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National Center for Small-Angle Scattering Research

Reports on Measurements Carried Out
by Users of the Facilities of the NCSASR

S. Spooner
L. B. Maddox

December 1, 1985--September 30, 1987

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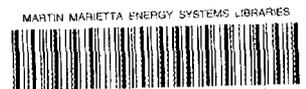
ORNL/TM-10614

**NATIONAL CENTER FOR SMALL-ANGLE
SCATTERING RESEARCH**

**Reports on Measurements Carried Out
by Users of the Facilities of the NCSASR**

December 1, 1985--September 30, 1987

Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
operated by
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for the
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under Contract No. DE-AC05-84OR21400



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Reports on measurements carried out at the NCSASR. The reports are organized by category: materials science, chemistry and colloid science, biology, polymers, and interdisciplinary experiments (calibration, fractal physics, etc.).

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30-M SANS

Title SANS from Commercial Li-Al Alloys

(Feasibility Experiment)

Research Sponsor Aeritalia S.p.A

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

R. Triolo

To Be Completed by ORNL

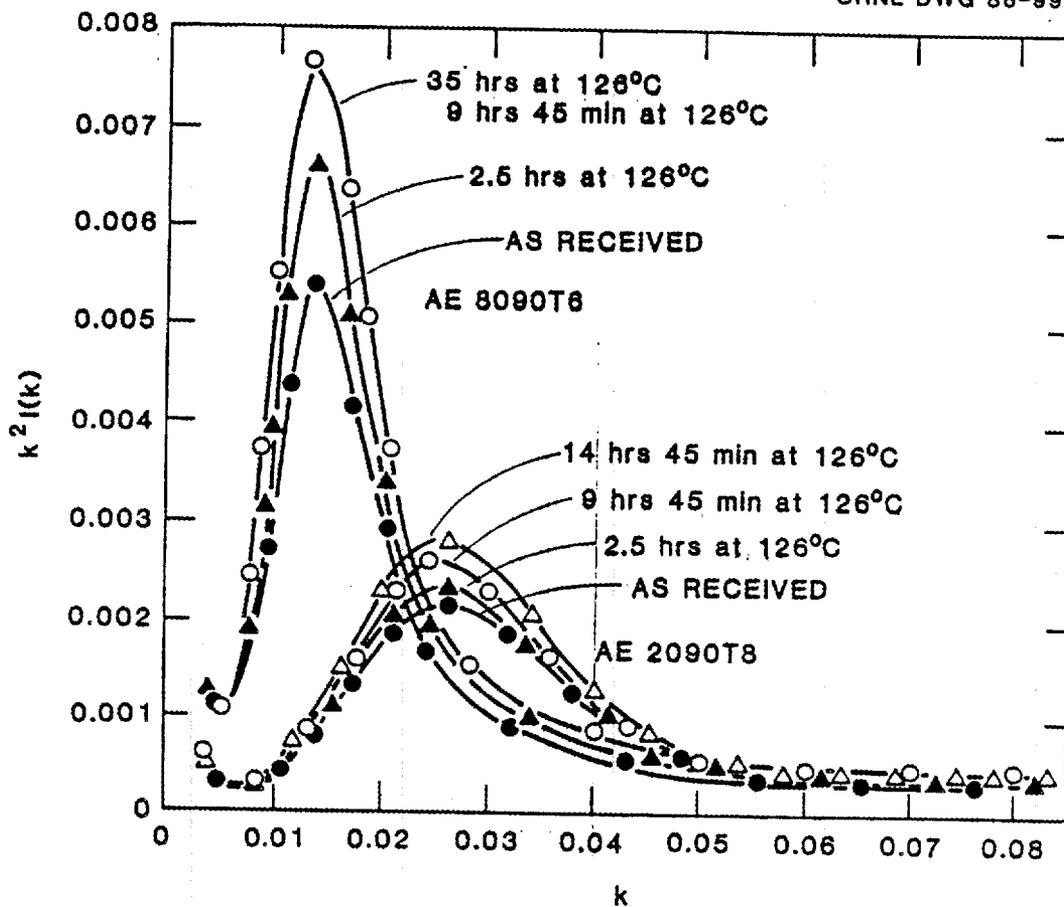
Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

We have performed preliminary SANS experiments on two different commercial Al-Li samples (A = 2090T8, B = 8090T6). We have measured the scattering intensity as a function of k at 19, 6, and 3 m corresponding to $0.003 \text{ \AA} < k < 0.35$. The "as received samples" have been heat treated at 126°C with different heating profiles. All the samples show a sharp increase of intensity for $k < 0.01 \text{ \AA}^{-1}$. In addition, one of the samples B has been treated for 9 hrs and 45 m at 126°C . After measuring the intensity curve the sample has been treated at 126°C for 26 more hrs. Surprisingly the scattering intensities of the two samples are identical. We plan to investigate further the effect of interrupting the aging treatment, as well as the origin of the scattering at $k > 0.01 \text{ \AA}^{-1}$.



References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASRInstrument(s) 30 m SANSTitle SANS Investigation of Pore Removal in Al₂O₃ During SinteringResearch Sponsor DOE, Office of Basic Energy Sciences Grant or Contact No. DE-FG05-84ER45063

Participants and NCSASR Collaborator(s)

R. A. PageS. Spooner

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

**PORE EVOLUTION DURING GLOW DISCHARGE^(1,2)
SINTERING OF ALUMINA****Abstract****R. A. Page, S. Spooner, W. B. Sanderson, and D. L. Johnson**

A series of experiments have been performed to demonstrate the applicability of small-angle neutron scattering to the study of pore evolution during sintering. Samples of α -Al₂O₃ which had been zone sintered in a hydrogen hollow cathode glow discharge to densities exceeding 94 percent of theoretical were employed in these preliminary measurements. The neutron scattering results indicate that densification during the final stages of glow discharge sintering occurs primarily through a reduction in the number of pores present with only a small change in the average pore size.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

- (1) R. A. Page, S. Spooner, W. B. Sanderson, and D. L. Johnson, J. Am. Ceram. Soc. (submitted).
- (2) R. A. Page, S. Spooner, W. B. Sanderson, and D. L. Johnson, American Ceramic Society Annual Meeting, Pittsburgh, PA, April, 1987.

Report of Measurements Carried Out at the NCSASRInstrument(s) 30 m SANSTitle SANS Investigation of Creep Cavitation in Ceramics Containing a Continuous Grain Boundary Glassy PhaseResearch Sponsor DOE, Office of Basic Energy Sciences Grant or Contact No. DE-EG05-84ER45063

Participants and NCSASR Collaborator(s)

R. A. PageJ. LankfordS. Spooner

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report **CREEP CAVITATION IN LIQUID-PHASE-SINTERED ALUMINA⁽¹⁾****R. A. Page, J. Lankford, K. S. Chan, K. Hardman-Rhyme, and S. Spooner****Abstract**

The early stages of cavitation during compressive creep of a liquid-phase-sintered alumina have been characterized using small-angle neutron scattering. Grain-boundary cavities were found to nucleate throughout creep, although at a steadily decreasing rate. The cavities were located on two-grain junctions as well as triple points and were spaced approximately 100 to 200 nm apart. The cavity spacing corresponded to the spacings observed for grain-boundary ledges, suggesting that the ledges were the cavity nucleation sites. Cavity nucleation was also found to be relatively independent of the applied stress. This behavior has been rationalized based on the decreasing ratio of $\epsilon_{gbs}/\epsilon_t$, where ϵ_{gbs} is the strain due

to grain-boundary sliding and ϵ_t is the total strain, at increasing stresses. Cavity growth, on the other hand, was highly stress dependent. Above a certain "threshold" stress cavity growth was observed. In all cases, however, the observed growth was transient; i.e., the cavity growth rate decreased with time. Lowering the stress below the "threshold" resulted in a condition in which cavities nucleated but continued growth of the cavities did not occur. In all cases the cavities nucleated and grew, when growth did occur, with relatively equiaxed shapes.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

- (1) R. A. Page, J. Lankford, K. S. Chan, K. Hardman-Rhyne, and S. Spooner, J. Am. Ceram. Soc., Vol. 70, pp. 137-145, 1987.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30 meter SANS

Title (preliminary) SANS Investigation of Microstructural Changes in Nickel-based Superalloy Single Crystals due to Creep

Research Sponsor _____ Grant or Contact No. _____

Participants and NCSASR Collaborator(s)	To Be Completed by ORNL
<u>J. Chene</u>	Date Received _____
<u>S. Spooner</u>	Proposal No. _____
_____	Date of Experiment(s) _____

Report

SANS measurements were made on single crystal superalloy CMSX which is a nickel-based composition having a γ' precipitate oriented in a fixed habit in a γ matrix. It was anticipated that there would be a strong scattering from the γ' precipitates but it was hoped that due to the anisotropic nature of the scattering that changes in scattering could be measured in the low intensity part of the pattern. Samples differing in the amount of charged hydrogen were compared. No readily measured differences could be found in these experiments. It is concluded that the γ' scattering is too strong a "background" over which to measure the subtle effects of hydrogen.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASRInstrument(s) 30 meter SANS

Title Exploratory SANS Investigation of the Shape of ^{Cobalt} Precipitates
in Cu(Co) Single Crystals

Research Sponsor _____ Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

H. I. AaronsonS. Spooner

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

With the unavailability of Cu(Co) crystals (several attempts having failed) SANS investigation of the early stages of precipitation was made on polycrystalline samples of a 0.5 at. % alloy. Heat treatment for 1, 2 and 3 hours at 560°C, 580°C and 600°C. Under these conditions the nucleation and growth stages of precipitation could be observed. Use of the absolute~~d~~ calibrated intensity permitted the estimate of the number density of precipitates which increased with time. The apparent nucleation rates were found to agree to an order of magnitude with rates found in TEM studies.

While it was expected that the large angle scattering part of the the SANS pattern would reveal some indication of finite boundary width, the interference of scattering background from incoherent^{ent} and possibly paramagneticⁿ scattering obscured the subtle variations in the Porod law scattering that were sought.

Until large single crystals and large magnetic field capabilities are available studies are not likely to yield the desired information on the shape and boundary chemistry of nuclei in the Cu(Co) system.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30-M SANS

Title Kinetics of Phase Separation in Mn_{0.67}Cu_{0.33}

Research Sponsor _____ Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

B. D. Gaulin

S. Spooner

Y. Morii

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

We have examined the kinetics of phase separation in $\text{Mn}_{0.67}\text{Cu}_{0.33}$ using time-resolved neutron-scattering techniques. In an early-time regime, the kinetics follows the Cahn-Hilliard-Cook linear theory of spinodal decomposition. There is an intermediate stage. Then, at a late time, dynamic scaling is obeyed. The time dependence of the wave vector at maximum scattering intensity (which is inversely proportional to the average linear domain size) can be well described over the entire late-time regime and much of the intermediate-time regime by arguments recently put forward for earlier-time corrections to the limitingly late-time stages of phase separation.

References

Give references if the work has been published or submitted to conferences, symposia, etc.
Physical Review Letters 59, 668 (1987).

Report of Measurements Carried Out at the NCSASR

Instrument(s) Small Angle X-ray Scattering

Title Determination of the Al-Li Phase Diagram by SAXS/TEM

Research Sponsor Alcoa

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

CHANGMO SUNG

Dr. D. B. Williams

Dr. S. Spooner

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report Aluminum alloys containing lithium offer attractive possibilities for the aviation industry and for other structural applications due to their low density and high stiffness properties. The major strengthening increment in all Al-Li alloys is afforded by the widespread precipitation of ordered, metastable δ' (Al_3Li) during aging. At present there is still considerable uncertainty surrounding the $\alpha + \delta'$ phase field, which limits our understanding of the precipitation behavior of the important δ' phase.

SAXS is sensitive to non-periodic structures on a scale from 0.5nm to 200nm in diameter, and the SAXS spectrum is obtained from a region of specimen $3\text{mm}^2 \times 100\mu\text{m}$ thick. Therefore, SAXS gives information characteristic of bulk material due to scattering from many centers. While the scattering statistics are excellent, the effects of small sub-micron variation in the scattering centers cannot be accounted for and therefore limit the quantification of the SAXS data. In other words the SAXS spectrum does not give a unique structure identification and a specific model is essential in order to interpret the spectrum. Deviation from the model in the real specimen limits the interpretation. Only when the range and type of scattering centers is known can the separate contribution to the SAXS spectrum be separated. However, these separate scattering contributions can be obtained using TEM imaging.

Single crystals of Al-7.4at% and 9.1at% Li alloys was used to study the $\alpha + \delta'$ phase boundary at aging temperatures above 150°C. It is known that volume fraction of δ' precipitates and hence the solute removed from the matrix is proportional to the integrated small angle scattering intensity. Thus, it is important that the precipitates and matrix are in local equilibrium so that the integrated intensity is independent of aging time. Several aging times were chosen at each aging temperature based upon δ' precipitates coarsening data. In addition to two single crystal alloys, one large grain polycrystal Al-12.7at% alloy was used to investigate the $\alpha + \delta'$ phase boundary because we can obtain more reliable compositions of the α matrix and δ' precipitates from a SAXS experiment if more than two kinds of Al-Li alloys are used (S. Spooner, private communication).

Fig. 1 shows the Kratky plot of Al-12.7at%Li alloy aged at 230°C for 2 hrs (A), 0.5 hrs (B), and 10 mins (C). Fig. 2 shows the microstructure of sample A which contains δ' and δ precipitates. We can determine the composition of δ' precipitates at each aging temperature and predict phase diagram of Al-Li alloys using the integrated intensity (Fig. 1) and TEM results (Fig. 2). Complete results will be published later.

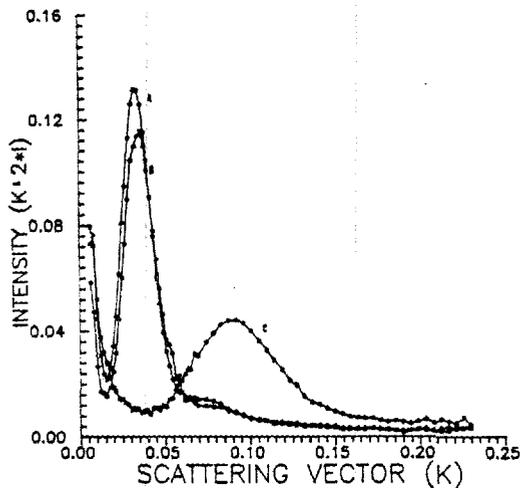


Fig. 1

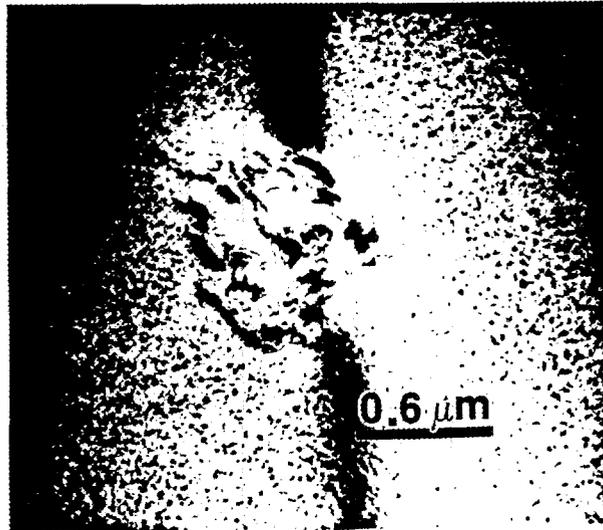


Fig. 2

References

Give references if the work has been published or submitted to conferences, symposia, etc.

"Combined SAXS and TEM Studies of Al-Li Alloys", S. Spooner, D. B. Williams, and C. M. Sung. Oxford Conf. on Al-Li Alloys III, pp. 329-336, January 1986.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 10-m SAXS camera

Title A Search for Cu₅Mn Ordered Phase in Neutron-Irradiated Cu-5 at. % Mn

Research Sponsor _____

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

S. J. Zinkle

S. Spooner

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

The alloy Cu-5 at. % Mn was irradiated with 14-MeV neutrons at room temperature to a fluence of 2×10^{21} n/m² ($\sim 10^{-3}$ displacements per atom). This alloy composition should be single-phase according to published phase diagrams, but some researchers have claimed that an ordered phase Cu₅Mn occurs near this composition at temperatures below 400°C. Electrical resistivity measurements on the irradiated alloy suggested that short-range order (SRO) had occurred as a result of the irradiation. This study was therefore intended to examine whether any clustering had occurred during the neutron irradiation.

We did not observe any evidence of clustering from small angle X-ray scattering measurements. Furthermore, electron microscopy and diffraction measurements did not reveal a second phase. We therefore conclude that there is no appreciable clustering in this alloy. The observed resistivity behavior is most likely due to short-range ordering that does not involve the creation of a second discrete phase.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 10-M SAXS, 10-M SANS (ORR)

Title Measurement of Magnetic Domain Size (Preliminary)

Research Sponsor _____

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

W. A. Challener

S. Spooner

J. S. Lin

G. D. Wignall

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Samples of a magnetic amorphous alloy similar to that used in erasable optical disks were given a preliminary examination by SANS and SAXS techniques. The samples were composed of 1000 angstroms of a magnetic amorphous alloy, protected from oxidation by 50 angstroms of a dielectric, deposited upon a kapton film substrate. The purpose of the experiment was to determine if the equipment available could be used to measure magnetic domain sizes which are presently believed to be on the order of 50 to 200 angstroms in diameter.

Because of the very small volume of the sample, multiple sample layers and long data collection times were used in both the SAXS and SANS experiments. The radius of gyration measured by SAXS was 77 angstroms, corresponding to an approximate diameter of 200 angstroms in the physical structure. The radius of gyration measured in the SANS experiment was 89 ± 11 angstroms. For the SANS experiment, the sample was also placed in a 4 kG external field, but the signal was too small to measure any change in the scattering.

This feasibility experiment indicated several ways in which a follow up experiment may be improved. Replacing the kapton film substrate with a very thin quartz or glass substrate or a deuterated plastic film would eliminate much of the background scattering. The thin films could be deposited on both sides of the substrate, and perhaps multiple layers could be deposited on one substrate. An order-of-magnitude increase in signal-to-noise ratio is expected by using the high flux reactor instead of the lower flux reactor used in these measurements.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASRInstrument(s) 10-Meter SAXS CameraTitle "Dispersoid Coarsening Kinetics in Commercial
Alumina Dispersion Strengthened Copper Alloys"

➤ Research Sponsor _____ Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

Dr. John J. Stephens^{*}, Lockheed Missiles and Space CoDr. Ron J. Livak, Los Alamos National LaboratoryDr. Stephen Spooner, NCSASR*formerly, Sandia National Laboratories

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Dispersoid Coarsening Kinetics in Commercial Alumina Dispersion Strengthened Copper

The aim of this investigation is to use Small Angle X-ray Scattering to characterize the rate of coarsening in Al_2O_3 dispersion strengthened copper (Glidcop Grades Al-15 and Al-60). Previous work (ref. 1) has demonstrated that SAXS is an effective tool for characterizing the dispersoid volume fraction and size distribution in the nickel base dispersion strengthened alloy, MA 754. The present investigation focuses on a dispersion strengthened copper which is currently a candidate material for various Tokamak Fusion Reactor application, where neutron resistance (ref. 2) and high temperature strength (ref. 3) are important issues.

Specimens of both Al-15 (0.3 wt.% alumina) and Al-60 (0.6 wt.% Alumina) were encapsulated in quartz with a high purity Argon backfill and Tantalum foil getter and subjected to long term annealing. Temperatures ranged from 850 to 1040 C, for times up to 2000 hrs. SAXS data was acquired during a one week visit to NCSASR in February, 1987. Preliminary analysis of the data indicate that dispersoid size stability is good, but that morphological changes occur during the long term annealing. In particular, asymmetric contours in 2-D intensity plots indicate a shape change from equiaxed to elongated particles. This is in qualitative agreement with TEM thin foil results for aged specimens.

A second trip to NCSASR is tentatively being planned for late summer by Drs. Livak and Stephens. This planned session will permit further data analysis, and hopefully lead to the outline of a journal publication.

References

1. J.J. Stephens, S. Spooner, "Determination of Dispersoid Size Distributions in Inconel MA 754 by Small Angle X-ray Scattering" *Acta Metall.*, 34, pp. 303-312 (1986).
2. R.J. Livak, T.G. Zocco and L.W. Hobbs, "Neutron Damage Microstructures of High-Conductivity Copper Alloys" *Journal of Nuclear Materials*, 1986.
3. J.J. Stephens, D.T. Schmale, "The Effect of High Temperature Braze Thermal Cycles on Mechanical Properties of a Dispersion Strengthened Copper Alloy", SAND 87-1296, Sandia National Laboratories, Albuquerque, N.M. May, 1987.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 10 meter SAXS

Title Low Temperature Solvus in Aluminum-Lithium Alloys

Research Sponsor _____ Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

S. Spooner

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Four aluminum-lithium alloys (4.1 at.%Li, 5.5 at.%Li, 6.5 at.%Li and 7.2 at.% Li) were reacted after direct quench to three temperatures (95°C, 110°C and 125°C) for times up to 16 hours. These samples were measured with SAXS for the main purpose of determining the presence or absence of precipitation product from the treatments. In the 4.1 at.% Li alloy no clear indication of precipitation was found. In the 5.5 at.% LI precipitation was evident except in the 125°C treatment. A phase boundary was inferred which came remarkably close to the prediction of Sigli and Sanchez. These results corroborate the earlier SAXS studies done in this laboratory. Study of the kinetics and the variation of the volume fraction of the precipitate with treatment should permit a more quantitative determination of the phase boundary limits in this system.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

S. Spooner, D. B. Williams and C. M. Sung, "Evidence for the Metastable Miscibility Gap in Al-Li from Small Angle X-ray Scattering," AIME-TMS Meeting Abstract, New Orleans, 1986.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 10 meter SAXS

Title Study of the Effect of Retained Helium in Metal (Pd) Lattices

Research Sponsor _____ Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

P. W. Seabaugh

C. R. Hudgens

S. Spooner

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

SAXS measurements on paladium powdered metal subjected to various cycles of hydriding and dehydriding were made to find structural changes resulting from the hydrogen treatment. This preliminary work was done in anticipation of the study of the effects of other hydrogen isotopes in paladium which may involve helium effects as well. The principal scattering effects appear to arise from the metal substrate powder. Variations in the scattering pattern can be correlated with the differences in the method of manufacturing the powder. No readily measured changes can be seen as a result of hydride cycle effects however. In one experiment a paladium sample pressurized with hydrogen was measured in situ and then measured over a period of time after release of the hydrogen from the sample. A small and tantalizing change seemed to be on the edge of measurability in the time series. The expectation is that a change from the hydrided to unhydrided condition would show a change in the scattering. Several attempts were made to repeat the experiments with no convincing corroboration of the initial indication. Improved hydrogen cell designed seems to be required to insure that hydrogen release can be controlled.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 10-meter SAXS

Title SAXS Study of Coarsening Kinetics at Low Temperature and Small Lithium
Content Al-Li Alloys: The Effects of Direct and Indierct Quenching

Research Sponsor _____ Grant or Contact No. _____

Participants and NCSASR Collaborator(s)
S. Spooner

To Be Completed by ORNL
Date Received _____
Proposal No. _____
Date of Experiment(s) _____

Report

SAXS measurements of 6.8 at.% Li at 126°C and 9.4 at.% Li at 100°C for times up to 30 hours were made in which two quenching methods were employed. In one method the sample is quenched to room temperature and then aged while in the second method the sample is directly quenched to the precipitation temperature. The evolution of average precipitate size and volume fraction depends on the quenching method. Direct quenching produces a larger precipitate size. With the 9.4 at.% Li alloy reacted at 100°C the direct quench gives a larger volume fraction of precipitates than in the case of the quench to room temperature and age. In the 6.8 at.% Li alloy direct quenching produces a lower volume fraction at 126°C. The implication is that a phase boundary such as a miscibility gap is traversed as temperature is lowered to 100°C degrees in the 9.4 at.% Li alloy while no such traverse is accomplished in the 6.4 at.% Li alloy at 126°C. It is suggested that a spinodal decomposition mode is possible in this system.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

S. Spooner, D. B. Williams and C. M. Sung, " Combined small angle X-ray scattering and transmission electron microscopy studies of Al-Li alloys", in Aluminum-Lithium Conference III, ed. C. Baker, P. J. Gregson, S. J. Harris and C. J. Pell, The Inst. Metals, London, 1986.

Report of Measurements Carried Out at the NCSASRInstrument(s) 10-m SAXS cameraTitle A Search for Cu₅Mn Ordered Phase in Neutron-Irradiated Cu-5 at. % Mn

Research Sponsor _____

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

S. J. ZinkleS. Spooner**To Be Completed by ORNL**

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

The alloy Cu-5 at. % Mn was irradiated with 14-MeV neutrons at room temperature to a fluence of 2×10^{21} n/m² ($\sim 10^{-3}$ displacements per atom). This alloy composition should be single-phase according to published phase diagrams, but some researchers have claimed that an ordered phase Cu₅Mn occurs near this composition at temperatures below 400°C. Electrical resistivity measurements on the irradiated alloy suggested that short-range order (SRO) had occurred as a result of the irradiation. This study was therefore intended to examine whether any clustering had occurred during the neutron irradiation.

We did not observe any evidence of clustering from small angle X-ray scattering measurements. Furthermore, electron microscopy and diffraction measurements did not reveal a second phase. We therefore conclude that there is no appreciable clustering in this alloy. The observed resistivity behavior is most likely due to short-range ordering that does not involve the creation of a second discrete phase.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) _____

Title Structure and Properties of 3-Component Microemulsions Near the Critical Point

Research Sponsor _____ Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

J. S. Huang

M. Kotlarchyk

S. H. Chen

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

We have used small angle neutron scattering and light scattering to study the structure and nature of the phase transition near the lower critical point of a 3-component AOT microemulsion system. We have found that both far and close to the critical point, the system exists as an assembly of surfactant coated spherical water droplets in oil, characterized by a well defined polydispersity. Upon approaching the critical point, the correlation length of the system diverges with a critical exponent of $\nu = 0.75$ for a number of field variables, namely, temperature, pressure, alkane number, and salinity. This divergence can be attributed to increased correlations between the basic droplets. Furthermore, the critical exponents for the correlation length and the osmotic compressibility appear to be Ising-like, with $\gamma = 2\nu$. The coexisting phases above the transition temperature are both water-in-oil microemulsions, differing only in the number density of droplets, and the nature of the phase transition is analogous to a simple liquid-gas coexistence. We have also determined that the critical phenomenon is driven by interdroplet attractions. Far below the cloud point temperature, the attraction is short-ranged. Near the transition, the interaction could become progressively longer-ranged and its strength increases linearly with temperature, consistent with the fact that the coexistence curve has a lower critical point.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

J S Huang, M Kotlarchyk, and S H Chen, Structure and Properties of 3-Component Microemulsions Near the Critical Point, Statistical Thermodynamics of Micelles and Microemulsion Systems, Edited by S H Chen and R. Rajagopalan, (Springer Verlag 1987)

Report of Measurements Carried Out at the NCSASR

Instrument(s) _____

Title ~~The Structure and Phase Transitions of a Three-Component Microemulsion System =~~
AOT/Water/Alkane

Research Sponsor _____ Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

Sow-Hsin Chen _____

Tsang-Lang Lin _____

John S. Huang _____

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

For the model microemulsion containing a surfactant known as AOT, because of its large solubility in alkanes (from C_6 to C_{12}) and of its asymmetric molecular geometry the anionic surfactant sodium di-2-ethylhexylsulfosuccinate (AOT) forms water-in-oil microemulsions over a large portion of its ternary phase diagram. Extensive small angle neutron scattering (SANS) measurements have been carried out by the MIT/Exxon group to determine the detailed structure of reverse micelles when the surfactant is dissolved in decane and of the water swollen reverse micelles (microemulsions) when an increasing amount of water is added. As a result the "droplet" picture of this microemulsion system is now firmly established not only in the dilute regime but also in the dense microemulsions when the volume fraction of the droplets is as high as 0.71. This article briefly reviews the droplet structure as well as the inter-droplet structure of this ternary system in the one-phase region and in the microemulsion two phase region. In particular, the nature of the fluctuations near the cloud points and its connection with the temperature dependent effective droplet-droplet attractive interaction are discussed.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

S H Chen, T L Lin, and J S Huang, The Structure and Phase Transitions of a Three-Component Microemulsion System: AOT-Water-Alkane, Physics of Complex and Supermolecular Fluids, Edited by S A Safran and N A Clark, (Wiley Interscience 1987) p.285-314

Report of Measurements Carried Out at the NCSASR

Instrument(s) _____

Title Phase Separation in Microemulsions

Research Sponsor _____ Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

S. A. Safran

L. A. Turkevich

J. S. Huang

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

We have constructed a phenomenological theory of microemulsion phase behavior, based on a model of interacting spherical globules. The model exhibits a critical point prior to a two-phase coexistence, a first-order phase separation ("emulsification failure"), and a three-phase coexistence. The results of the model are in accord with small angle neutron scattering measurements on AOT/water/decane microemulsion. Analysis of the neutron scattering data shows the interglobule interaction to scale with globule radius, consistent with a short range attraction, possibly due to overlap of surfactant tails.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

M. Kotlarchyk, J S Huang, M W Kim and S H Chen, Analysis of SANS Data From Dense Microemulsions, Surfactants in Solution, Vol 6, p1303, Edited by K L Mittal and P Bothorel, (Plenum Press, New York, 1986)

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30-Meter SANS

Title Structural Changes in Anionic Micelles Induced by Counterion Complexation with a Macrocyclic Ligand: Double- vs. Single-Chain Amphiphiles

Research Sponsor NSF Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

K. A. Payne

L. J. Magid

J. B. Hayter

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

We have been interested in how patterns of micellar aggregation differ for double-chain vs. single-chain amphiphiles; for sodium bis(n-alkyl)sulfosuccinates (C₁₈SS) in water, the first-formed spherical micelles have large areas per head group and low extents of counterion binding (fraction (β) of ca. 0.5), but with increasing surfactant concentration rapid micellar growth, deviation of the micellar shape from spherical and substantial increases in the fraction of counterions bound are observed. We supposed that Na⁺ complexation by macrocyclic ligands such as the cryptand C222 in dilute C₁₈SS solutions would produce minimum-sphere, highly ionized micelles (with β 's even lower than observed with C222 plus the single-chain amphiphile sodium dodecylsulfate, SDS).

Examination of representative scattering curves, presented in Figure 1, shows immediately, without recourse to curve-fitting, that the addition of one equivalent of C222 does indeed decrease the mean aggregation number (\bar{n}) of SDS micelles. Contrary to expectations (see Fig. 1 again), at some concentrations of C₁₈SS C222 has the opposite effect. Figure 2 shows typical fits for the scattering curves: the micelles are modelled as spheres at low concentration, prolate ellipsoids at the higher concentrations. More detail may be found in refs. 1 and 2; adjustable parameters were \bar{n} ,

evaluated for a given Z , micellar hard sphere diameter and volume fraction following Hayter, Penfold and Hansen (refs. 3 and 4).

Figures 3 and 4 present the evolution of \bar{n} 's for the two surfactants with and without C222 as a function of amphiphile concentration and supporting electrolyte (NaCl) concentration. For SDS, the presence of one C222 per Na^+ decreases the micellar size and makes it insensitive to increases in SDS and NaCl concentration; C222 also increases the extent of micellar ionization. For the C_{7}SS micelles, the decrease in mean \bar{n} occurs only in the more concentrated micellar solutions; the effect of added NaCl on micellar growth is muted somewhat but not eliminated.

The difference in behavior is rooted in geometrical considerations. The $\text{Na}^+:\text{C222}$ complex occupies 136 \AA^2 ; SDS micelles in the absence of C222 have areas per head group of less than 100 \AA^2 , so \bar{n} must decrease in order to accommodate the C222. However, the area per head group for C_{7}SS micelles is large enough (until ca. $0.2 \text{ M C}_{7}\text{SS}$) already; in fact, some increase in \bar{n} occurs upon addition of C222, as hydrocarbon-water contact at the micellar surface is minimized.

References

1. J. B. Hayter and J. Penfold, Colloid Polym. Sci. **261**, 1022 (1983).
2. L. J. Magid, Coll. Surf. **19**, 129 (1986).
3. J. B. Hayter and J. Penfold, Mol. Phys. **42**, 109 (1981).
4. J. P. Hansen and J. B. Hayter, Mol. Phys. **46**, 651 (1982).

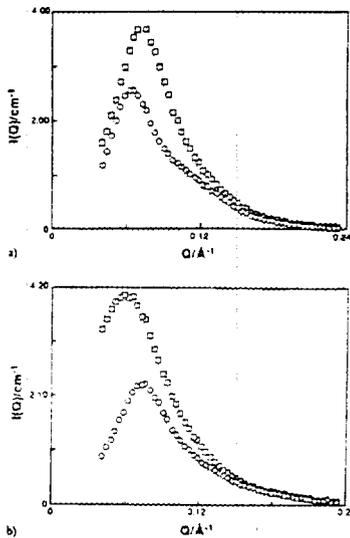


Fig. 1. SANS data for (a) 0.10 M SDS (at 25°C) and (b) $0.10 \text{ M C}_{7}\text{SS}$ (at 45°C) micellar solutions without (O) and with (□) C222.

References

Give references if the work has been pu

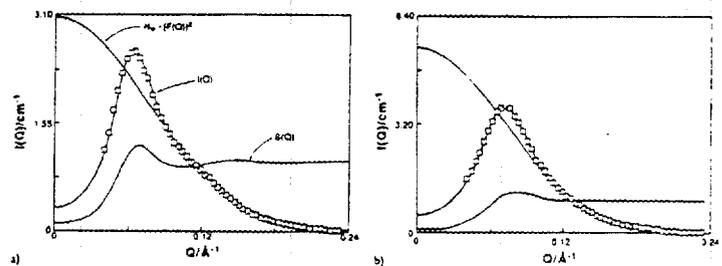


Fig. 2. Fits to the SANS curves for (a) 0.10 M SDS and (b) $0.10 \text{ M SDS} + \text{C222}$.

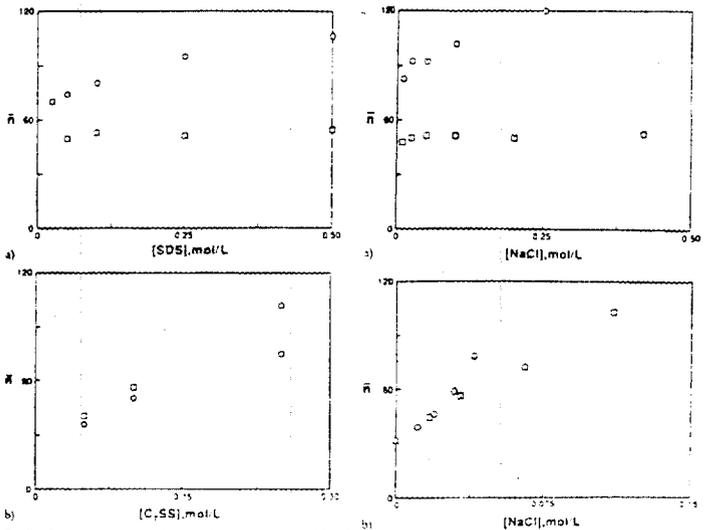


Fig. 3. Mean aggregation numbers for the micelles in (a) SDS and (b) C_{7}SS solutions. Without C222 (O); with (□).

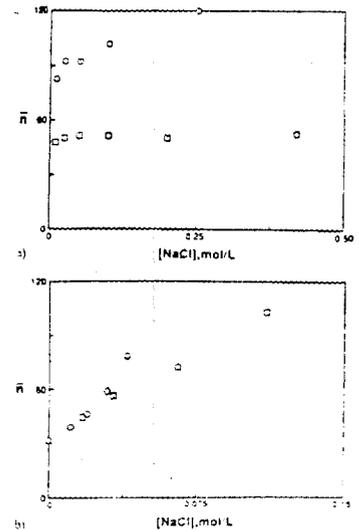


Fig. 4. Effect of NaCl on the mean aggregation numbers for the micelles in (a) 0.225 M SDS and (b) $0.225 \text{ M C}_{7}\text{SS}$. Without C222 (O); with (□).

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30M SANS

Title SMALL-ANGLE NEUTRON SCATTERING STUDIES OF SOLUBILIZATES IN SDS MICELLES

Research Sponsor EASTMAN-KODAK. Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

____ O. I. Thompson, J. M. O'Reilly, _____
 _____ W. C. Koehler* _____

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

The technique of SANS has been used to determine the change in size and aggregation number of SDS micelles with the solubilization of naphthol and decane. The results for decane were as expected; the radius and aggregation number increase with mol fraction of decane (0.1-0.4). Contrast variation experiments indicated that decane was localized near the center of the micelle. In the case of naphthol, similar increases in size and aggregation number were observed but the contrast valuation experiments did not clearly identify the locus of solubilization of naphthol.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

submitted for publication in Magnetic Resonance & Scattering
in Surfactant Systems (Proceedings of a Meeting) *PLENUM PRESS*

Report of Measurements Carried Out at the NCSASRInstrument(s) 30-M SANS

Title The Effect of Added Sodium and Lithium Chlorides on Intermicellar Interactions and Micellar Size of Aqueous Dodecyl Sulfate Aggregates as Determined by Small-Angle Neutron Scattering

Research Sponsor ORAU/DOE/NSF/3M

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

Stuart S. BerrRichard R. M. Jones

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

The effect of added electrolyte on ionic micelle size and interparticle interactions has been studied by small-angle neutron scattering (SANS). The surfactants, lithium and sodium dodecyl sulfate (LDS and SDS) were kept at a fixed concentration (0.05 M), while their respective chloride concentrations (LiCl and NaCl) were increased. As the concentration of added salt was raised, coulombic interactions decreased to the point where Van der Waals forces could dominate. Furthermore, the added electrolyte was able to screen intramicellar headgroup repulsions, allowing the micelles to grow in terms of an increased aggregation number, N . Sodium was found to be much more effective than lithium at screening charge. N for SDS micelles increased from 54 to 928 and the contact potential decreased from 16 to -221 kJ/mol when [NaCl] was increased from 0.0 to 0.6 M. N for LDS, on the other hand, went from 53 to 91 and the contact potential decreased from 14 to -2.5 kJ/mol as [LiCl] was increased from 0.0 to 0.8 M.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Langmuir

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30-Meter SANS

Title Scattering Investigations of a Three Component Nonionic Microemulsion

Research Sponsor NSF Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

P. B. Butler

L. J. Magid

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

SANS measurements were performed for the ternary microemulsion D_2O -octane- $C_{12}E_5$ at several compositions: (1) as a function of $C_{12}E_5$ wt% (Υ) at constant oil/water wt. ratio ($\alpha = 40$, so the oil-to-water volume ratio is one) in both the high and low temperature arms of the fish tail (Fig. 1a); and (2) as a function of α (at $\Upsilon = 7$ wt%) through the main isotropic channel (Fig. 1b). All of the scattering curves showed a Q^{-4} decay at large Q , indicating the presence of an interfacial film at which the change in scattering length density from ρ_{D_2O} to ρ_{oil} is sharp.

The majority of the curves also display a peak at low Q ; in series 1 it decreases in intensity and moves to higher Q as Υ increases (see Fig. 2), while in series 2 I_{peak} and Q_{max} show a parabolic dependence on α (Fig. 3 expresses the latter trend as $2\pi/Q_{max}^{peak}$). In series 2 at low and high α (10 and > 80 respectively), the scattering is consistent with that expected from oil-in-water or water-in-oil microemulsion droplets: Guinier radii, the maximum in $P(r)$ and D_{max} for each sample give the same radius; the droplet radii increase, as expected, with increasing volume fraction of the dispersed phase. However, when substantial amounts of water and oil are both present, this is no longer the case. Electron micrographs of the microemulsions show intertwined domains of oil and water rather than droplets; translational self-diffusion coefficients (measured by PGSE FTNMR)

of oil and water are consistent with the connectivity. The experimental D_{\max} values (Fig. 3) are roughly equal to the sum of the average diameters of the oil and water domains seen in the micrographs; D_{\max} is proportional to the product $\phi_o \cdot \phi_w$.

Recently Teubner and Strey have shown that SANS curves such as those in Fig. 2 can be represented by $I(Q) \sim (a_2 + c_2 Q^2 + c_2 Q^4)^{-1}$; this arises from the use of a particular order parameter expansion in describing the free energy density in a Landau theory. The correlation function in real space which yields this $I(Q)$ representation is given by $\Upsilon(r) = (d/2\pi r) \cdot (\exp(-r/\xi)) \sin(2\pi r/d)$; d is characteristic for the domain size (the periodicity; roughly D_{\max}), while ξ is the correlation (or persistence) length. As observed already by others studying microemulsions, ξ may be obtained from the Porod's law regime, as well as from fitting the full scattering curve.

The following values for d (and ξ) were obtained for the scattering curves in Fig. 2, using the Teubner-Strey formalism: at 6 wt%, 809 Å (236 Å); at 12 wt%, 379 Å (126 Å); at 21 wt%, 183 Å (82 Å).

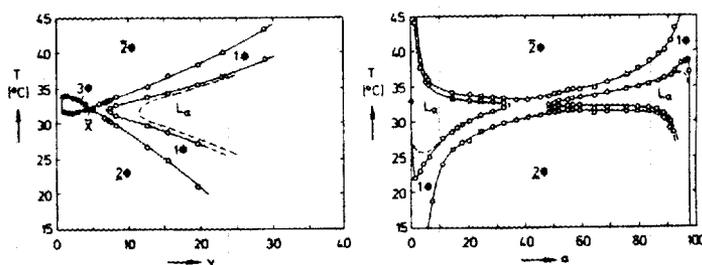


Figure 1.

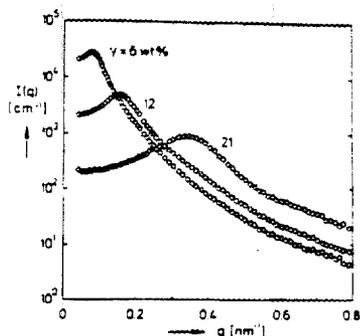


Figure 2.

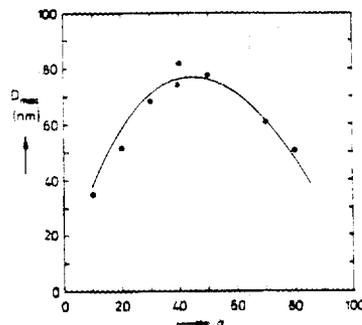


Figure 3.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

M. Kahlweit, R. Strey, D. Haase, H. Kuneida, T. Schmeling, B. Faulhaber, M. Borkovec, H.-F. Eicke, G. Busse, F. Eggers, Th. Funck, H. Richmann, L. Magid, O. Soederman, P. Stilbs, J. Winkler, A. Dittrich and W. Jahn, J. Colloid Interface Sci., to appear August, 1987.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30-M SANS

Title SMALL-ANGLE NEUTRON SCATTERING FROM HEXADECYLTRIMETHYLAMMONIUM BROMIDE
MICELLES IN AQUEOUS SOLUTIONS

Research Sponsor Wake Forest Univ/ORAU/DOE/NSF/Univ.
Palermo/3M Company

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

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E. Caponetti

James S. Johnson, Jr., Richard R. M. Jones

Linda J. Magid

To Be Completed by ORNL

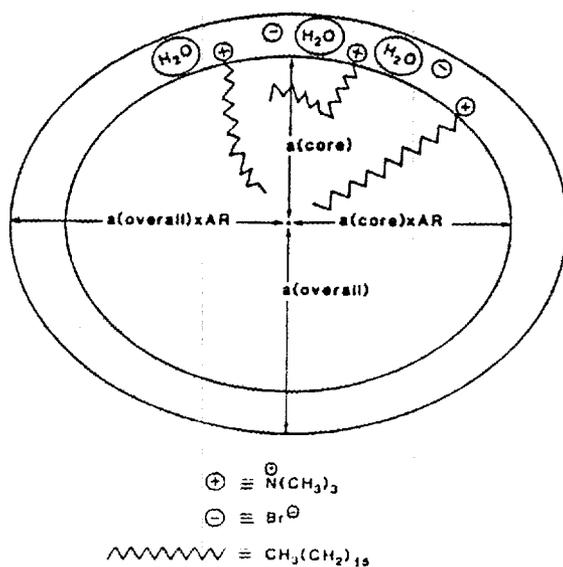
Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Small-angle neutron scattering measurements have been carried out at 50°C as a function of external contrast (different ratios of H₂O to D₂O) on 0.12 M solutions of hexadecyltrimethylammonium bromide, with the methyls of the ammonium group protiated and deuterated. The results indicate that most of the surfactant hydrocarbon is in a micellar core penetrated by little, if any, solvent. The micelles are described adequately by a dispersion of monodisperse prolate ellipsoids. There is a significant effect on the size of the aggregates by the isotopic composition of the solvent.



References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASRInstrument(s) 30-M SANSTitle Small-Angle Neutron Scattering Study of the Structural Effects of Substitution
of Tetramethylammonium for Sodium as the Counterion in Dodecyl Sulfate MicellesResearch Sponsor Wake Forest Univ./DOE/NSF

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

Stuart S. BerrMichael J. ColemanRichard R. Marriott Jones

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Small-angle neutron scattering (SANS) data have been obtained at 303 K for aqueous micellar solutions of $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4 \text{Na}$ (sodium dodecyl sulfate, SDS) and $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4 \text{N}(\text{CH}_3)_4$ (tetramethylammonium dodecyl sulfate, TMADS) and their deuterated analogues $\text{CH}_3(\text{CH}_2)_{10}\text{CD}_2\text{SO}_4 \text{Na}$ (D_2 -SDS) and $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4 \text{N}(\text{CD}_3)_4$ (D_{12} -TMADS). Results have been obtained for 0.4 mol dm^{-3} surfactant in various $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures and for TMADS as a function of surfactant concentration in D_2O . The SANS data are well described by charged, monodisperse hard spheres interacting through a screened coulomb potential. The asphericity and the polydispersity of the systems were estimated to be small. The deuterium for the deuterated surfactants lies mainly in the Stern region of the micelle and increases contrast between the hydrocarbon core and the water saturated Stern layer. Therefore, these deuterated micellar systems were used to determine the radius of the dry core which was then used in the determination of the structural parameters for the micellar systems. The degree of hydration was determined without resorting to the assignment of values for the water of hydration for the individual ions present. It was found that TMADS micelles are smaller, have a higher charge, smaller degree of aggregation, and less but more deeply penetrating water than do SDS micelles. Both SDS and TMADS micelles had substantial amounts of hydrocarbon residing in the aqueous Stern layer.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

J. Phys. Chem. 90, 6492 (1986).

Report of Measurements Carried Out at the NCSASRInstrument(s) 10 and 30-m SANSTitle SANS Study of Volcanic Rocks

Research Sponsor _____

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

Roberto Triolo**To Be Completed by ORNL**

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report**Experimental**

The volcanic rock samples were mounted on cylindrical aluminum holders about 1" in diameter. The thickness of the samples was such to have an absorption coefficient about 0.5. Scattering intensities were recorded at the 10-m (Oak Ridge Research Reactor) and 30-m (High Flux Isotope Reactor) SANS cameras. We used neutrons of 4.75 Å wavelength with a sample to detector distance of 19, 6, and 4.56 m. This geometry gave us a range of momentum transfer between 0.003 \AA^{-1} and 0.1 \AA^{-1} . During measurements the samples were kept at room temperature.

Scattering equation

For a sample of monodisperse noninteracting particles inbedded in a uniform matrix, with rough particle-matrix interface the scattered intensity as a function of the modulus of the scattering vector, Q is given by¹

$$I(k) = A(k^{-4} + a k^{-3}(c+x)) \quad (1)$$

where A is merely a collection of constants and depends on the concentration of dispersed phase, x is an universal positive parameter which characterizes the surface roughness, while a is a function of the roughness of the interface between the particles and the matrix ($a=0$ for smooth surfaces). Noncrystalline rocks usually give measurable neutron scattering signals in the small angle region ($0.003 \text{ \AA}^{-1} < k < 0.1 \text{ \AA}^{-1}$) and hence give information for distances roughly in the range from 100 to $\sim 2000 \text{ \AA}$.

Discussion

If the scattering intensity of a rock sample follows a k^{-4} dependence, one can conclude that only the first term of equation (1) is important, and hence that $a \approx 0$. Roughness is therefore unimportant in the mentioned length scale. However, it is possible that $I(k)$ obeys a single power law with exponent other than -4 . For rocks this should be the rule rather than the exception, and for this reason we shall devote more words to the description of this situation. First we must keep in mind that if the scattering originates not from the contrast at the interface particle-matrix, but rather from the particle volume, and if the volume is fractal then $I(k)$ should obey a single power law dependence with exponent > -3 (Schaefer et al. 1984). However, if $I(k)$ obeys a single power law dependence with exponent < -4 or if a portion of the scattering curve obeys a single power law dependence with exponent < -4 , then the surface is a fractal. In any other case, roughness is the dominating factor in determining the scattering intensity. We wish to point out that the previous conclusions would hold even for systems of interacting particles as are valid for $kR \gg 1$ (R being the size of the particles). Of course, if the particles are interacting then the shape of $I(k)$ for $kR \approx 1$ would strongly depend on the interaction between the particles. $I(k)$ could possibly show interaction peaks and/or power law dependences other than the one discussed previously.

In the k range $0.003\text{--}0.1 \text{ \AA}^{-1}$ the intensity of all our samples obey a single power law dependence with the exponents greater than -4 . The exponent of the power law varies for all the samples between -3.5 and -3.8 . We can then conclude that in no case the scattering particle have fractal volumes. If we assume that the particles are monodisperse then we can conclude that the interface roughness is of dominant importance for all the samples. The analysis of the scattering curves allowed us to exclude the possibility that the scattering particles of our rock samples are fractal volumes. Due to the chemical and physical complexity of the systems under investigation, no conclusion has been reached at this stage concerning the possibility that the particle-matrix interface might be a fractal surface. Further work is progress in this direction.

-
1. P.-Z. Wong, Phys. Rev. B 32, 7417 (1985).

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30-M SANS

Title Solvent Isotope Effects on Alkytrimethylammonium Bromide Micelles as a
Function of Alkyl Chain Length

Research Sponsor Wake Forest Univ, DOE, NSF

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

S. S. Berr

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

The effect on micellar structure of changing the solvent from H_2O to D_2O for C_n TAB (C_n TAB $\equiv C_nH_{2n+1}N(CH_3)_3Br$) with $n = 12, 14,$ and 16) has been examined. The energetics of micellization have been determined by measuring critical micelle concentrations using surface tensiometry. The micellar structure has been elucidated through the use of small-angle neutron scattering (SANS). It was found that there is a solvent isotope effect that is small for C_{12} TAB, but increases with n . This effect is manifest mainly by an increase in aggregation number and is attributed to solvent-hydrocarbon interactions of the dissolved monomers. The fractional charge of the micelle is not altered by the isotopic composition of the solvent. C_n TAB micelles are found to be drier than are micelles formed by the corresponding sodium alkyl sulfates and this results in a larger solvent effect for the quaternary ammonium bromides.

References

Give references if the work has been published or submitted to conferences, symposia, etc.
J. PHYS. CHEM. (in press).

Report of Measurements Carried Out at the NCSASRInstrument(s) 30-M SANSTitle The Effect of Substitution of Hydrogen by Fluorine on the Structure of Aqueous Sodium Octanoate Micelles as Seen by Small-Angle Neutron ScatteringResearch Sponsor Univ. VA/3M/NSF/DOE

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

Richard R.M. JonesStuart S. Berr

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Fluorinated surfactants are more hydrophobic than their protiated counterparts as is evidenced by their smaller cmc's and larger surface activity. The charge (Z) and aggregation number (N) are determined for $C_7F_{15}COONa$ as a function of surfactant concentration by small-angle neutron scattering (SANS). The fluorine atoms provide excellent contrast between the micelles and the aqueous (1H_2O) solvent. The values for Z and N are compared to previously determined values for $C_7H_{15}COONa$. N for the fluorinated surfactant is found to be greater than twice that of the protiated one. The fluorinated micelles are well described by a spherical micelle model in which all of the alkyl tails reside in a water-free core.

References

Give references if the work has been published or submitted to conferences, symposia, etc.
Dissertation for the degree of Doctor of Philosophy, Wake Forest University, NC

Report of Measurements Carried Out at the NCSASR

Instrument(s) _____

Title Analytical Structure Function of a Polydisperse Percus-Yevick Fluid and
Schulz (Gamma) Distributed DiametersResearch Sponsor DOE/NSF/Univ. Palermo Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

W. L. GriffithR. TrioloA. Compere

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Analytical expressions for the static structure function for a polydisperse Percus-Yevick fluid with Schulz (gamma) distributed particle diameters have been obtained. Results obtained with the expression for selected width factors and particle densities are presented.

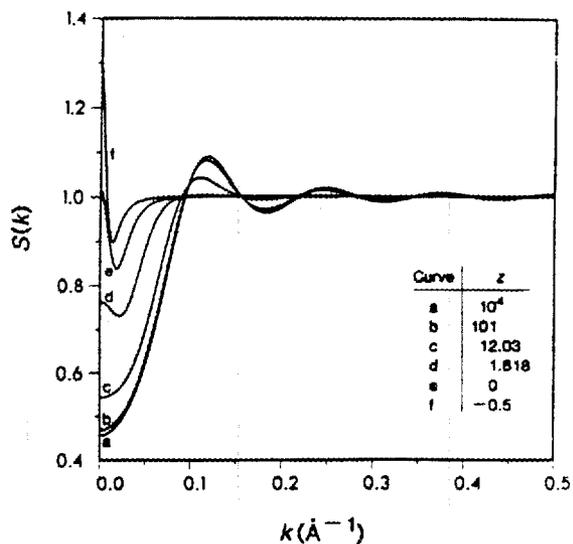


FIG. 1. Polydisperse structure functions calculated for selected Schulz width parameters z and a packing fraction, $\eta = 0.1$.

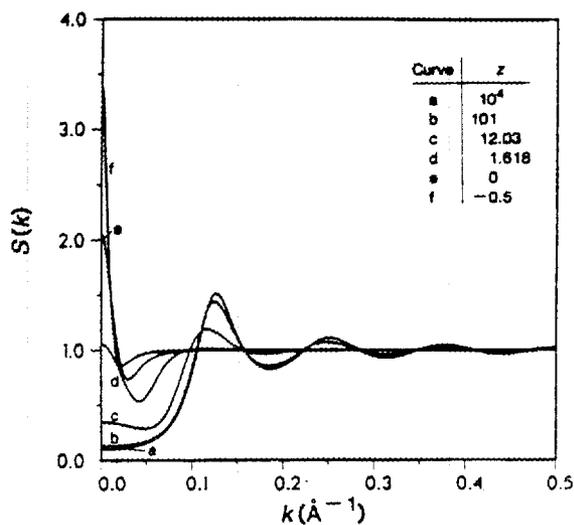


FIG. 2. Polydisperse structure functions calculated for selected Schulz width parameters z and a packing fraction $\eta = 0.3$.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Phys. Rev. A35, 2200 (1987).

Euchem Conf. on Microaggregates in Homogeneous Solution, Reactivity and Structure, June 1987, Assis (Italy).

Report of Measurements Carried Out at the NCSASR

Instrument(s) _____

Title Analytical Scattering Function of a Polydisperse Percus-Yevick Fluid with
with Schulz- (Γ -) Distributed DiametersResearch Sponsor DOE/NSF/Univ. Palermo Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

W. L. GriffithR. TrioloA. Compere

To Be Completed by ORNL

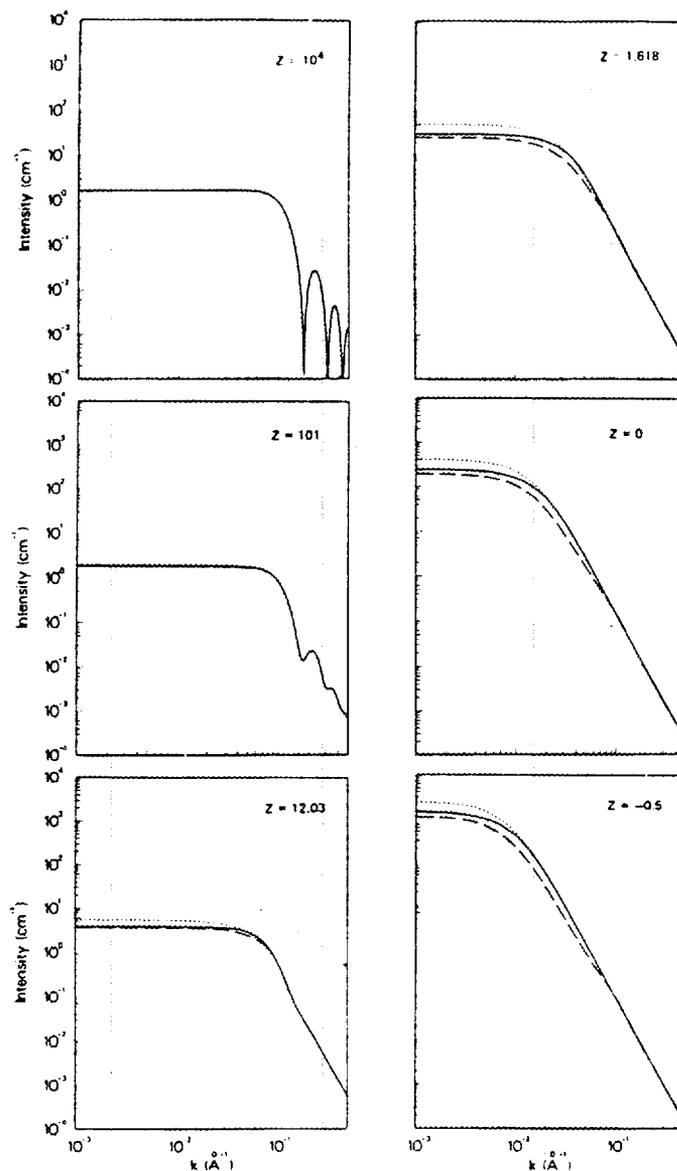
Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Analytical expressions for the scattering function for a polydisperse Percus-Yevick fluid with Schulz- (Γ -) distributed particle diameters have been obtained. Results obtained with the expression for selected width factors and particle densities are presented. Comparisons have been made with approximations routinely used to model small-angle scattering curves. The expression derived is shown to yield the static structure function as a special case.



Scattering intensity calculated for selected Schulz width parameters z and a packing fraction $\eta=0.1$. Legend: analytical solution, solid line; model-*A* approximation, dotted line; model-*B* approximation, dashed line.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Phys. Rev. A35, 2200 (1987).

Euchem Conf. on Microaggregates in Homogeneous Solution, Reactivity and Structure, June 1987, Assisi (Italy).

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30-M SANS

Title A Small Angle Neutron Scattering (SANS) Study of Micellar Structure and Growth of
A Straight-Chain Benzene Sulfonate: Comparison with an Isomeric Branched Chain
Surfactant

Research Sponsor U. Palermo, ORNL, and UT

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

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R. Triolo

Patience C. Ho, J. S. Johnson Jr.

L. J. Magid, P. Butler, and K. A. Payne

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Sodium p-n-dodecylbenzenesulfonate solutions have been studied by means of small angle neutron scattering (SANS) measurements at 65°C as a function of the surfactant concentration, as a function of the contrast of the solvent and as a function of the concentration of added electrolyte. In addition micelles of the isomeric branched chain surfactant sodium p-1-(pentyl-heptyl)benzenesulfonate have been studied at the same temperature as a function of the contrast of the solvent and as a function of the concentration of added electrolyte to compare the structure and the micellar growth of the two surfactants. Good fits to the experimental results have been obtained by calculating the structure factor by means of the mean spherical approximation (MSA) using a screened coulombic potential plus hard core repulsions. Several different models have been used to calculate the particle form factor. For some of the models, the measured geometry and the charge of the aggregates are, within the experimental uncertainties, independent of the contrast between the micelles and the solvent. The thickness of the shell which surrounds the hydrocarbon core implies a rough micellar surface for both surfactants; thus we propose that the planar phenyl group functions as a sort of supplementary head group, leading to a thicker polar shell.

References

Give references if the work has been published or submitted to conferences, symposia, etc.
J. Colloid and Interface Science 116, 200 (1987).

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30 m SANS

Title NON-EQUILIBRIUM FRACTAL STRUCTURES NEAR CRITICAL POINTS

Research Sponsor DOE

Grant or Contact No. DE-AC-04-76DP00789

Participants and NCSASR Collaborator(s)

J. P. Wilcoxon, D. W. Schaefer, and

E. W. Kaler

To Be Completed by ORNL

Date Received _____

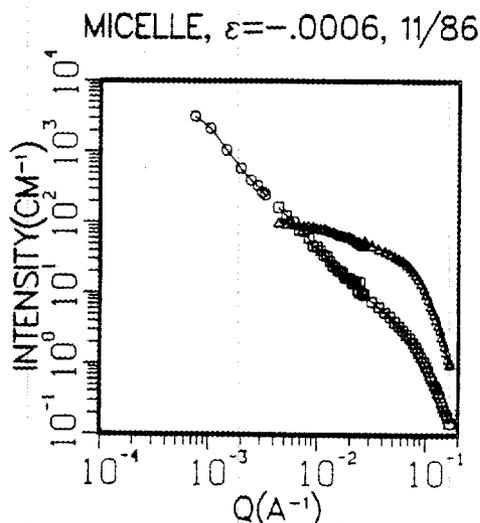
Proposal No. _____

Date of Experiment(s) _____

Report

SANS measurements in the two phase region near the critical point of a non-ionic surfactant system ($C_{12}E_6$ in D_2O) have been combined with previously obtained data taken by static light scattering to demonstrate that non-equilibrium structures develop whose scattering intensity deviates significantly from the simple long-wavelength Ornstein-Zernike form $I \sim Q^{-2}$ found in the single phase region. This deviation is first observed even in the single phase region very near the critical point and is likely due to the reversible formation of aggregates, whose elementary constituents are themselves spherical aggregates (micelles). Meanwhile, the single particle form factor retains the characteristics observed far from the critical point. These fractal correlations in space eventually extend to length scales of greater than 2000 Å in the early (less than 2 hours) stages of the very slow phase separation process. (Equilibration time ~ 24 hrs). Figure 1 shows a comparison of a critical and off-critical temperature quench performed in a tall scattering cell which allowed observation of both coexisting phases in the two phase region. We observed the formation of fractal clusters of micelles in both surfactant poor and surfactant rich regions of the scattering cell. The scattering behavior was identical in shape differing solely in the total intensity (due the smaller amount of micelles present in the poor phase). Finally, we observed that the small Q region of the scattering curves flattened out with quench time as these self-similar correlations in space decrease in length scale. Continuing to follow this evolution to equilibrium via light scattering, we observed that all remnants of the fractal structures are absent on length scales from 300 to 3000 Å, and that the equilibrium structures consist of small ordinary micelles with weak interparticle interactions (short correlation length). Furthermore, a change in individual micelle form factor was observed upon quenching into the two phase region indicating the order parameter (micelle number density) is not conserved across the phase boundary. The importance of proximity to the critical point is demonstrated by comparison of these results with the off-critical (15% wt) quench also shown in Fig. 1. No intermediate or long-range fractal correlations are observed in this case.

Fig. 1. Absolute intensity vs. wavevector (Q) for the $C_{12}E_6$ micelle system shallowly ($T=0.1^\circ C$) quenched into the two-phase region. In the early stages (time 1 hr.) of phase separation. The scattering follows a power law in Q for on-critical (circles, squares) but not for off-critical (triangles) quenches.



References

Give references if the work has been published or submitted to conferences, symposia, etc.

J. P. Wilcoxon, D. W. Schaefer, and E. W. Kaler, "Equilibrium and Non-Equilibrium Aggregate Structures Near Critical Points in Micellar Solutions," 61st ACS Colloid and Surface Science Symposium.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30-Meter SANS

Title A Search for the Vesicle-to-Micelle Transition in Aqueous
Didodecyldimethylammonium Acetate Solutions

Research Sponsor NSF Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

L. J. Magid

J. B. Hayter

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Recently Evans and coworkers observed using microscopy populations of vesicles in dilute aqueous dispersions of didodecyldimethylammonium acetate (DDAOAc); with increasing DDAOAc concentration the vesicles disappeared. The surfactant inventory (amount in vesicles plus amount in micelles) was quantitated using a fluorescence quenching technique; however, the scattering data reported here established that the interpretation of the fluorescence data was in error. The inventory has recently been redetermined (ref. 1); there are in fact essentially no vesicles in the surfactant solutions studied by SANS. The original inventory indicated that from 5 to 100 mM DDAOAc, the percent of surfactant present in the vesicles declined from 68 to 0%. Neither the Q dependence of the scattering nor its magnitude supports the original contention.

Figure 1 shows the scattering curves, which are typical of those displayed by dilute solutions of strongly interacting charged micelles. For the 5 and 61 mM samples, measurements were extended to a Q_{\min} of 0.01 \AA^{-1} in order to detect scattering from vesicles if present.

Figure 2 compares the experimental scattering curve for 5 mM DDAOAc to the computed scattering for a mixed vesicle-micelle population. The vesicles were assumed to have inner compartments (Gaussian distribution) of mean radius \bar{R} and std. deviation $0.26 \cdot \bar{R}$; the bilayer was assumed to be 26Å thick. The vesicle form factor has a single shoulder (from the "shell" spectrum) which shifts to lower Q as \bar{R} increases. (The peak at lowest Q comes from the micellar structure factor.) For $\bar{R} = 100\text{Å}$, the shoulder occurs at the experimental Q_{peak} , but the calculated intensity at $Q < Q_{\text{peak}}$ bears no relation to the experimental. In addition, the experimental intensity is higher than the calculated beyond $Q = 0.07 \text{Å}^{-1}$; this occurs because only 32% of the total DDAOAc was assumed to be in the micelles, when in fact all of it is already at 5 mM.

Each of the scattering curves is fit well if one assumes that all of the surfactant (above the cmc) is present in micellar rather than vesicular form; Figure 3 illustrates a typical fit. The adjustable parameters were the micellar aggregation numbers (n), apparent charges and axial ratio (the micelles are prolate ellipsoids); note that the absolute scattered intensities are correctly predicted. From 5 to 100 mM DDAOAc, n increase from 38 to 118; the micellar ionization is about 50% at 5 and 10 mM, which is typical for micelles of double-chained surfactants.

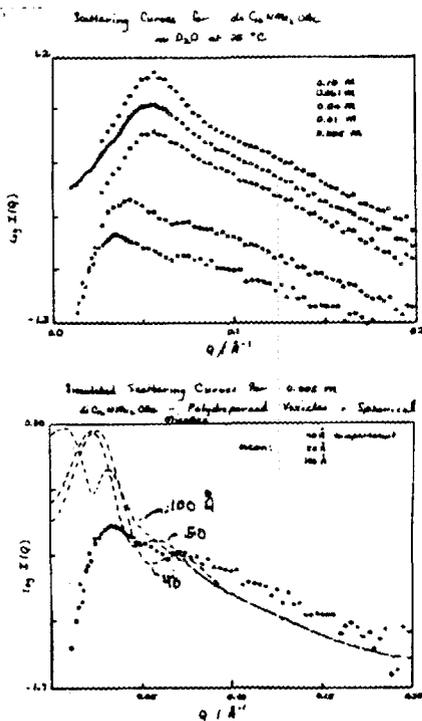


Figure 2.

Figure 1.

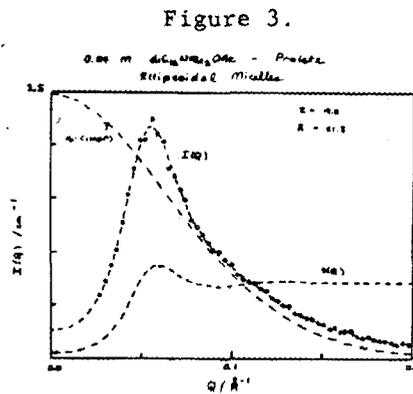


Figure 3.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Ref. 1: D. D. Miller, G. G. Warr, D. F. Evans and L. J. Magid, manuscript in preparation.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30-M SANS and 10-M SANS

Title Small Angle Neutron Scattering from Micelles of Alkylpolyoxyethylene Sulfate:
Effect of Chain Length

Research Sponsor DOE/NSF/Univ. Palermo

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

E. Caponetti

R. Triolo

J. S. Johnson Jr.

To Be Completed by ORNL

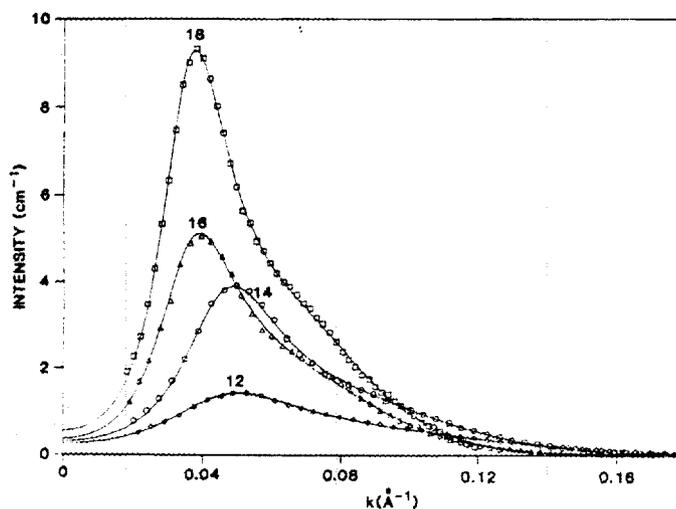
Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Small-angle neutron scattering (SANS) data have been obtained for (i) a series of solutions of $C_m H_{2m+1} (OCH_2-CH_2)_2 SO_4 Na$, for $m = 18, 16,$ and 14 ; (ii) an approximately $0.07M$ solution of $C_{14} H_{29} (OCH_2-CH_2)_2 SO_4 Na$ to which different amounts of $NaCl$ were added; and (iii) a series of solutions of variable concentration of $C_{12} H_{25} (OCH_2-CH_2)_2 SO_4 Na$. The increase of the number of carbon atoms of the hydrocarbon chain produces a noticeable increase of the aggregation number of the micelles, while the salt tolerance decreases with increasing m . All the data can be described in terms of a monodispersed, charged, hard-spheres model interacting via a screened Coulombic potential, except the run at highest salt concentration, for which an ellipsoid model gives better results. The figure shows fits of the data with $m=12, 14, 16,$ and 18 .



References

Give references if the work has been published or submitted to conferences, symposia, etc.

J. Sol. Chem. 16, 295 (1987).

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30-m

Title SANS Studies of Middle Phase Microemulsions

Research Sponsor NSF Grant or Contact No. PYIA 8351179

Participants and NCSASR Collaborator(s)
E.W. Kaler
J.F. Billman
J.P. Wilcoxon

To Be Completed by ORNL
Date Received _____
Proposal No. _____
Date of Experiment(s) _____

Report

The 30-m. SANS instrument has been used to study the structure of a five-component microemulsion (sodium 4-(1'-heptylnonyl) benzene-sulfonate; i-butanol; NaCl; D₂O; various alkanes). Recently the effect of hydrocarbon chain length upon the progression of microemulsion structure as the salinity of the brine phase varies was investigated. The evolution of microstructure in the dodecane system as salinity changes has been determined previously using SANS and has been reported.¹⁻² In these latest experiments microemulsions formed with the even, normal hydrocarbons (octane-hexadecane) were studied. The scattered intensities of most of the samples were recorded for a scattering vector range of 0.003-0.12 Å⁻¹.

The scattered intensities for all microemulsions were observed to obey Porod's law, indicating that the interface between the oil and water domains is sharp. The area per unit volume of this surfactant/co-surfactant rich interface has been calculated to be approximately a constant and independent of salinity and hydrocarbon type. Given this information, the area/surfactant molecule is calculated to vary inversely with both hydrocarbon chain length and salinity.

The observed scattering patterns of the microemulsion samples have been successfully modeled when the microemulsion is extremely rich in either water or oil. Within these regimes the observed scattering is consistent with models of the microemulsion as a dispersion of droplets. The scattering of the water-in-oil regime (aqueous fraction less than 25%) is in agreement with that predicted by a model treating the water droplets as polydisperse hard spheres. This model successfully describes the scattering patterns observed for the shorter hydrocarbons (octane-dodecane). The scattering patterns of the microemulsions formed with the longer hydrocarbons are inconsistent with this hard sphere model as these patterns possess an anomalous low-q behavior suggestive of critical scattering phenomena. The scattering patterns of the oil-in-water microemulsions (oleic fraction less than 25%) are consistent with that predicted for a dispersion of charged prolate ellipsoids for all hydrocarbon chain lengths. This later model considers the particles as macroions (J. B. Hayter, *Farad. Discuss. Chem. Soc.* 11, 76, 7, 1983) and assumes that the orientations and separations of the particles are independent. The aspect ratio of the ellipsoids is approximately 3.5 for all compositions.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

- 1) N. Y. J. Chang, J. F. Billman, R. A. Licklider, and E. W. Kaler in "Statistical Thermodynamics of Micellar and Microemulsion Systems", Chen, H.-S. ed., Springer-Verlag, 1986
- 2) J. F. Billman, E. W. Kaler, "Water-in-Oil and Oil-in-Water Microemulsions", To be submitted.

Report of Measurements Carried Out at the NCSASRInstrument(s) 10-m SAXSTitle Structure of Cubic Phase in DDAB / H₂O / Oil SystemsResearch Sponsor ANU, DOE Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

I. N. Zemb Australian National UniversityJ. B. Hayter Oak Ridge National Laboratory

To Be Completed by ORNL

Date Received 3/16/87Proposal No. 401Date of Experiment(s) 3/9-13/87

Report

In the DDAB/ water / hexene ternary phase diagram, a new cubic phase of uncommon behaviour has recently been identified: this cubic phase, instead of being located in a very narrow concentration range, extends over the whole composition range, from the oil to the water corner of the phase diagram. The aim of this experiment was to obtain a first insight into its structure. Five samples were measured, on an absolute scale, using water as a reference. The composition of the samples was in the range DDAB: 20-55%, H₂O: 3-14%, Hexene: 77-31%. As a counter-experiment, a lamellar sample was also prepared by evaporating hexene from the sample with highest hexene content. The low scattering of water in SAXS is of the same order of magnitude as that from the samples and therefore provides an ideal calibration. The scattering was measured at 298K and 343K, using two Sample-Detector distances to obtain an overall ratio $Q_{min}:Q_{max}$ of 0.15:5.0 nm⁻¹. The following observations were made:

1. For all samples studied, the expected symmetry was found. The cubic lattice constants varied from $a=2.8$ nm to $a=13.4$ nm on going from lowest to highest hexene content. Detailed investigation of the spacing variation with composition should give geometric information on the water/oil interface.

2. All spectra exhibit, as well as Bragg peaks, broad diffuse scattering extending to high Q-values. Unfortunately, due to high parasitic scattering, this result is not yet quantitative and needs to be confirmed with an improved experimental geometry. We do not know if the scattering at high angle is a modulation of the form factor of the elementary cell by higher order Bragg peaks, or if the Bragg peaks are so broad that they overlap. In the first case, one would have more precision in spacing measurements, whereas in the second case, one would face a new type of structure, like a supermolecular fluid, where the cubic symmetry is confined to remain local, due to a very high number of defects. At the present stage, it is not possible to discriminate between these two possible structures. It is striking to see the similarity of the scattering at large angles of a "cubic" phase and a disordered microemulsion.

3. At high water content, both in the adjacent lamellar phase and in the cubic phase, the viscosity decreases, allowing relaxation of the system to a monocrystal of macroscopic size: Bragg spots are seen on the 2-D detector. Even after shaking the sample, the Bragg scattering indicates a monocrystalline structure of the order of one mm. In the case of the lamellar phase, lamellae usually orient parallel to the Kapton cell windows, but we have observed perpendicular orientation as well (Fig. 1). In the case of cubic symmetry, both $\langle 100 \rangle$ and $\langle 111 \rangle$ planes parallel to the sample windows have been observed. We have also observed a sample in which lamellar and cubic phases coexist: the microscopic directions were correlated, suggesting that the lamellar phase can grow out of the cubic phase, in correlated directions.

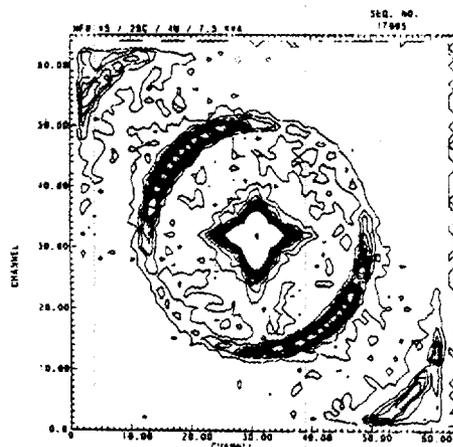


Figure 1. Scattering from lamellar sample at 298K, showing the orientation of the lamellae perpendicular to the cell windows.

4. The sample with the smallest spacing, near the phase boundary with the L2-phase, exhibits a cubic-to-microemulsion phase transition on heating. In this case, we know precisely the characteristic surface, and this melting transition of a cubic phase towards a microemulsion should be studied with small temperature intervals together with a precise calorimetric measurement.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) SMALL ANGLE X-RAY SCATTERING SPECTROMETER

Title DIRECT MEASUREMENTS OF COUNTERION CONDENSATION OF A CHARGED COMB-SHAPED
COPOLYMER IN WATER STUDIED BY SAXS

Research Sponsor S. C. Johnson & Son, Inc., and NSF grant Grant or Contact No. _____
to S. H. Chen

Participants and NCSASR Collaborator(s)

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S. H. Chen (MIT)

L. B. Shih (SCJ)

J. S. Lin (ORNL)

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) have been used to determine the distribution of counterions and the structure of aggregates formed by a charged, comb-shaped copolymer, poly(1-octadecene-co-maleic anhydride), abbreviated as PODMA, in D₂O. The copolymer is fully neutralized with CsOH and the structure of aggregates in solution is determined by SANS as cylindrical-shaped with a radius of 20 Å and a length of 110 Å and the number of repeating units of the copolymer per micelle 233 at low copolymer concentrations. At full neutralization, each repeating unit carries two negative charges and the linear charge density at the micellar surface is a function of the added anionic surfactant, sodium dodecyl sulfate. Since the electron densities of the micellar core and the bulk solvent are nearly equal, SAXS intensity distribution function is a direct Bessel transform of the Cs ion distribution around the cylindrical micelles. In our system, the dimensionless linear charge density parameter, ξ , is varied from 1.4 to 3.0 where $\xi = l_B/b$, where l_B is the Bjerrum length and b the linear spacing between unit charges on micellar surface. The data are analyzed according to both Manning's counterion condensation theory and the solution of the cylindrical Poisson-Boltzmann equation.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

A poster has been submitted to the Summer, 1987 Gordon Conferences on "Ion-Containing Polymers".

Report of Measurements Carried Out at the NCSASRInstrument(s) 30-M SANSTitle Structure of PhosphofructokinaseResearch Sponsor NIHGrant or Contact No. NS-14269
Am 21489

Participants and NCSASR Collaborator(s)

J. C. LeeT. G. ConslerGuang-Zuan CaiG. J. Bunick and E. C. Uberbacher

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Phosphofructokinase (PFK) (ATP: D-fructose 6-phosphate 1-phosphotransferase, EC 2.7.1.11) catalyzes the transfer of the terminal phosphate of ATP to the C-1 hydroxy of fructose 6-phosphate to produce fructose 1,6-diphosphate. Since the catalyzed reaction represents a key regulatory point in the regulation, e.g., conformational changes, subunit assembly, and post-translational modifications.

One of the most significant conformational changes involves the substantial change in sedimentation coefficient of the tetrameric form of PFK during its conversion from an inactive to that of an active form (1-4).

Active enzyme centrifugation studies at pH 7.0 and $23 \pm 1^\circ\text{C}$ showed that PFK sediments as a single component with a sedimentation coefficient of 12.2 ± 0.5 S. Boundary sedimentation studies of PFK in the presence of 1.0 mM fructose-6-phosphate, 0.1 mM adenylyl imidodiphosphate at pH 7.0 and $23 \pm 1^\circ\text{C}$ showed that the sedimentation coefficient of PFK remains constant within the range of protein concentration studied and assumes a value of 12.4 S. The molecular weights of the subunit and the 12.4 S component were measured by sedimentation equilibrium yielding values of 83,000 and 330,000 for the monomeric and polymeric species, respectively.

The physical properties of the inactivated form (reversible inactivated by oxidized glutathione) were characterized by sedimentation studies. In the presence of saturating amounts of fructose 6-phosphate and the nonhydrolyzable ATP analogue, 5'-adenylyl imidodiphosphate, the inactivated PFK sediments as a 13.5 S component. Sedimentation equilibrium study identifies it to be a tetramer with a molecular weight of 320,000. Although a significant change in the hydrodynamic properties of PFK has been documented, the detail structural features that are associated with this change are not defined. There is no crystallographic information on the rabbit muscle enzyme, hence, small angle neutron scattering was chosen and possible domain-interactions in the regulation of normal functioning of this protein.

The inactivated form of PFK was prepared at concentrations of 5 and 10 mg/ml in both H_2O and D_2O buffers. The active form of PFK was prepared at 5 and 10 mg/ml in H_2O buffer, and at 9 and 14 mg/ml in D_2O buffer. The presence of a precipitate was noted in some samples after data collection, especially in the H_2O samples containing inactive enzyme. Guinier plots for all samples were nonlinear. R_g 's calculated over selected regions in the Guinier plots were 66 Å and 70 Å for the inactive and active enzyme, respectively. These results are contrary to sedimentation experiments which indicate that the active form is the more compact structure.

The aggregation and precipitation observed in this neutron scattering experiment was unexpected based upon the prior sedimentation studies. Apparently, the enzyme concentrations in this study were significantly higher than in the sedimentation experiments or the small percentage of high M.W. aggregates present in the samples went undetected in the type of sedimentation experiments performed. This experiment should be repeated after modifying the buffer conditions to eliminate aggregation at the enzyme concentrations required for neutron scattering.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30M Small Angle Neutron Scattering

Title Polydispersity in Bovine Nasal Cartilage Proteoglycan from Small Angle Neutron Scattering

Research Sponsor Stevens Institute of Technology Grant or Contact No. nil

Participants and NCSASR Collaborator(s)

S. S. Stivala and A. Patel

Stevens Institute of Technology

J.D. Gregory and E. C. Uberbacher, NCSASR

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report The AIDI preparation for proteoglycan subunit (PGS) was further purified by eluting through a column of sepharose CL-2B equilibrated with 0.5M lithium acetate of PH 6.2. The three fractions, 1st, 2nd and 3rd, of the polydisperse preparation were studied by small angle neutron scattering that yielded molecular weight, M_w , the radius of gyration, (R_g) and the radius of gyration of the cross section, (R_g^c) for three fractions, i.e., $M_w = 7.06, 0.96, 0.48 \times 10^6$, $R_g = 796, 674, 554 \text{ \AA}$ and $R_g^c = 528, 404, 255 \text{ \AA}$, respectively.

It is clear from the various methods used in obtaining physico chemical data on bovine nasal cartilage PGS that its M_w lies in the range of $2.5 - 5 \times 10^6 \text{ g/mol}$. The variation may be due, in part, to (a) range of polydispersity of various preparations (b) approximations used in various methods (c) variation in the nature or condition of the various bovine nasal cartilage tissues used for extraction of PGS (d) calculations based on assumed hydrodynamic models (e) the particular fraction of the polydisperse preparation taken and (f) insufficient addition of supporting electrolyte. Therefore, we intended to estimate the extent of polydispersity of bovine nasal cartilage proteoglycan.

Neutron scattering measurements were performed on the 30 m small angle neutron scattering instrument at the National Center for Small Angle Scattering Research, Oak Ridge National Laboratory. The instrument selects neutrons of $\lambda = 4.75 \text{ \AA}$ with $\Delta\lambda/\lambda$ of 6%. The detector to sample distance was 17 m which allowed measurement of a large radius of gyration and high molecular weight of PGS. The scattered neutrons were detected by a two dimensional position sensitive ^3He detector with $64 \times 64 \text{ cm}^2$ elements. Sample and buffer were run in a pair of matched quartz cells to avoid error due to cell thickness and transmission. The three fractions were repeatedly run for 4 hr. 40 mins. and scattered intensities were added. The scattering due to buffer was subtracted from that of each fraction, and data were treated as per the general procedure laid down at the National Center for Small Angle Scattering Research.

It is observed that there is a wide range of polydispersity in AIDI preparation. This range is quite comparable to the range of molecular weight i.e., less than 1.0×10^6 to greater than 4.0×10^6 , observed by others. Interestingly, the average value of M (2.83×10^6) of the three fractions is closely in agreement with the M values (2.25, 2.55 and 2.90×10^6) reported by us from small angle x-ray scattering (SAXS) study of different salts of PGS. In our work on SAXS, we have used 2nd fraction to minimize the polydispersity. Since the scattering experiments determine the weight average molecular weight and the value of M strongly depends on how one chooses the boundary for three different fractions, the M values obtained in this work are acceptable. As polydispersity depends on many factors this study singles out the polydispersity that may arise due to boundary selection for three different fractions and helps to focus the attention on other factors.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

This work was presented in the poster session of the Third IPNS User Meeting, Dec. 8-9, 1986, Argonne National Laboratory.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30-m small angle neutron-scattering instrument

Title Small-angle Neutron-scattering and Electron Microscopy studies of the
Chicken Liver Fatty Acid Synthase

Research Sponsor NIH and NSF Grant or Contact No. _____

NIH GM 19091; NSF DMR-7724459

Participants and NCSASR Collaborator(s)

James K. Stoops

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Edward C. Uberbacher - NCSASR

Gerard J. Bunick - NCSASR

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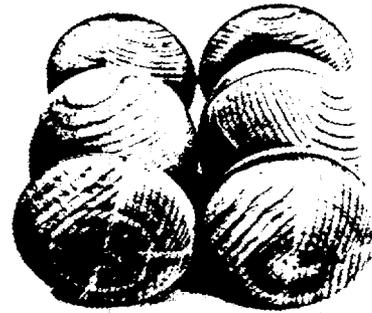
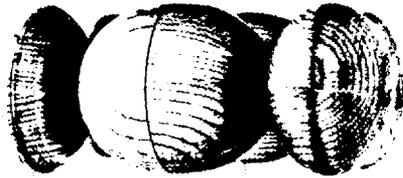
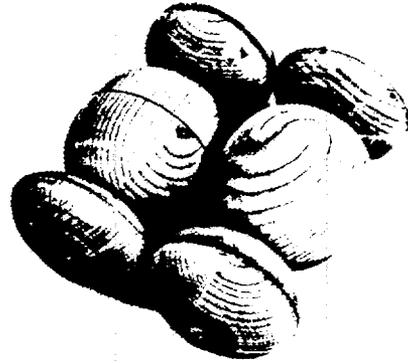
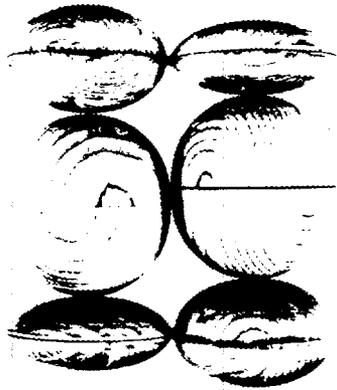
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Proposal No. _____

Date of Experiment(s) _____

Report

A structural model for the chicken liver fatty acid synthase is proposed based on electron microscope and small-angle neutron-scattering studies of the enzyme. The model (see Figure) has the overall appearance of two side by side cylinders with dimensions of $160 \times 146 \times 73 \text{ \AA}$, with each subunit 160 \AA in length and 73 \AA in diameter. The model was constructed by dividing each cylinder into three domains having lengths of 32, 82, and 46 \AA , with the domain structures in the two subunits being related to each other by a dyad axis. The model is consistent with chemical cross-linking studies which indicated that the subunits are arranged in a head to tail fashion. The cross-linking studies further showed that the β -ketoacyl synthase active site contains a cysteine and a pantetheine residue from adjacent subunits. It is proposed that the domains which catalyze the addition of C_2 units from malonate to the growing fatty acid chain lie in the crevice between the two subunits and that the two independent sets of fatty acid-synthesizing centers lie on the major axis of the model on opposite ends of the molecular dyad.



References

Give references if the work has been published or submitted to conferences, symposia, etc.

James K. Stoops, Salih J. Wakil, Edward C. Uberbacher, and Gerard J. Bunick
J. Biol. Chem. 262, 10246-10251 (1987).

J. K. Stoops, S. J. Wakil, E. C. Uberbacher, and G. J. Bunick. Electron microscope and small angle neutron scattering studies of chicken liver fatty acid synthase. *Federation Proceedings* 45, 1532 (1986).

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30 -m SANS Camera

Title Effects of Ligands on the Shape of Rabbit Muscle Pyruvate Kinase

Research Sponsor NIH Grant or Contact No. DK-21489

Participants and NCSASR Collaborator(s)
Edward C. Uberbacher
Gerald J. Bunick

To Be Completed by ORNL
Date Received _____
Proposal No. _____
Date of Experiment(s) _____

Report

The effects of ligands on the structure of rabbit muscle pyruvate kinase were studied by small angle neutron scattering. The radius of gyration R_G , decreases by about 1A in the presence of the substrate, phosphoenolpyruvate, but increases by about the same magnitude in the presence of the allosteric inhibitor, phenylalanine. With increasing pH or in the absence of Mg^{++} and K^+ , the R_G of pyruvate kinase increases. Hence, there is a 2A difference in R_G between two alternate conformations. Length distribution analysis indicates that under all experimental conditions which increase the radius of gyration, there is a pronounced increase observed in the probability for interatomic distance between 80-110A. These small angle neutron scattering results indicate a "contraction" and "expansion" of the enzyme when it transforms between its active and inactive forms. Using the α -carbon coordinates of crystalline cat muscle pyruvate kinase, a length distribution profile was calculated, and it matches the scattering profile of the inactive form. These observations are expected since the crystals were grown in the absence of divalent cations (Stuart et al., J. Mol. Biol. 134, 109-142, 1979). Hence, results from neutron scattering, X-ray crystallographic and sedimentation studies (Oberfelder et al., Biochemistry 23, 3822-3826, 1984) are totally consistent with each other.

With the aid of computer modeling, the crystal structure has been manipulated in order to effect changes that are consistent with the conformational change described by the solution scattering data. The structural manipulation involves the rotation of the B domain relative to the A domain, leading to the closure of the cleft between these domains. These manipulations resulted in the generation of new sets of atomic (C- α) coordinates, which were utilized in calculations, the result of which compared favorably with the solution data.

Submitted to J. Biol. Chem.

References

Preliminary reports published in Biophys. J. 51, 81a, 1987.

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30-M SANS

Title Analysis of phase structure of bacterial lipopolysaccharide and lipid A

Research Sponsor Cystic Fibrosis Foundation

Grant or Contact No. G136-01

Participants and NCSASR Collaborator(s)

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Biochemistry Department, Michigan State Univ.

2. John B. Hayter

Solid State Division, ORNL

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

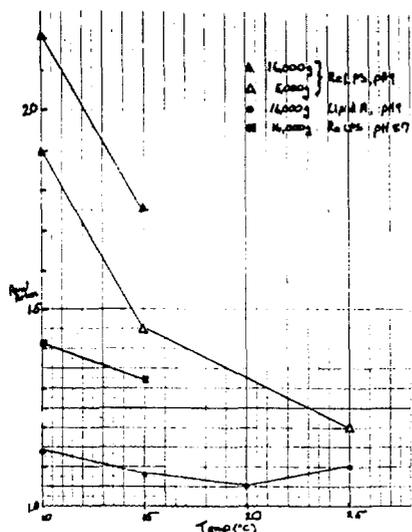


FIGURE 1

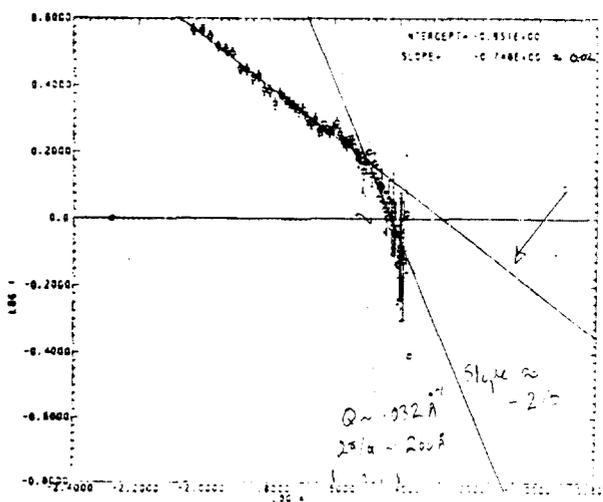


FIGURE 2

Our studies, carried out 10/14/86-10/16/86, were extensions of work carried out a year before on deep rough (Re chemotype) LPS. In our first studies (1), we analyzed the particle size and shape of LPS aggregates from Escherichia coli D21f2 using static neutron scattering measurements and analysis of anisotropic scatter of aggregates aligned in a shear cell. In these studies, we found that the scattering patterns were dependent on pH, and the ability to align the aggregates increased with decreasing temperature. From our results, we proposed that at pH 9.1 this LPS formed a unique aggregate, paired tubes of uniform separation.

In our experiments last October, we analyzed the particle size and shape of two chemically related molecules and attempted to determine if the aggregates showed similar changes with pH and temperature. The sample studied in most detail was a derivative of the ReLPS, diphosphoryl lipid A. This molecule was formed by cleaving two sugar acid residues from the ReLPS samples. The scattering intensity results of lipid A at 25°C at pH 7.5 and 9.1, when plotted on log I vs. log K plots, showed a single line with a slope of -2, consistent with a random coil structure. In addition, the scattering data of the pH 9.1 sample, when analyzed with a Kratky plot, yielded a straight line again, consistent with a random coil. The sample at pH 9 was rather viscous and could be subjected to relatively high shear forces in the shear cell.

Analysis of the anisotropy of scatter of this sample at 4 temperatures also indicates an aggregate that did not readily align itself (Fig. 1). We propose that upon removal of the two acidic groups from the ReLPS, the lipid A head group decreases its curvature as a result of decreased charge repulsion, and the aggregates were more like floppy random coils.

The second sample measured, LPS from strain D21, has an additional 7-8 sugars and 5 phosphate groups compared to the ReLPS. Thus, we supposed that with an increased head group size and charge, at pH values above the pKa's of the phosphates, this LPS would also form tubular micelles. When the anisotropy of the scatter of samples in the shear cell were measured, it was seen that the RaLPS was more aligned than the lipid A, but not as much as the ReLPS analyzed under similar conditions (Fig. 1). Even more surprising were the analyses of the static scattering measurements. At 15°C, the RaLPS at pH 8.7 showed a Kratky plot of scattering with two lines, one with slope of -2.3 and a second with slope of -0.75 (Fig. 2). Thus, the LPS aggregate shape of RaLPS, at high pH, is distinctly different from that of ReLPS and lipid A. Future work will be required to better define this particle shape and how it changes with pH and temperature.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Hayter, J.B., M. Rivera and E. J. McGroarty. 1987. Neutron Scattering Analysis of Bacterial Lipopolysaccharide Phase Structure. Changes at High pH. *J. Biol. Chem.* 262, 5100-5105.

Report of Measurements Carried Out at the NCSASRInstrument(s) 30 - m SANS CameraTitle Structure of PhosphofructokinaseResearch Sponsor NIHGrant or Contact No. DK-21489

Participants and NCSASR Collaborator(s)

Edward C. UberbacherGerald J. Bunick**To Be Completed by ORNL**

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Rabbit muscle phosphofructokinase (PFK) was subjected to small-angle neutron scattering in 25 mM Tris-carbonate, 6 mM $MgCl_2$, 3 mM $(NH_4)_2SO_4$, 1 mM EDTA at pH 7.0, 23°C. In order to detect the difference between the active and inactive forms of the enzyme the study was conducted in the presence of substrates i.e. 1 mM fructose 6-phosphate and 1 mM AMP-PNP, a non-hydrolyzable ATP analogue. The inactive conformation was achieved by exposing the enzyme to oxidized glutathione.

Samples at approximately 5 to 15 mg/ml were dialyzed against buffers in >90% and 0% D_2O . The scattering data were analyzed by the Guinier plots to yield apparent² radii of gyration, R_G . In all circumstances these plots showed pronounced curvature indicating heterogeneity, most likely self-aggregation as shown by Fig. 1A and B. The limiting slopes at the low angles of observation were dependent on protein concentration, as summarized in Table I.

Since the system showed significant amount of self-aggregation under the experimental conditions, the scattering intensities not only contain information on the shape of the enzyme but also change in mass. Hence, an extensive study on protein concentration dependence is necessary to resolve the contribution of self-aggregation from the data before any information on the conformational change can be extracted.

Table I

Sample	Radius of Gyration in Å	
	H_2O	D_2O
Inactivated		
5 mg/ml	65	65
10 mg/ml	72	67
Activated		
9 mg/ml		71
14 mg/ml		71
5 mg/ml	68	
10 mg/ml	68	

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) The 30-m SANS camera. $\lambda = 4.75 \text{ \AA}$

Title Investigation of the Shape of the Active Form of Eukaryotic Fatty Acid Synthetase by Small Angle Neutron Scattering

Research Sponsor National Institute of General Medical Sciences Grant or Contact No. GM19091

Participants and NCSASR Collaborator(s)

Dr. James K. Stoops

Dr. G. J. Bunick

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

The purpose of the investigation was to distinguish between two electron microscope models of the chicken liver fatty acid synthase. The enzyme is a homodimer of 480,000 molecular weight and each subunit is known to contain the seven activities involved in fatty acid synthesis: acetyl and malonyl transacylase, acyl carrier protein, β -ketoacyl synthase, β -ketoacyl reductase, β -hydroxylacyl dehydrase, enoyl reductase and thioesterase.

Electron microscope fields are comprised of molecules in various shapes and sizes. The monomer structures could be related to each other by assuming the subunit is rod-like in open form and is capable of nearly closing to form a C. Similarly, the dimeric structures may consist of two rods or two stacked C's and forms between these. The rods measure 200 \AA and 50 \AA on their major and minor axes, respectively. If the rods close to form a ring, the diameter of the ring would be 64 \AA . The C shaped structures in the micrographs have a diameter ranging from 70-100 \AA , representing the degree to which they are closed. These models were distinguished by small angle neutron scattering studies of the active enzyme and resulted in considerable refinement of the electron microscope model of the enzyme. The scattering data

was best fit by a model in which the molecule consists of two side by side elipsoidal cyclinders with overall dimensions of 150 Å X 136 Å X 60 Å. The dimeric structure has a cleft extending the length of the major axis. The elipsoid has major and minor axes of 70 Å and 60 Å, respectively, and there is a 5.16 Å overlap between the two cylinders. Many structural models were considered including those with variable overlapping cylinders, hollow cylinders, and stacked C's, however, these models were inconsistent with the scattering curves. A manuscript for publication of these studies is in preparation.

As a result of the determination of the small angle neutron scattering model of the enzyme it is proposed to continue these studies in order to locate some of the component activity domains in the multifunctional enzyme. The thioesterase domain can be readily isolated from the complex by limited proteolysis followed by gel filtration chromatography. This operation yields an active 35,000 molecular weight thioesterase component and the core enzyme of 420,000 molecular weight with all the activities intact. Small angle neutron scattering studies of these enzymes may result in further refinement of the model of the dimeric enzyme and the determination of the location and structure of the thioesterase domain in the complex.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASRInstrument(s) 10-m SAXSTitle Investigation of the Structural Organization of Fatty
Acid Synthase from Chicken Liver.Research Sponsor National Institute of General
Medical SciencesGrant or Contact No. USPS GM19091

Participants and NCSASR Collaborator(s)

G. J. BUNICKE. C. UBERBACHER**To Be Completed by ORNL**

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

The purpose of this investigation was to determine the distance between the two condensation centers in chicken liver fatty acid synthase using small-angle x-ray scattering and the mercury probe tetrakis(acetoxy-mercuri) methane (TAMM).

A structural model for the enzyme has been proposed based on electron microscopy and small-angle neutron scattering studies (1). The enzyme is a homodimer of 480,000 molecular weight with the subunits organized in a head to tail fashion. Each subunit is approximately 160 Å in length and 73 Å in diameter. The domains which catalyze the addition of C₂ units from malonate to the growing fatty acid chain are thought to lie along the major axis of the molecule in the crevice between the two subunits.

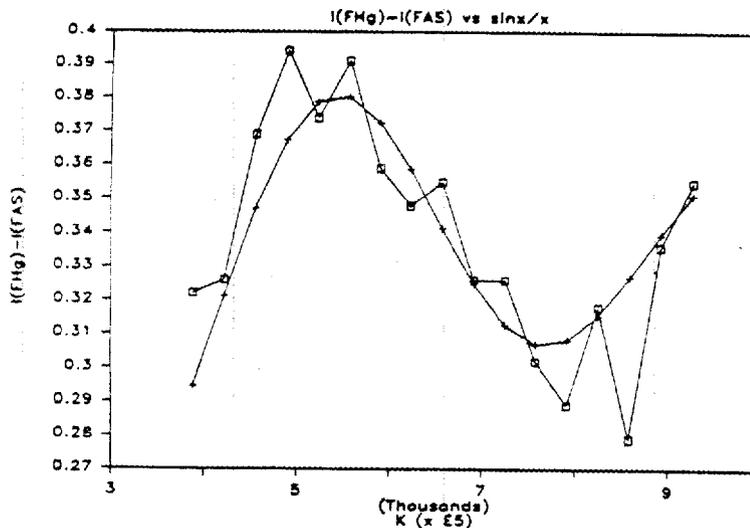
The condensation centers have been shown to contain three reactive thiol groups, two cysteine residues and a pantetheine residue (2). It has been shown that four moles of TAMM bound to the enzyme inactivate it, and that two molecules of TAMM are bound to the reactive thiols at each condensation site. Thus each center of fatty acid synthesis is labelled by eight mercury atoms.

Experimental

Scatter curves were collected on native FAS and heavy atom labelled FAS using the 10-m SAXS instrument. The method of Vainshtein (3) was used to analyze the data. Application of this method consists of calculating the difference curve between the labelled and native enzyme. The resulting curve primarily contains scattering from the markers and also from protein-marker cross terms. In the region of the scatter curve subsidiary maxima the cross term contribution is much less than from the markers. This region of the difference scattering curve displays an oscillatory behavior which can be fit to an equation of the form $(1+\sin(kr)/kr)$ to determine the distance between the markers, r .

Results

The value of r for which the $\sin(x)/x$ function best fit the experimental data is 142 Å. The centers of fatty acid synthesis containing the reactive thiols which the TAMM labelled thus appear to be located along the molecule's major axis near the ends of the 160 Å long enzyme.



Plot of the difference curve (FAS_{Hg}-FAS) in the k range of interest and the $\sin(x)/x$ function calculated for $r=142$ Å.

References

- (1) J. K. Stoops, S. J. Wakil, E. C. Uberbacher, G. J. Bunick (1987) *J. Biol. Chem.* **262**, 10246-10251.
- (2) J. K. Stoops, S. J. Wakil (1982) *J. Biol. Chem.* **257**, 3230-3235.
- (3) B. K. Vainshtein, L. A. Feigin, Yu. M. Lvov, R. I. Gvozdev, S.A. Marakushev, G. I. Likhtenshtein (1980) *Febs Letts.* **116**, 107-110.

Report of Measurements Carried Out at the NCSASRInstrument(s) 30 m SANSTitle Interactions In Mixtures of Poly(ethylene oxide) and
Poly(methyl methacrylate)Research Sponsor IBM Grant or Contact No. _____Participants and NCSASR Collaborator(s)
T. P. Russell
H. Ito
G. D. Wignall**To Be Completed by ORNL**

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

INTERACTIONS IN MIXTURES
OF POLY(ETHYLENE OXIDE) AND POLY(METHYL METHACRYLATE)

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ABSTRACT: Small angle neutron scattering measurements have been performed on mixtures of poly(ethylene oxide), PEO, with proteo and deuterio poly (methyl methacrylate), PMMAH and PMMAD, respectively, to evaluate the Flory-Huggins interaction parameter χ_{AB} . It has been found that χ_{AB} varies from -5×10^{-3} to -1×10^{-3} as the total PMMA concentration increases from 0.3 to 0.7. The temperature dependence of the scattering combined with other results indicate that entropic, rather than enthalpic, contributions dominate χ_{AB} . The magnitude of χ_{AB} is found to be on the same order of magnitude as that expected between PMMAH and PMMAD, particularly at high total concentrations of PMMA. Studies of PMMA at higher scattering vectors show that down to length scales of 25\AA no changes are observed in the conformation of PMMA in the mixtures in comparison to that of PMMA in the bulk. However, pronounced differences are seen at distances less than 25\AA suggesting that some changes in the local conformation of PMMA occur in order to enhance interactions with PEO.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

1. Amer. Phys. Soc., March, 1986.
2. Gordon Conference on Polymer, Poster Session, January, 1986.
3. Macromolecules, accepted, 1987.

Report of Measurements Carried Out at the NCSASR

Instrument(s) Small Angle Neutron Scattering Facility

Title A Deformation-Induced Phase Separation In The Solid State

Research Sponsor NSF INT-8417651

Grant or Contact No. 5-22791

Participants and NCSASR Collaborator(s)

J.M. Lefebvre, R.S. Porter and G.D. Wignall

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

SYNOPSIS

Amorphous polymethylmethacrylate/polyethyleneoxide blends deformed by solid-state coextrusion exhibit anomalous anisotropic small angle neutron scattering patterns in the low q range. It is shown that upon drawing the samples have undergone phase separation to some extent. The resulting structure of the system is characterized by combining scattering techniques with Differential Scanning Calorimetry.

References

Give references if the work has been published or submitted to conferences, symposia, etc.
Journal of Materials Science, to be published in June 1987.

Report of Measurements Carried Out at the NCSASRInstrument(s) 30 M SANS FacilityTitle Morphological Characterization of Block Copolymer/Homopolymer Blends

Research Sponsor _____

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

X. QuanG.D. WignallI. GancarzJ.T. Koberstein**To Be Completed by ORNL**

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

The properties and morphology of block copolymers which have been blended with a homopolymer diluent have been widely studied due to the importance of these blends in various processing and mechanical applications. However, there has been less work on the structure of the blends on a molecular level since it is difficult to separate the contributions of the components, especially when the homopolymer has the same chemical structure as one of the blocks. We have begun a series of small-angle neutron (SANS) and x-ray (SAXS) scattering experiments to characterize the morphology of a block copolymer matrix containing a homopolymer diluent. The blends are based on a styrene-hydrogenated butadiene-styrene triblock copolymer. The technique of *phase-matching* is used to isolate the scattering from each of the copolymer blocks and from homopolymer chains which are chemically identical to the midblock segments of the block copolymer. In this method, one of the blend components has been partially deuterated in order to match its scattering density to that of one of the other components. By various combinations of phase-matched and protonated components, the concentration profiles of endblock, midblock, and homopolymer segments can be determined. Because the morphology is not affected by deuteration of the components, the entire microstructure can be determined from these experiments.

Several results have been obtained:

1. The addition of low molecular weight homopolymer to the midblock microdomain leads to contraction of the microdomain structure. Intermediate molecular weight homopolymers cause expansion of the microdomains. Blends containing homopolymers with molecular weights greater than that of the midblock have the microdomain dimensions of the pure block copolymer since most of the homopolymer is excluded from the microdomains. This behavior can be qualitatively understood by considering the configurational constraints imposed on the homopolymer molecules and midblock sequences.
2. Scattering studies of block copolymer blends containing phase-matched polymers show that a homopolymer diluent which is chemically identical to the midblock of a triblock copolymer matrix is segregated into the microphases formed by the midblock segments. The homopolymer appears to be localized within the center of these microdomains creating higher concentrations of midblock segments at the domain interfaces. This is in qualitative agreement with several theories describing these systems.
3. Diblock copolymer matrices can be phase-matched as well as triblock matrices. However, blends based on diblock copolymer do not maintain a lamellar morphology and analysis of the SANS data is not straightforward.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

- PhD dissertation, Princeton University, May 1986.
- J. Polym. Sci.: Polym. Phys. Ed. 25 641 (1987).
- Macromolecules 20 1431 (1987).
- APS March Meeting, 1986, Las Vegas, NV.
- Polymer Physics Gordon Research Conference, July 1986, Andover, NH.
- MRS Meeting, December 1986, Boston, MA.

Report of Measurements Carried Out at the NCSASRInstrument(s) 30-m HFIRTitle Evidence for a Modified Spinodal Decomposition Phase
Separation in cross-Poly Butadiene -inter-cross-Polystyrene
Sequential Interpenetrating Polymer NetworksResearch Sponsor National Science Foundation Grant or Contact No. DMR-8405053

Participants and NCSASR Collaborator(s)

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Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Cross-polybutadiene-inter-cross-polystyrene sequential interpenetrating polymer networks, IPN's, were synthesized by four different techniques, and phase dimensions were studied by small-angle neutron scattering, SANS, and transmission electron microscopy, TEM. The specific interfacial surface area increases with styrene polymerization up to about 250 m²/gm, depending on polymerization method, reaching a maximum at about 50% polystyrene. At that level of polymerization, the polymer morphology changes from spheres or cylinders to one of interconnected cylinders. The transverse length of the polystyrene domains ranges from about 75 Å to 225 Å.

The presence of maxima or shoulders in the SANS angular patterns and characteristic interconnected morphologies support a modified spinodal decomposition model of phase separation.

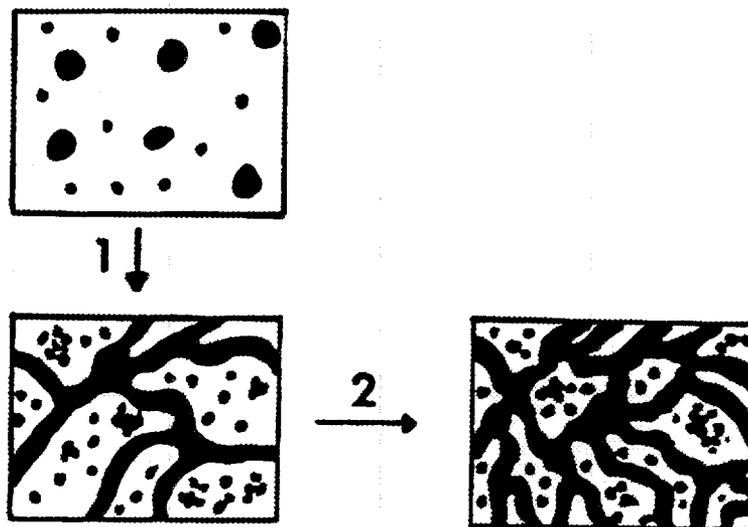


Figure 1. The development of cylinders and then interconnected cylinders is modeled. First, domains are postulated to form via nucleation and growth, spheres, followed by cylinders, spinodal decomposition.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Submitted to Polymer, and presented at the ACS meeting in Denver, April, 1987.

See also, J. H. AN, A. M. Fernandez, and L. H. Sperling, *Macromolecules*, 20, 191 (1987).

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30-M SANS

Title Small-Angle Neutron Scattering Studies of Diffusion in Bulk Polymers:
Experimental Procedures

Research Sponsor Ford Motor Company

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

J. E. Anderson

J. H. Jou

G. D. Wignall

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

ABSTRACT: This research addresses experimental issues arising in SANS diffusion studies of bulk polymers. Sample preparation, annealing protocols, reproducibility of replicate samples, data reduction, and analysis procedures are considered. Experimental SANS data for 68000 MW polystyrene are examined in detail. These data were obtained on specimens containing 50 wt % protonated and deuteriated polymer. The initial specimens were heterogeneous, containing domains of protonated and deuteriated polystyrene. Heterogeneities were destroyed, by interdiffusion, during sample annealing at 130 °C. SANS results, made as a function of annealing time, were analyzed to characterize diffusion. This analysis yielded diffusion coefficients that appeared to increase with scattering angle: values between 9×10^{-16} and 1.8×10^{-15} cm²/s were obtained over the range $Q = (4.0-8.0) \times 10^6$ cm⁻¹. We attribute this apparent Q dependence to instrumental effects, specifically, to "smearing" of experimental data. Simulation of scattering results, using an appropriate "smearing" function, generates values that match experiment. Simulation indicates that "smearing" has a minimal effect on diffusion coefficients measured at higher scattering angles. A constant (Q -independent) value $D = 1.8 \times 10^{-15}$ cm²/s is suggested for 68000 MW polystyrene at 130 °C.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Macromolecules, 1987, 20, 1544.

Report of Measurements Carried Out at the NCSASRInstrument(s) 30 M SANSTitle Influence of Homopolymer on the Correlation Hole in a Homogeneous
Diblock Copolymer.Research Sponsor AT&T Bell Labs

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

F. S. BatesAT&T Bell Labs

To Be Completed by ORNL

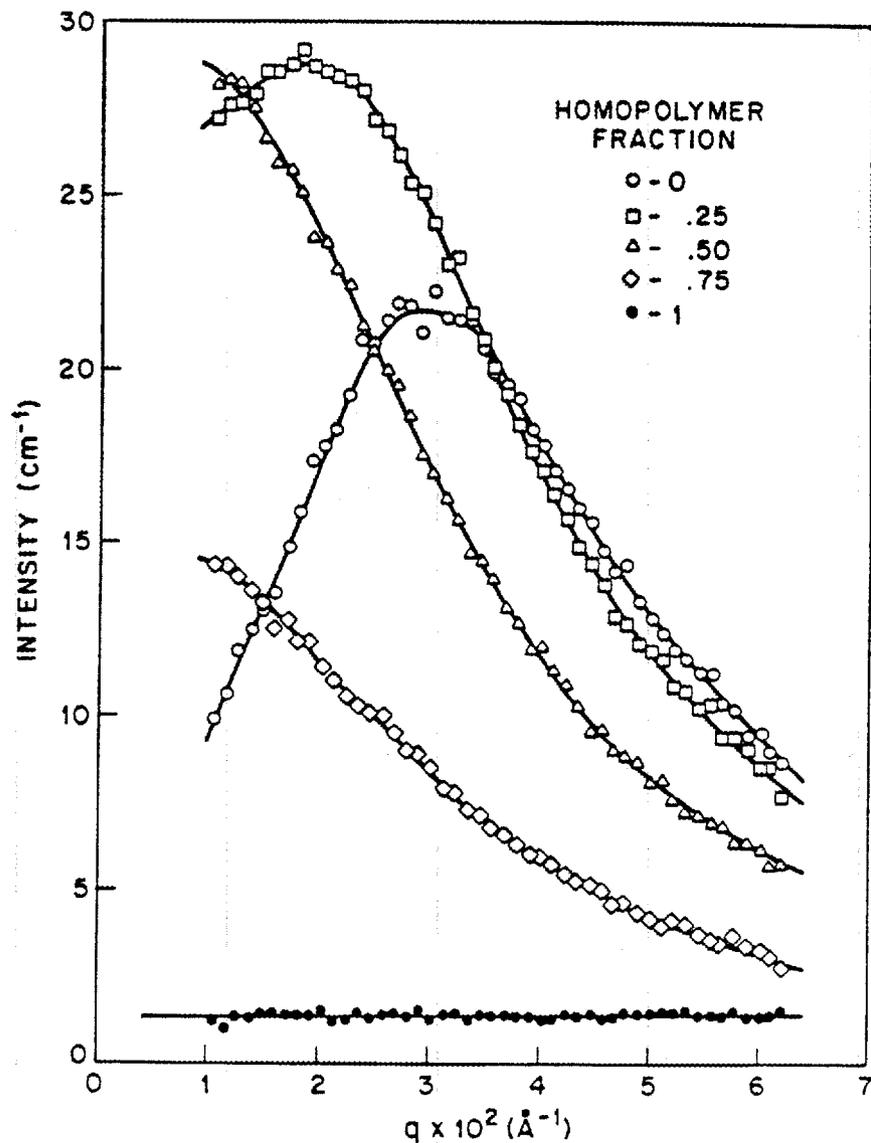
Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

A homogeneous, symmetric 1,4-polybutadiene-1,2-polybutadiene diblock copolymer containing a perdeuterated 1,4-polybutadiene block has been mixed with equal molecular weight 1,2-polybutadiene homopolymer and examined by small-angle neutron scattering (SANS). The undiluted diblock copolymer exhibits a well defined peak as measured by SANS which derives from the correlation hole effect. Addition of homopolymer initially shifts this peak to smaller scattering wavevectors and subsequently eliminates the correlation hole scattering. These results are in close agreement with the theoretically predicted scattering from homogeneous diblock copolymer-homopolymer mixtures, thus providing a method for determining the Flory-Huggins interaction parameter χ . The composition dependence of χ for the mixtures is found to be equivalent to that previously determined for undiluted diblock copolymer containing the same monomers.



Small angle neutron scattering from homogeneous mixtures of a 1,4-perdeuteropolybutadiene-1,2-polybutadiene diblock copolymer and 1,2-polybutadiene homopolymer. Open symbols represent coherent scattering while the closed circles correspond to the total scattering which is dominated by incoherent scattering events. The solid lines are guides for the eye.

References

Give references if the work has been published or submitted to conferences, symposia, etc. to appear in Macromolecules.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30 m S.A.N.S. Spectrometer

Title A Small Angle Neutron Scattering investigation on a deformed amorphous miscible blend : Poly(methylmethacrylate)/Poly(ethyleneoxide)

Research Sponsor U.MASS Polymer Science Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

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Dr. G.D. Wignall N.C.S.A.S.R.

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Amorphous blends of poly(methylmethacrylate) with poly(ethyleneoxide) (PMMA/PEO) have been uniaxially drawn by the solid state coextrusion process. A small angle neutron scattering (SANS) characterization was attempted for both isotropic and deformed samples.

The molecular dimensions and interaction parameter χ deduced in the former case were indicative of the miscibility of the system thus confirming previous work using different techniques. χ was found to be very small and positive ($\approx 10^{-3}$) for the particular composition under investigation (90/10% by weight). In the latter case however, anomalous scattering behavior at small angles precluded any determinations of the molecular anisotropy retained at various correlation distances, as well as a measurement of χ .¹

A combination of differential scanning calorimetry and small angle scattering techniques has revealed marked structural changes induced by deformation. Both methods point to a certain extent of phase separation in the originally miscible system.² Such a structural change could not be thermally induced within the temperature range of chemical stability of the blend. Over an 80°C range above T_g , the value of χ remained constant within experimental error. These results are consistent with recent F.T.I.R. studies which concluded that interactions in the blend are very weak.

To the present a better knowledge of the PMMA/PEO phase diagram is required but a reasonable conjecture would be to assume a stress modified upper critical solution temperature behavior. A more quantitative interpretation of the random two-phase system is not achievable on the basis of the current SANS data.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

- 1 J.M. Lefebvre, R.S. Porter and G.D. Wignall, *Polymer Eng. and Sci.* 27, 643 (1987)
- 2 J.M. Lefebvre, R.S. Porter and G.D. Wignall, *Mat. Res. Soc. Symp. Proc.* vol. 79 (1987)
J.M. Lefebvre, R.S. Porter and G.D. Wignall, submitted for publication.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30 M SANS

Title Thermodynamics of Isotopic Polymer Mixtures: Poly(vinylethylene)
and Poly(ethylethylene).

Research Sponsor AT&T Bell Labs; Exxon; ORNL

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

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L. J. Fetters Exxon Research

G. D. Wignall NCSASR

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

**Thermodynamics of Isotopic Polymer Mixtures: Poly(vinylethylene) and
Poly(ethylethylene)**

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G. D. Wignall

National Center for Small Angle Scattering Research
Oak Ridge National Laboratory
Oak Ridge, TN 37831

Binary mixtures of normal (protonated) and perdeuterated poly(vinylethylene), and of poly(ethylethylene), containing 50% by volume deuterated polymer, have been examined by small angle neutron scattering (SANS). Evaluation of SANS data obtained between 26 and 100°C, using the RPA theory for binary polymer mixtures, reveals that both isotopic systems are characterized by a small positive Flory-Huggins segment-segment interaction parameter, $5 \cdot 10^{-4} < \chi < 10^{-3}$, and an upper critical solution temperature (UCST). This isotope effect primarily derives from the reduction in carbon-hydrogen bond length which results from substituting deuterium for hydrogen in non-polar organic liquids; the shorter carbon deuterium bonds are directly manifested as a smaller segment volume, $(V_H - V_D)/V = 0.0019 \pm 0.0004$ and 0.0039 ± 0.0004 for poly(vinylethylene) and poly(ethylethylene) respectively. A prediction for the excess free energy of mixing for isotopic polymer mixtures, based on the measured differences in segment volumes and the associated differences in segment polarizabilities, accounts for the experimental findings. Two other published theories, based solely on the segment volume isotope effect, are also discussed. We conclude that non-ideal mixing is a universal characteristic of deuterated and protonated polymers.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Macromolecules, submitted.

Report of Measurements Carried Out at the NCSASR

Instrument(s) SANS HFIR 30 METER SPECTROMETER

Title PLASTICIZATION OF PVC

Research Sponsor MONSANTO Grant or Contact No. ERD-84-433

Participants and NCSASR Collaborator(s)

NCSASR: G. D. WIGNALL

MONSANTO: D. DUFOUR

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

SEE ABSTRACT

EFFECT OF COMPOSITION ON INTERFACE IN PVC BLENDS. Judith A. Lefelar, Monsanto Chemical Company, 730 Worcester Street, Springfield, MA. 01151.

The microstructure of a PVC based three component system (PVC/Methyl Methacrylate, Butadiene, Styrene (MBS)/Styrene, Maleic Anhydride, Methyl Methacrylate (SMA)) has been investigated using wide angle x-ray diffraction, phase contrast microscopy, differential scanning calorimetry, and small angle neutron scattering. The physical properties have been characterized using IZOD impact testing and heat distortion under load. When the Methyl Methacrylate level of the SMA component is held constant while the styrene/maleic anhydride ratio is varied, dimensions increase as the level of maleic anhydride increases. Physical Properties of the materials go through a maximum at a particular styrene/maleic anhydride ratio. It is hypothesized that specific interactions between PVC and maleic anhydride lead to the growth of a diffuse interface region which at high enough levels becomes a phase in itself.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Poster submitted for presentation at MRS Symposium on Polymer Surfaces, Interfaces and Adhesion to be held in Boston 11/30/87 - 12/5/87.

Report of Measurements Carried Out at the NCSASRInstrument(s) 30-m HFIRTitle Development of Supermolecular Structure in Polystyrene
LatexesResearch Sponsor National Science Foundation Grant or Contact No. CBT-8512923Participants and NCSASR Collaborator(s)
L. H. Sperling Lehigh UniversityA. Klein " "Se-In Yang " "Dr. G. D. Wignall NCSASR**To Be Completed by ORNL**

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

The development of supermolecular structure in polystyrene latex particles was investigated by small-angle neutron scattering. Seed latexes of deuterated polystyrene were swollen to equilibrium with protonated styrene monomer, and polymerized to complete conversion. The scattering patterns reflect the extent of supermolecular structure development inside the particle. A new method of analyzing the extent of segregation is proposed by separating the data with Debye single chain and spherical scattering form factors.

The extent of segregation was found to depend on the relative size of the chains compared with that of the particle, going through a maximum at the ratio M_w/D_w^2 of about 0.1. When the chain dimensions are relatively very small, uniform molecular mixing is obtained. At higher ratios of M_w/D_w^2 , the present data support the core-shell model of supermolecular structure.

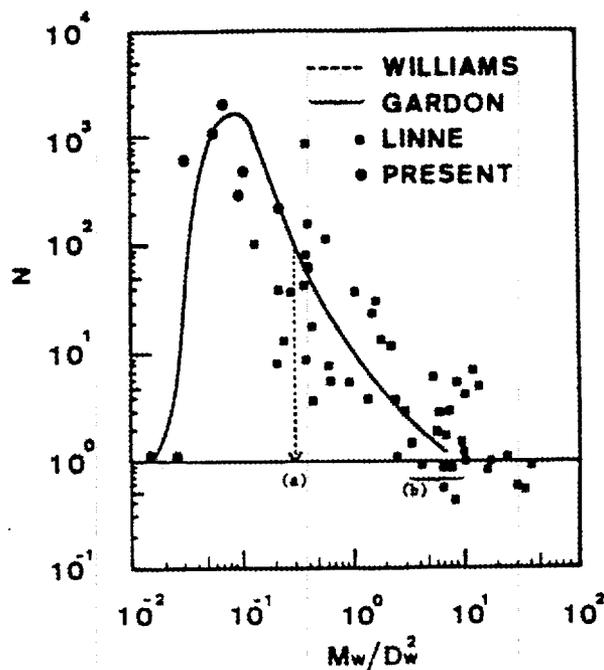


Figure 1. Development of segregation as a function of the ratio of the molecular weight of the polymer vs. the latex diameter, squared. The maximum in segregation comes approximately when the chains are half the diameter of the latex particle.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Submitted to J. Macromolecular Sci., Physics Edition and Polymer Communications.

Report of Measurements Carried Out at the NCSASRInstrument(s) 30 M SANSTitle Nonideal Mixing in Binary Blends of Perdeuterated and
Protonated Polystyrenes.Research Sponsor AT&T Bell Labs; ORNL Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

F. S. Bates AT&T Bell LabsG. D. Wignall NCSASR**To Be Completed by ORNL**

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Binary mixtures of perdeuterated and normal (protonated) atactic polystyrenes are shown by small-angle neutron scattering measurements to be characterized by a small positive segment-segment (Flory) interaction parameter ($\chi = (1.7 \pm 0.4) \times 10^{-4}$ at 160°C) and an upper critical solution temperature. These findings parallel our previous discovery of non-ideal solution behavior in isotopic mixtures of 1,4-polybutadienes, and corroborate the prediction of a universal isotope effect in amorphous polymers.

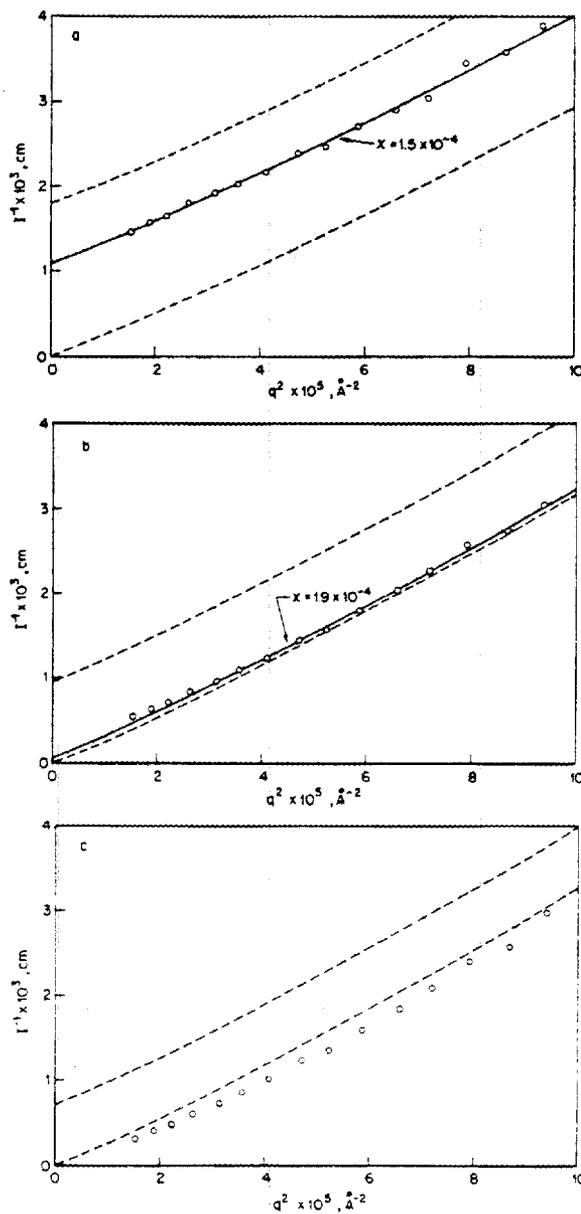


Figure 1. Coherent small-angle neutron scattering from binary mixtures of perdeuterated (50% by volume) and normal atactic polystyrenes (annealed at 160 °C) in order of increasing degree of polymerization: (a) PSHD1; (b) PSHD2; (c) PSHD3. The curves have been calculated from the theoretical correlation function for homogeneous binary polymer mixtures (eq 4), where the upper and lower dashed curves in each panel correspond to the limits of ideal mixing ($\chi = 0$) and single-phase stability ($\chi = \chi_s$), respectively.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Macromolecules (1986), 19, 932.

Report of Measurements Carried Out at the NCSASRInstrument(s) SANS HFIR 30 METER SPECTROMETERTitle PLASTICIZER EFFECT IN POLY(BUTYRAL-CO-VINYL ALCOHOL)Research Sponsor MONSANTOGrant or Contact No. ERD-84-433

Participants and NCSASR Collaborator(s)

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J. SCHAEFER
E. O. STEJSKAL**To Be Completed by ORNL**

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Date of Experiment(s) _____

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SEE ABSTRACT

The partitioning of polymer and plasticizer into soft and hard regions for mixtures of poly(butyrac-co-vinyl alcohol) and dihexyladipate has been determined by magic-angle spinning ^{13}C NMR. The soft regions are detected by Fourier-transform techniques with scalar decoupling, and the hard regions by cross-polarization with dipolar decoupling. This two-phase character of plasticized polybutyral is also observed in small-angle neutron scattering experiments in which integrated scattering intensity increases linearly with plasticizer concentration. We attribute the soft regions to liquid plasticizer containing mobile polymer, and the hard regions to solid polymer associated with partially immobilized plasticizer. There is no chemical exchange between hard and soft regions on a 1-sec time scale. The frequencies but not the amplitudes of cooperative main-chain motions of the polymer in the hard regions are influenced by interactions with the soft regions. This result is incorporated into a two-phase domain model which is used to rationalize the macroscopic stress-relaxation properties of these plasticized polymers.

References

Give references if the work has been published or submitted to conferences, symposia, etc.
J. Schaefer, J.R. Garbow, E.O. Stejskal, J.A. Lefelar, "Plasticization of Poly(butyrac-co-vinyl alcohol)," *Macromolecules*, 20, 1271 (1987).
Reprint enclosed.

Report of Measurements Carried Out at the NCSASRInstrument(s) 30 M SANSTitle Phase Behavior of Amorphous Binary Mixtures of Perdeuterated
and Normal 1,4-Polybutadienes.Research Sponsor AT&T Bell Labs; ORNL

Grant or Contact No. _____

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Date of Experiment(s) _____

Report

Phase Behavior of Amorphous Binary Mixtures of Perdeuterated and Normal 1,4-Polybutadienes

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A series of amorphous binary mixtures of normal and perdeuterated 1,4-polybutadienes has been examined by small-angle neutron scattering (SANS). Contrary to the generally held assumption that isotopic polymer mixtures form ideal solutions, we conclusively demonstrate that these mixtures are characterized by an upper critical solution temperature (UCST). This isotope effect derives from a small, measurable difference in segment volume between normal and perdeuterated species. Above the UCST, the SANS results are quantitatively predicted by the mean-field theory of deGennes for homogeneous binary polymer mixtures. Increasing the degree of polymerization raises the critical temperature, resulting in phase separation. Owing to the combined effects of the close proximity to the consolute point and a small segment-segment interaction parameter ($\chi \approx 10^{-3}$), the phase separated mixtures exhibit extensive interfacial mixing; Porod analysis of the SANS results reveals an average interfacial thickness of $\langle D \rangle = 250 \text{ \AA}$. Overall, these findings demonstrate that normal and perdeuterated amorphous polymers represent a new class of materials with which to study polymer-polymer phase behavior.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Macromolecules (1986), 19, 1938.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30 M SANS

Title Small-Angle Neutron Scattering Studies of PEC-PET Blends.

Research Sponsor Allied-Signal Inc. Grant or Contact No. _____

Participants and NCSASR Collaborator(s)
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Shaul M. Aharoni
George D. Wignall

To Be Completed by ORNL
Date Received _____
Proposal No. _____
Date of Experiment(s) _____

Report

Quenched blends of poly(ester carbonate) (PEC) and poly (ethylene terephthalate) (PET) have a single T_g and behave as single phase amorphous alloys up to 67% PET. However, small-angle neutron scattering (SANS) data show that the PET molecules are not statistically distributed as classical Gaussian coils in the PEC matrix. In quenched amorphous PEC-rich films (a single phase), PET-rich domains of varying PET concentration appear to be randomly distributed in the PEC matrix, and the excess SANS intensity is attributable to fluctuations in PET concentration. Wide- and small-angle x-ray scattering data and SANS results show incomplete phase separation of PET and PEC molecules upon annealing. A possible model for annealed blends (two phases) might be domains of folded chain, crystalline PET with interlamellar amorphous regions composed of a mixture of PET and PEC molecules. These domains are dispersed in the amorphous PEC matrix.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

To be Published in Polymer (1988)

Report of Measurements Carried Out at the NCSASRInstrument(s) 30 Meter SANSTitle Coil Dimensions of Polystyrenes in Isorefractive Viscous SolventsResearch Sponsor NSF-DMR Grant or Contact No. 8319291

Participants and NCSASR Collaborator(s)

T.P. LodgeK.C. HermannG.D. Wignall**To Be Completed by ORNL**

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Date of Experiment(s) _____

Report

We attempted to test a fundamental assumption in polymer solution dynamics experiments, namely, that the time-temperature superposition principle may be applied safely over a wide range of temperature for polystyrene dissolved in Aroclor solvents. The key issue is whether the solvent quality is sufficiently high that the coil dimensions are independent of temperature, from 0° to 50°C. We attempted to measure R_g for dPS, $M = 100,000$ in Aroclor 1248 at 0°, 25°, and 50°C. It appears that, within experimental error, R_g is independent of T . However, the signal-to-noise is always poor for this system, and the data scatter was greater than we would like. In particular, the detector leak was a problem. Thus, we hope to repeat these measurements in the future before publishing the results.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASRInstrument(s) 30 M SANSTitle Critical Behavior of Binary Liquid Mixtures of Deuterated
and Protonated Polymers.Research Sponsor AT&T Bell Labs; ORNL

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Proposal No. _____

Date of Experiment(s) _____

Report

Critical Behavior of Binary Liquid Mixtures of Deuterated and Protonated Polymers

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(Received 1 July 1985)

Binary mixtures of protonated and perdeuterated 1,4-polybutadiene have been examined by small-angle neutron scattering and are shown to exhibit an upper critical solution temperature. The scattering results above the critical temperature are described by the mean-field theory of de Gennes for homogeneous binary polymer mixtures. These results contradict the universally held assumption that mixtures of deuterated and protonated polymers of otherwise identical chemical structure form ideal solutions.

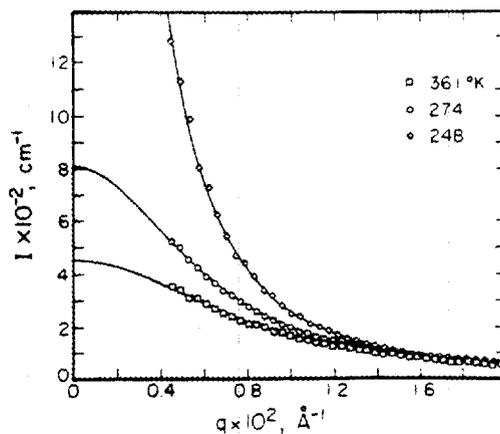


FIG. 1. Coherent small-angle neutron scattering from sample B2B5(0.31), a binary mixture of protonated and perdeuterated 1,4-polybutadiene at the critical composition. The curves were obtained from the predicted homogeneous-mixture scattering function by adjusting the segment-segment interaction parameter χ .

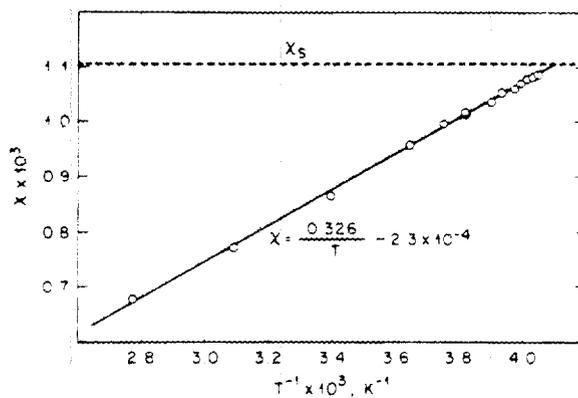


FIG. 3. Temperature dependence of the segment-segment interaction parameter χ , obtained by fitting the theoretical homogeneous binary-blend correlation function to the small-angle neutron-scattering data from sample B2B5(0.31).

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Physical Review Letters (1985), 55, 2425.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30 m SANS

Title LIQUID CRYSTALLINE TO ISOTROPIC PHASE TRANSITIONS

Research Sponsor DOE

Grant or Contact No. DE-AC-04-76DP00789

Participants and NCSASR Collaborator(s)

J. P. Wilcoxon

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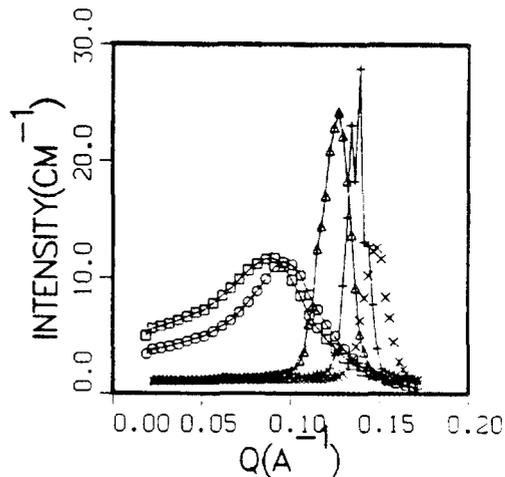
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Date of Experiment(s) _____

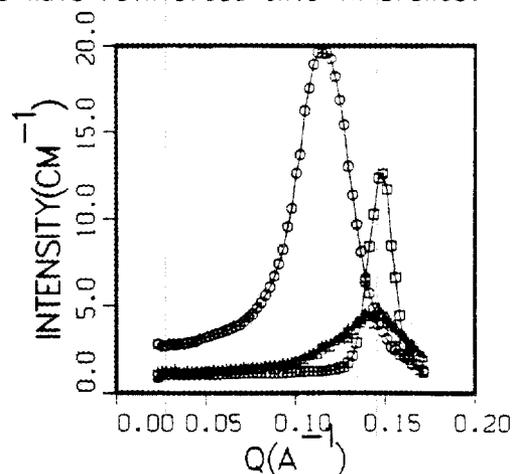
Report

Fig. 1. SANS data obtained in the isotropic 32% (squares), 40% (circles), hexagonal (triangles), cubic (pluses), and lamellar (crosses) phases of the $C_{12}E_6$ surfactant system.



SANS measurements of the lamellar, hexagonal and cubic phases of a non-ionic surfactant are used to study the nature of the order to disorder transition in this system ($C_{12}E_6$ in D_2O). Of particular interest is whether shape (e.g. sphere to rod) transitions occur prior to entering the ordered phase and whether the elementary constituents of the lamellar phase are micelles or individual surfactant molecules. The phase boundaries were approached either by changing temperature at constant amphiphile concentration (thermotropic l.c. transition), or by changing amphiphile concentration at a constant temperature (lyotropic l.c. transition). Distinct Bragg peaks are observed within the ordered phase accompanied by thermal diffuse scattering. The width (amount of disorder) and position (repeat spacing) is strongly dependent on the volume fraction surfactant. Figure 1 shows a concentration scan through the isotropic (32%, 40%) phases into the hexagonal (50%), cubic (65%) to lamellar (75%) phases. The cubic phase exhibits the most long range order. The peak spacing is not simply proportional to the volume fraction surfactant, but rather shows the largest shift between isotropic and ordered phases. The spacing in the hexagonal phase is 42 Å, a value consistent with the amphiphile chain length. A very significant increase in the compressibility (intensity at $Q=0$) is seen upon entering the disordered isotropic phase. Figure 2 shows a temperature scan through the lamellar phase of this surfactant system. The phase boundary is at 45 °C. A major increase in the compressibility is observed from the scattering at 45 °C. However, distinct peaks in the scattering function are observed at roughly the same spacing far above the l.c. phase boundary. Because of the high viscosity associated with the l.c. phase there is reason to believe that the shift in Bragg spacing near the transition temperature is due to a rearrangement of a metastable state that was trapped by too rapid cooling from the high temperature liquid state shown in the 75 °C and 83 °C curves. This metastable state undoubtedly consists of a packing of spherical micelles rather than the formation of layers consisting of individual surfactant molecules separated by solvent (the curve corresponding to $T=45$ °C). Subsequent SAXS measurements have reinforced this inference.

Fig. 2. SANS data obtained in the lamellar ordered phase (squares), at $T = 22$ °C, then at $T = 45$ °C (phase boundary, circles), and finally $T = 75$ °C (isotropic, triangles).



References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASRInstrument(s) Neutron ScatteringTitle Two-dimensional Phase Separation Behavior in the Langmuir-Blodgett FilmsPrepared from Mixtures of Protonated and Deuterated Stearic AcidsResearch Sponsor AT&T Bell Laboratories

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

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Date of Experiment(s) _____

Report

The objective of this study was to probe the two-dimensional phase separation behavior in the mixtures of protonated stearic acid and its deuterated analog. Preliminary results indicate the scattering signals to be too weak because of extremely small thickness of the films (ca. 50 Å). While we are planning to prepare films with greater thicknesses for further study, the project is not active at the moment because of other commitments.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30M SANS

Title Correlation Hole Analysis of Star-Block Copolymers

Research Sponsor _____ Grant or Contact No. _____

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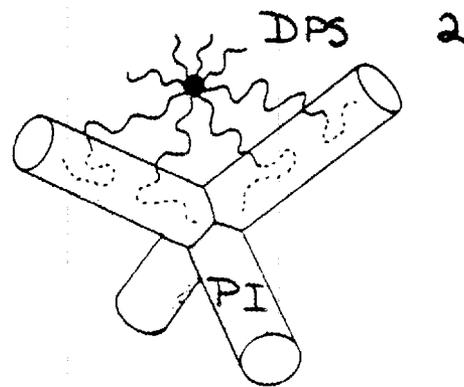
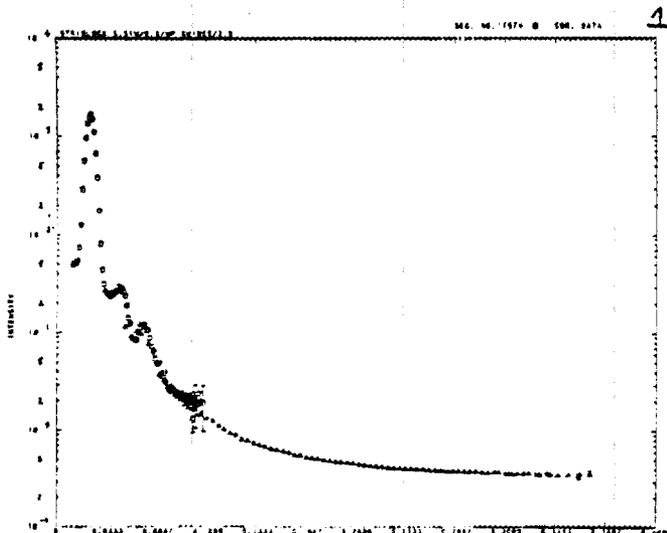
Proposal No. _____

Date of Experiment(s) _____

Report

Small angle neutron scattering measurements have been made over a wide Q range on star diblock copolymers in which both composition and arm number were varied. For totally hydrogenous materials a series of discrete Bragg peaks were observed, which corresponded exactly with those previously observed by small angle x-ray scattering¹.

The major purpose of these experiments was to determine the interfacial diffuse layer thickness in block copolymers with an ordered bicontinuous double diamond structure. For this purpose copolymers with 73 wt. % deuterostyrene were synthesized by Dr. L. J. Fetters of Exxon. The deuterostyrene constituted the cores of these stars and the samples studied were a linear star (tri-block) and a 12-arm star. Figure 1 shows the log of the radially averaged scattered intensity obtained for the deuterio-triblock at two different sample-detector distances. The Bragg peaks are clearly evident and even for the highest Q range used a constant level of scattering intensity is not obtained. Analysis of scattering data for diffuse layer thickness requires accurate subtraction of the incoherent scattering². For this purpose the incoherent scattering from a mixture of hydrogenous and deuterotoluene was used in which the scattering length density was equal to the average of the star diblock copolymers. Notwithstanding this correction, the data did not agree with expectations; i.e. attenuation in scattering being describable (in the first instance) by the single particle form factor for a cylinder. It is known, however³, that the form of the attenuation at intermediate Q is dependent on the form of the single particle form factor. Since this is not yet known for the tetrapods which make up the scattering particles (Fig 2), it is perhaps not surprising that an unusual attenuation is observed. Data are currently (August 1986) being further analyzed.



¹R.W. Richards and E.L. Thomas, unpublished data.

²R.J. Roe, *J. Appl. Cryst.*, 1982, **15**, 182.

³R.W. Richards and J.L. Thomason, *Polymer*, 1983, **24**, 1089.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASRInstrument(s) 30m small angle neutron scattering facility at HFIRTitle Determining Incoherent Scattering from Poly(ethylene terephthalate):Investigation of a General Correction Method for PolymersResearch Sponsor NSF, Oak Ridge Assoc. UniversityGrant or Contact No. T-416

Participants and NCSASR Collaborator(s)

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Report

Poly(ethylene terephthalate), PET, is unusual because it may undergo transesterification. Advantage was made of this reaction to allow measurement of the incoherent scattering from hydrogen and deuterium chain blends. Polymer chains containing either deuterium or hydrogen were mixed to make samples of various concentrations. Transesterification of the PET was performed at polymer melt temperatures to increase the speed of chain randomization. There is no coherent scattering from properly randomized chains; therefore, the entire signal from this type of sample is due to incoherent scattering effects.

The samples prepared showed that the total scattering cross section was linearly related to the deuterium concentration. This result allows the straightforward use of concentration in the Beer-Lambert Law for 4.75 nm neutrons.

Other results seem to indicate that incoherent scattering from PET behaves similarly to that from water. For high hydrogen concentrations, the incoherent scattering scales as 1 minus the sample transmission. Care must be taken when using low concentrations of hydrogen since this rule breaks down at intermediate levels of hydrogen. Furthermore, sample thickness at high hydrogen concentrations (scattering cross sections) may affect the incoherent scattering distribution, perhaps due to inelastic or multiple scattering events.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASRInstrument(s) 30 M SANSTitle Isotope Induced Quantum Phase Transitions in the Liquid StateResearch Sponsor AT&T Bell Labs; ORNL Grant or Contact No. _____

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Report

Isotope-Induced Quantum-Phase Transitions in the Liquid State

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(Received 8 May 1986)

Isotopic binary liquid mixtures are universally characterized by an upper critical solution temperature as a consequence of zero-point motion in conjunction with the anharmonicity of the interatomic potential. This quantum effect is predicted, and demonstrated by small-angle neutron-scattering measurements, to be manifest at ambient temperatures for mixtures of deuterated and protonated polymers. Prior evidence of such phase behavior has been restricted to liquid mixtures of ^3He and ^4He .

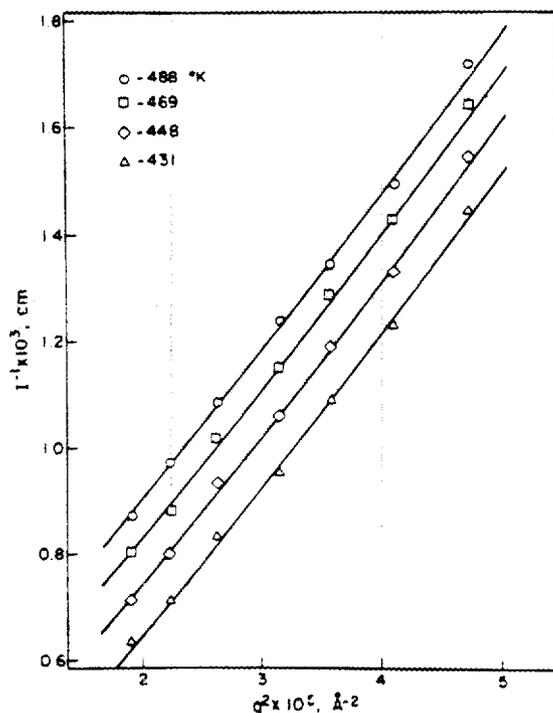


FIG. 2. Coherent small-angle neutron scattering from a homogeneous binary liquid mixture of fully deuterated and protonated polystyrenes near the critical point for demixing. The curves were obtained by use of the predicted homogeneous-mixture scattering function with adjustment of the segment-segment interaction parameter χ .

References

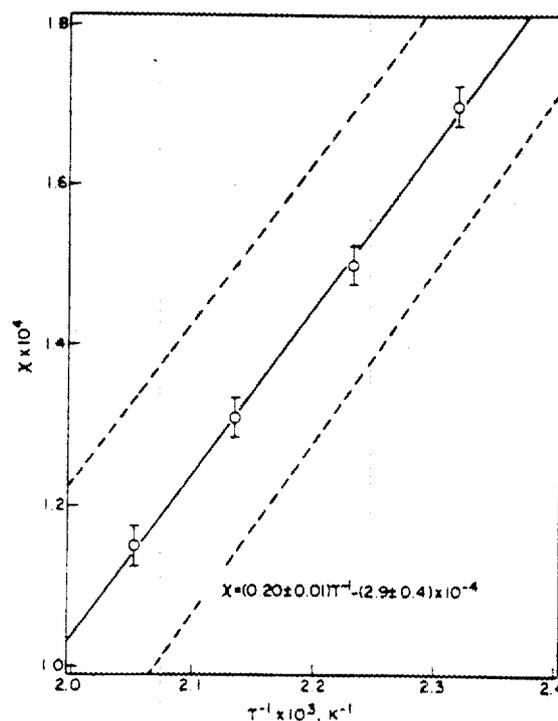


FIG. 3. Temperature dependence of the segment-segment interaction parameter obtained from the SANS results for a binary mixture of fully deuterated and protonated polystyrenes near the critical point. The dashed curves indicate the uncertainty in $\chi(T)$ corresponding to the estimated uncertainty in degree of polymerization N and SANS intensity calibration.

Give references if the work has been published or submitted to conferences, symposia, etc.

Physical Review Letters (1986), 57, 1429.

Report of Measurements Carried Out at the NCSASRInstrument(s) 30 m SANSTitle Scattering Studies on Mixtures of Poly(ethylene oxide) With
Poly(methylmethacrylate)Research Sponsor IBM Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

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Report

SCATTERING STUDIES ON MIXTURES OF POLY(ETHYLENE OXIDE)
WITH POLY(METHYL METHACRYLATE)

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ABSTRACT

Molten and semi-crystalline mixtures of PEO and PMMA have been investigated by small angle neutron and X-ray scattering. It has been found that the Flory Huggins interaction parameter, evaluated from the intermolecular scattering function, is quite small and is apparently dominated by entropic contributions. Scattering profiles from the semi-crystalline mixtures clearly show that the PMMA is incorporated within the amorphous phase between the crystalline PEO lamellae.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

1. Gordon Research Conference (Polymer Physics), Poster Session
July, 1986.
2. Materials Research Society Mtg. and Proceedings, Boston,
December, 1986

Report of Measurements Carried Out at the NCSASRInstrument(s) 30m small angle neutron scattering facility at HFIRTitle Determining Incoherent Scattering from Poly(ethylene terephthalate):Investigation of a General Correction Method for PolymersResearch Sponsor NSF, Oak Ridge Assoc. Universities Grant or Contact No. T-416

Participants and NCSASR Collaborator(s)

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Date of Experiment(s) _____

Report

The intensity measured during a scattering experiment can be broken up into contributions from several effects: elastic and inelastic scattering, along with coherent and incoherent scattering. For small angles and low energy neutron sources, inelastic scattering is small. The elastic coherent scattering contains structural information resulting from phase relationships between scatterers within a correlation volume. Elastic incoherent scattering carries no structural information and is principally isotropic over the full solid angle, 4π . For this reason, the incoherent scattering might be considered a flat background. This incoherent scattering is generally not important at small angles; however, it does become significant at intermediate angles, where the coherent signal is weak, and therefore must be subtracted accurately from the total scattering to obtain useful information.

Currently there are several techniques which have been employed to infer the incoherent scattering from polymer systems. Most employ the fact that incoherent scattering is principally due to hydrogen, which is a large and almost wholly incoherent scatterer. This assumption has been shown to hold for thin water samples; but has not been tested for polymers.

A property of poly(ethylene terephthalate), PET, enables one to measure incoherent scattering for this polymer. The technique employs different concentrations of H and D-PET chains. The samples are then heated to randomize the hydrogen and deuterium on inter and intramolecular levels by transesterification. For such a material, there should be no small angle coherent scattering. The incoherent scattering can then be directly measured because it is the entire signal.

As a result of its relatively small hydrogen content (poor isotope contrast), PET is extremely sensitive to sample preparation techniques. A method due to McAlea has been used to prepare specimens. Scattering experiments were performed on untransesterified samples to verify the effectiveness of this technique. Initial experiments on the transesterified samples showed that longer transesterification times would be necessary, along with other slight modifications to the sample preparation technique.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASRInstrument(s) 30-M SANS SpectrometerTitle Polymer Chain Expansion in Deformed Polystyrene NetworksResearch Sponsor National Science Foundation Grant or Contact No. DMR-8217460

Participants and NCSASR Collaborator(s)

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Date Received _____

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Date of Experiment(s) _____

Report

The molecular model of rubber elasticity was studied by small angle neutron scattering (SANS). SANS experiments can provide a direct measure of the changes in size and shape of the polymer chains which take place when the network is deformed.

The polystyrene networks were prepared by hot-molding mixtures of polystyrene and deuteriopolystyrene of molecular weight 100,000 with crosslinking agent, m-benzenedisulfonyl azide, at 155°C for about 1-1/2 hours. The nominal crosslink densities of these random networks were five, seven and nine, and the actual numbers were about 60% of each of these. These dumbbell-shaped polystyrene networks were stretched in a heated Instron to various extents and allowed to relax underload before quenching to room temperature.

The SANS results showed that the deformation of the networks is not segment affine and the radius of gyration is a function of the extent of deformation only, and is independent of the crosslink density. Deformation in parallel direction is closer to the phantom network; while in perpendicular direction the fixed junction model prevails.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Polymer Preprints, April 1986, 27, No.1, pp.87.

Presented at the ACS National Meeting, New York City, April 1986;
ACS Great Lake Regional Meeting, Milwaukee, June 1986.

Report of Measurements Carried Out at the NCSASR

Instrument(s) Small Angle Neutron Scattering Facility

Title A Double-Tilt Small Angle Neutron Scattering Experiment On Deformed
Polymer Systems

Research Sponsor NSF-Eng.-8416031

Grant or Contact No. 5-22775

Participants and NCSASR Collaborator(s)

R.F. Saraf, J.M. Lefebvre, R.S. Porter and

G.D. Wignall

To Be Completed by ORNL

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Proposal No. _____

Date of Experiment(s) _____

Report

SYNOPSIS

A double rotation goniometer has been mounted in the neutron beam in order to characterize the molecular deformation in polymers subjected to various strain conditions.

The results provide a direct verification of the fiber symmetry in solid state coextruded polymethylmethacrylate (PMMA) and polypropylene (PP) homopolymers.

In the case of the shear banding phenomenon, we have been able to test the validity of the simple shear assumption; it also provides a direct estimate of the finite shear strain involved in the process. As a last illustration of the method, we also consider the biaxial deformation of PP and PMMA squeezed under various temperature and strain-rate conditions.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

J. Materials Res. Soc., 1987, to be published.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 10-M SANS/30-M SANS

Title SMALL ANGLE NEUTRON SCATTERING STUDIES ON MISCIBILITY OF POLYSTYRENE AND
TETRAMETHYL-BISPHENOL A-POLYCARBONATE BLENDS

Research Sponsor Eastman Kodak Company

Grant or Contact No. _____

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Date of Experiment(s) _____

Report

The miscible blend of polystyrene (PSH) and tetramethyl-bisphenol A-polycarbonate (TMPC) has been previously studied by differential scanning calorimetry (DSC), viscoelasticity, and microscopy. In this study, small-angle neutron scattering (SANS) has been applied to obtain the quantitative interaction parameter (χ) of this blend at room temperature. Deuterated polystyrene (PSD) was used for the scattering contrast in the study. The PSD/TMPC blends show a single T_g over the whole range of composition from the DSC measurements, which is the same as the T_g of PSH/TMPC blend.

The interaction parameter was calculated from the de Gennes scattering intensity function of miscible polymer blends, which is based on the random phase approximation. As expected for a miscible system, all χ values are negative over the range of composition. It is also found that the χ is composition-dependent and can be expressed as: $\chi(\phi)/v_0 = (-0.66 \times 10^{-4}) - 1.35 \times 10^{-4}\phi - 2.44 \times 10^{-4}\phi^2$ where ϕ is the volume fraction of PSD and v_0 is the volume of the unit cell. Furthermore, the correlation length of the concentration fluctuation (10~17Å) is approximately twice the segment length of the component polymer (PSD = 6.7Å and TMPC = 7.4Å), implying that the mixing of this blend is effectively at segmental level.

References

Give references if the work has been published or submitted to conferences, symposia, etc.
Materials Research Society Symposium "Scattering Deformation and Fracture in Polymers, Boston, MA (December 1-5, 1986), MRS Proceedings 79, 129 (1987).

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30-M SANS

Title Plasticization of Poly(butyrac-co-vinyl alcohol)

Research Sponsor Monsanto Company Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

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To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

ABSTRACT: The partitioning of polymer and plasticizer into soft and hard regions for mixtures of poly-(butyral-co-vinyl alcohol) and dihexyl adipate has been determined by magic-angle-spinning ^{13}C NMR. The soft regions are detected by Fourier-transform techniques with scalar decoupling and the hard regions by cross-polarization with dipolar decoupling. This two-phase character of plasticized polybutyral is also observed in small-angle neutron scattering experiments in which integrated scattering intensity increases linearly with plasticizer concentration. We attribute the soft regions to liquid plasticizer containing mobile polymer and the hard regions to solid polymer associated with partially immobilized plasticizer. There is no chemical exchange between hard and soft regions on a 1-s time scale. The frequencies but not the amplitudes of cooperative main-chain motions of the polymer in the hard regions are influenced by interactions with the soft regions. This result is incorporated into a two-phase domain model that is used to rationalize the macroscopic stress-relaxation properties of these plasticized polymers.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Macromolecules, 1987, 20, 1271.

Report of Measurements Carried Out at the NCSASRInstrument(s) 30-M SANSTitle SANS from Sulfonate Ionomer Solutions Polyelectrolyte Effects in Polar SolventsResearch Sponsor Exxon Research and U. Mass

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

C. W. LantmanW. J. MacKnightS. K. Sinha, D. G. PeifferR. D. Lundberg and G. D. Wignall**To Be Completed by ORNL**

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Dimethyl formamide solutions of lightly sulfonated polystyrene (SPS) ionomers have been studied. These SPS polymers possess a narrow molecular weight distribution and are in the form of sodium salts. A combination of reduced viscosity and small-angle neutron scattering measurements reveal polyelectrolyte effects in these solutions. Mixed labelling experiments were performed to provide a molecular basis for understanding these effects.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

To appear in *Macromolecules*

Report of Measurements Carried Out at the NCSASRInstrument(s) 30-M SANS, 10-M SANSTitle A SANS Study of the Structure of Plasticized PVCResearch Sponsor IBM, Case Western Reserve University Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

H. R. BrownM. KasakevichG. D. Wignall**To Be Completed by ORNL**

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

ABSTRACT: The structure and crystallinity of plasticized poly(vinylchloride) (PVC) has been examined using Small Angle Neutron Scattering (SANS) and a deuterated plasticizer. The scattering curve, which shows a prominent peak at a Bragg spacing of ~11 nm, has been interpreted using a two phase model where the phases are assumed to be plasticized amorphous material and unplasticized, probably crystalline material. The volume fraction of the PVC that was unplasticized was obtained from the SANS invariant. The value found, 0.29, was relatively insensitive to the assumed amorphous density and consistent with the dependence of the scattering peak height on the fraction of the plasticizer that was deuterated.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30-M SANS

Title Small-Angle Neutron Scattering Study on the Morphology of Seeded Emulsion-Polymerized Latex Particles

Research Sponsor Hercules Research

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

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R. H. Hoerl and G. D. Wignall

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

A statistical copolymer of styrene and methyl methacrylate was used as seed particles for further polymerization of methyl-d₃ methacrylate in a starved monomer feed technique. The resulting polymer latex was shown to have a core/shell morphological structure as determined by small-angle neutron scattering. The overall size of the particle was in excellent agreement with the values obtained by light scattering and transmission electron microscopy.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30 m SANS, 10 m SAXS

Title SILICA SILOXANE MOLECULAR COMPOSITES

Research Sponsor DOEGrant or Contact No. DE-AC-04-76DP00789

Participants and NCSASR Collaborator(s)

D. W. Schaefer, J. E. Mark, andJ. P. Wilcoxon

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Silica siloxane molecular composites are typically made by simultaneous or sequential polymerization of a rubbery siloxane polymer with a glassy silicon alkyoxide. We have studied the type of structures which form in these molecular composites as a function of the polymerization sequence and chemical conditions. In the first sequence of experiments, we studied conditions which we anticipated would produce particulate fillers, basically colloidal silica precipitated in a rubbery siloxane matrix.

The small-angle scattering curves of all these materials, regardless of polymerization sequence or chemistry, were strikingly similar. Porod analysis of the scattering curves indicate that all samples consisted of a smooth surface two-phase structure on length scales below $\sim 50 \text{ \AA}$. On longer length scales, a peak in the scattering curve was observed as well as a divergence near $Q \rightarrow 0$. We interpret this long length scale structure as a bicontinuous network formed by a spinodal phase separation process.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

J. E. Mark, "In Situ Generation of Ceramic Particles in Elastomeric Materials," to be published.

Report of Measurements Carried Out at the NCSASRInstrument(s) 10-m SAXS facilityTitle Thorium Nitrate Hydroxide Polymer Solutions (#1)Research Sponsor DOE - BES - Chemical SciencesGrant or Contact No. FTP/A 68
KC 03 02 02 0

Participants and NCSASR Collaborator(s)

L. M. Toth (Chemical Technology Div)J. S. Lin (Solid State Div)L. K. Felker (Chemical Technology Div)**To Be Completed by ORNL**

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Small angle x-ray scattering, SAXS, studies of Th(IV) hydrous polymers have been conducted on 0.01 M Th(NO₃)₄ aqueous suspensions and organic extractants that have been contacted with them. Assuming spherical geometries, fresh Th(IV) polymer suspensions consist of particles that vary in size from 2.5 to 8.4 nm whereas aged (by reflux) Th(IV) polymer suspensions consist of particles that range in size from 1.6 to 17.4 nm. The decrease in size of the small extreme on aging is consistent with a dehydration and shrinkage process during conversion of hydroxyl bridges to oxygen bridges between Th atoms. These suspensions have been shown to be extracted by 0.5 M dibutylphosphate in n-dodecane, NDD, but not by 0.1 M trioctylphosphine oxide in NDD or 0.1 M dihexyl-[(diethylcarbamoyl)-methyl] phosphonate in NDD. The particle size distribution in the organic extractant was similar to that in the aqueous phase showing that there was no size segregation as a result of extraction. Attempts to alter the size of the polymers by growing them in the presence of UO₂²⁺ produced no differences in particle size distribution; it has since been realized, though, that the 0.5/1 ratio of UO₂²⁺/Th(IV) would probably have to be increased to 10/1 before measureable effects could be obtained.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Abstract of poster to be presented at the Fourth Users' Group Meeting at the National Center for Small Angle Scattering Research, Oak Ridge, TN. May 12-14, 1987.

Report of Measurements Carried Out at the NCSASR

Instrument(s) SAXS

Title Processing and Characterization of Cellulose Triacetate Films from
Istropic and Liquid Crystalline Solutions

Research Sponsor Celanese Fibers Company Grant or Contact No. _____

Participants and NCSASR Collaborator(s)
J. S. Lin

To Be Completed by ORNL
Date Received _____
Proposal No. _____
Date of Experiment(s) _____

Report

Processing and Characterization of Cellulose Triacetate Films from Isotropic and Liquid Crystalline Solutions

O. O. OMATETE,[†] HASSAN BODAGHI,[°] JOHN F. FELLERS,
and COLIN L. BROWNE,^{*} *Materials Science and Engineering,*
University of Tennessee, Knoxville, TN 37996

Synopsis

Cellulose triacetate (CTA) films have been prepared by extrusion of various liquid crystalline and isotropic CTA solutions in a mixture of dichloroacetic acid (DCA) and formic acid (FA) through an annular die. The extrudate was either given a uniaxial drawdown into a coagulation bath or biaxially deformed via expansion with recirculating coagulant to the inside of the extrudate. Thus solutions with CTA concentrations ranging from 23 to 30% were extruded as uniaxially- and biaxially-oriented films.

A survey of solvent systems to produce liquid crystalline CTA showed DCA or DCA/FA to be the only reasonable choices from among the solvents tried. Rheological characterization showed that CTA/DCA/FA could be processed in the 23 to 30% concentration range. A maximum in the viscosity vs. concentration curve, plastic flow stresses, and viscosity-shear rate behavior typical of liquid crystalline systems were observed. At 60°C, the system reverts to isotropic and provides for some comparisons between isotropic and anisotropic behavior.

The CTA films were characterized by small angle x-ray scattering (SAXS), mass density, scanning electron microscopy (SEM), permeation studies, differential scanning calorimetry (DSC), wide angle x-ray diffraction (WAXS), and birefringence. The latter two methods were used to characterize the molecular orientation produced with various processing conditions. The volume fraction of microvoids was computed by SAXS invariant analysis and found to vary from 0.01 to 0.18%. This is low compared to results from mass density measurements. Density and SAXS measurements indicate a void content decreasing with decreasing solution concentration and heat treatment. SEM locates micron-size voids in the cross-section of films produced from high solution concentrations. Fibrillar structure was observed for "peeled" uniaxial films. This is increased with an increase in solution concentration. Biaxial films could not be peeled.

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© 1986 by The Society of Rheology, Inc. Published by John Wiley & Sons, Inc. Journal of Rheology, 30(3), 629-659 (1986) CCC 0148-6055/86/030629-31\$04.00

References

Give references if the work has been published or submitted to conferences, symposia, etc.

- O. O. Omatete, Hassan Bodaghi, John F. Fellers, and Colin L. Browne, "Processing and Characterization of Cellulose Triacetate Films from Isotropic and Liquid Crystalline Solutions," *Journal of Rheology*, 30(3), 629-659 (1986).

Report of Measurements Carried Out at the NCSASRInstrument(s) 10 meter SAXS cameraTitle The Fibrillar Structure of Melt Spun and Drawn Polypropylene FilamentsResearch Sponsor University of Tennessee
Center for Materials Processing

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

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To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

ABSTRACT

A basic study of fibrillation and void development during drawing of melt spun polypropylene filaments is presented. The filaments are characterized by small angle x-ray scattering (SAXS), density, differential scanning calorimetry (DSC), scanning electron microscopy (SEM), wide angle x-ray diffraction (WAXS) and birefringence. The latter two methods were used to characterize the molecular orientation produced by processing while SEM studies of peeled filaments revealed, qualitatively, the development of the fibrillated internal superstructure. The volume fraction of microvoids was computed from the intensity of SAXS and from a combination of DSC and density measurements. The microvoid fractions determined by these two

techniques were in good agreement. Volume per cent of microvoids varied from 0.04 to 2.8%. It was found that the fibrillation observed qualitatively by SEM and the measured volume fraction and number density of microvoids increased with (i) increase in draw ratio, (ii) decrease in draw temperature, (iii) increased orientation of melt spun filaments, and (iv) increased molecular weight of the polypropylene. Using Guinier analysis of the SAXS data it was found that the voids had dimensions of 25-40 nm, parallel to the fiber axis and of order 15-30 nm perpendicular to the fiber axis. As the drawing temperature increased the SAXS void size increased and void number density decreased. The longitudinal mechanical properties of the fibers were found to be mainly a function of the orientation and were not very much affected by changes in fibrillation or void structure per se.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

"The Fibrillar Structure of Melt Spun and Drawn Polypropylene Filaments,"
J. International Polymer Processing, accepted for publication.

Report of Measurements Carried Out at the NCSASRInstrument(s) 10 m SAXSTitle The effect of Solvents on the Microstructure of Polystyrene IonomersResearch Sponsor NSF Grant or Contact No. DMR 8407098

Participants and NCSASR Collaborator(s)

R. A. WeissJ. J. FitzgeraldJ. S. Lin (NCSASR)**To Be Completed by ORNL**

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

The effect of polar and nonpolar diluents on the morphology of SPS ionomers was characterized by SAXS. The addition of methanol to SPS reduces the intensity of the peak characteristic of ionic clusters and shifts the peak to lower scattering vector. The reduction in intensity indicates that the methanol partially destroys the structural heterogeneity responsible for the peak, i.e., the ionic cluster. In the case of a MnSPS sample with 10% methanol no peak was observed, though a substantial amount of low angle scattering was observed. We believe that these results indicate phase mixing has occurred which is consistent with ESR data that show that methanol weakens the interactions between the ionic entities. The shift of the SAXS peak to lower scattering vector, k , corresponds to a larger characteristic distance.

The effect of a nonpolar solvent, dodecane, on the SAXS curve of the SPS was studied. The addition of 3.4% (wt) had no effect on the scattering curve. If the dodecane were present in the ionic clusters a reduction in the electron density difference between the ionic aggregates and the hydrocarbon matrix would be expected, which should result in a decrease in the intensity of the scattering peak. This and the fact that no change in the position of the SAXS peak was observed indicate that the dodecane must be absent from the scattering entity, or in other words, it partitions into the hydrocarbon matrix.

The effects of dioctyl phthalate (DOP) and glycerol on the SAXS curves of 1.65 MnSPS were studied. In the case of addition of DOP to the ionomer, the intensity of the ionic peak decreased as DOP was added, but the shape of the peak and its position did not change. This is what would be expected if DOP preferentially partitions into the hydrocarbon-rich matrix. Swelling of the matrix should decrease the volume fraction of clusters, which would account for the observed decrease in intensity of the SAXS curve.

Adding glycerol to the 2.65 MnSPS ionomer increased the intensity of the ionic peak and shifted it to smaller scattering vector (larger characteristic distance). This suggests that the glycerol swells the cluster, which would enhance the electron density contrast in the system and increase the volume fraction occupied the cluster. In swelling the cluster, the glycerol must also be weakening the strength of the intermolecular interactions, as demonstrated by the diminution of the rubbery plateau and shifting of the "cluster Tg" to lower temperature as shown in dynamic mechanical experiments.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

1. J. Polym. Sci., Part C: Polymer Letters, 24, 263 (1986)
2. Polymer, 27, 3 (1986)
3. Weiss and Fitzgerald, in Structure and Properties of Ionomers, M. Pineri and A. Eisenberg, Eds., NATO ASI Ser., Series C, 198, 361 (1987)

Report of Measurements Carried Out at the NCSASRInstrument(s) 10 - m SAXS CameraTitle Small-angle x-ray Scattering Studies of CopolymersResearch Sponsor Allied Corporation Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

N. S. Murthy**To Be Completed by ORNL**

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

The thermal stress cracking properties of ethylene-chlorotrifluoroethylene copolymer (E/CTFE copolymer, marketed as Halar[®] by Ausimont U.S.A. Inc.) was improved considerably by using 2 to 6 wt. % hexafluoroisobutylene (HFIB) as a termonomer. This improvement arises from the increased flexibility of the polymer molecule in the presence of HFIB units, which also reduces the average lamellar-repeat from 300-400 Å for the copolymer to 135-185 Å for the terpolymer. We postulate that crystalline lamellae consist entirely of alternating units of ethylene and chlorotrifluoroethylene, while the HFIB substituted E-CTFE segments are segregated in the interlamellar amorphous regions. These structural features are used to explain the role of HFIB in enhancing the resistance of the terpolymer to environmental stress-cracking.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Submitted to Polymer (July 1987)

Report of Measurements Carried Out at the NCSASRInstrument(s) ORNL 10-m SAXS CameraTitle On the Wear Behavior of Doubly-Oriented PolymersI. Nylon 6Research Sponsor Alexander von Humboldt Foundation Grant or Contact No. _____Oak Ridge Associated Universities.

Participants and NCSASR Collaborator(s)

H. Voss, Technical University of HamburgJ. H. Magill, University of PittsburghK. Friedrich, Technical University of HamburgJ. S. Lin, Oak Ridge National Laboratory**To Be Completed by ORNL**

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

On the Wear Behavior of Doubly-Oriented Polymers. I. Nylon 6

H. VOSS, J. H. MAGILL, * and K. FRIEDRICH, *Technical
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Synopsis

Wear behavior correlations with morphology and orientation directions have been established from commercially produced nylon 6 with different draw ratios between 1 and 7 approximately. The wear rate is least in a direction perpendicular to the draw direction for highly drawn samples. It correlates with surface microstructure and the inherent molecular characteristics induced by sample preparation. Well-characterized polymer specimens were used in this investigation.

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Journal of Applied Polymer Science, Vol. 33, 1745-1761 (1987)

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CCC 0021-8995/87/051745-17\$04.00

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) SAXS

Title Structure and Orientation Development in Biaxial Stretching
of UHMWPE GEL Films

Research Sponsor NSF Grant or Contact No. MSM-8519906

Participants and NCSASR Collaborator(s)

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Kenichi Fujita

Myung H. Cho

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

The major concern with the biaxially stretched UHMWPE film has been associated with the microvoiding. Some preliminary SAXS experiments were undertaken at the University of Akron using photographic technique. It was difficult to judge from the SAXS picture, therefore we requested the SAXS beam time from ORNL. Quantitative SAXS studies suggest that there is no appreciable voids in the biaxially stretched UHMWPE gels. This permits us to investigate the lamellar deformation during uniaxial and biaxial deformation.

A preliminary SAXS experiment was undertaken on 1x1, 6x6, and 10x10 stretched films in that the change of scattering pattern with biaxial deformation appears to be consistent with our SAXS photographs. Due to the misalignment of the SAXS beam the patterns were somewhat skew, thus no quantitative analysis was carried out. We intend to repeat the same experiment in the near future. Part of the work was reported at the APS meeting in New York City, March 1987.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

"Biaxial Stretching of UHMWPE Gel Films," T. Kyu, K. Fujita and M. H. Cho, APS Bulletin, New York, March 1987.

Report of Measurements Carried Out at the NCSASR

Instrument(s) SAXS

Title Fractal Analysis of Cotton Cellulose as Characterized by SAXS

Research Sponsor U.S. Department of Agriculture

Grant or Contact No. 5B-7B30-3-560.

CWU 6940-20551-043A

Participants and NCSASR Collaborator(s)

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To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Fractal Analysis of Cotton Cellulose
as Characterized by SAXS

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ABSTRACT

Complete small-angle x-ray scattering (SAXS) curves are reported and analyzed by conventional and fractal theories in this study of Valonia and eleven cotton cellulose samples. The scattering source is identified as voids in a solid matrix. The void volume fraction ranges from 0.7% to 3.4% in the various cotton samples and is 17% in Valonia. Modifications such as dewaxing, scouring, and bleaching improve the packing efficiency within aggregates, and additionally increase the void fraction. NaOH mecerization and NH₃ treatment destroy the packing efficiency slightly and decrease the void fraction. Two types of power-law decay were observed for the SAXS intensity $I(s)$. Hydrocellulose II and Valonia follow Porod's inverse fourth power law. Conventional analysis then determines the average pore size to be 8.5 nm and 12.5 nm, and specific inner surfaces of 15.3 and 45.2 m²/cm³, respectively. The other ten cotton samples follow power law decay with the exponent ranging from -2.7 to -2.1. The non-integer exponent is referred to as the Hausdorff dimension and suggests a fractal structure for the microcrystallites constituting the cellulose. The compliance of Hydrocellulose II and Valonia to Porod's law carries with it a model structure of a three dimensional void bounded by a smooth two dimensional surface. The other samples that have their fractal or Hausdorff dimension less than the Euclidian dimension implies there is a unit of measure small enough to sense discontinuities to the structure. The Hausdorff dimensions measured here suggest that native cellulose is a cluster aggregation of microcrystallites with the addition of rearrangement. Such speculations may stimulate some new insight to the growth mechanism of cotton.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

J. S. Lin, M. Y. Tang and J. F. Fellers, "Fractal Analysis of Cotton Cellulose as Characterized by SAXS." *The Structures of Cellulose, Characterization of the Solid States*, ed. by R. H. Atalla, ACS Symposium 340, Chap. 14, p. 233 (1987).

Report of Measurements Carried Out at the NCSASRInstrument(s) 10m SAXS - NCSASRTitle Annealing Behavior of Polyethylenes Designed for Underground Power Insulation

Research Sponsor _____

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

Y. D. Lee - UTPaul J. Phillips - UTY. S. Lin - NCSASR**To Be Completed by ORNL**

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

ANNEALING BEHAVIOR OF POLYETHYLENES
DESIGNED FOR UNDERGROUND POWER INSULATION

Most polymeric insulators are exposed to a high level of thermal stresses during their normal operation, since power transmission generates heat in the conductor. Thermal stresses not only change the structure of the materials but also modify their properties.

Studies of morphological changes resulting from annealing were carried out by the combined techniques of small-angle X-ray scattering (SAXS) and differential scanning calorimetry (DSC). The materials used are three different grades of

crosslinked low-density polyethylene (XLPE) and one grade of linear-low-density polyethylene (LLDPE).

The general shapes of radially averaged SAXS curves of XLPE are different from those of LLDPE. The SAXS plots of XLPE show well-defined Bragg maxima, indicating the presence of stackings of two entities with different electron densities, presumably amorphous and crystalline layers. On the other hand, the SAXS intensities of LLDPE decrease monotonically with very tiny hump-like Bragg maxima. Such patterns are considered to be due to the presence of poorly defined stacking structures with a wide distribution in their size.

Even though the shapes of the intensity curves of XLPEs are different from those of LLDPE, the effects of annealing on the structures of these polyethylenes are common. One sees three major principal effects—increasing long period spacing calculated from the Bragg peak, an overall increase of scattering intensity and a narrowing of the breadths of the Bragg peaks. These major effects become more pronounced as annealing time increases.

It is also noted that curing produces similar trends in the SAXS pattern as annealing. Once cured, the sample shows an increase in long periodicity and overall intensity. Upon curing, crystallinity values obtained from DSC decrease. Increase of long period on curing is considered therefore, to be due to a major thickening of the amorphous layer. Annealing was found however, to increase the crystallinity of the material. The increase in the long period of XLPE and LLDPE upon annealing is due to a major increase in the size of the crystalline layer, as expected.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASRInstrument(s) 10m SAXS cameraTitle Morphology and Thermal Aging of Crosslinked PolyethyleneResearch Sponsor EPRI Grant or Contact No. #7891

Participants and NCSASR Collaborator(s)

Ali Vatansever - UTPaul J. Phillips - UTY. S. Lin - NCSASR**To Be Completed by ORNL**

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

MORPHOLOGY AND THERMAL AGING OF
CROSSLINKED POLYETHYLENE

High voltage polyethylene (PE) and crosslinked polyethylene (XLPE) cables extruded and cured under different conditions were supplied by major cable producing companies. These original cables were subjected to various levels of thermal and thermoelectrical stresses. The materials were compared and studied to define their morphological structures and to assess the effect of thermal and thermoelectrical stresses on their structures, using optical and electrical microscopy, small and wide angle X-ray scattering techniques, and differential scanning calorimetry.

The morphologies throughout the cables are sheaf-like. The appearance of those morphological entities upon thermal and thermoelectrical aging remained unchanged. However, morphological structure was found to be altered on a lamellar scale upon aging in terms of the lamellar thickness and void content.

The overall shapes of radially averaged SAXS plots of all samples studied were quite similar, having broad Bragg peaks. The major difference between various cables of different history was in the intensity at low scattering angles, corresponding to entities bigger than 200-300Å. Higher intensity values at lower scattering angles observed in specimens subjected to high temperatures (ca. 107°C) are considered to reflect a melt separation between the gel network and the extractable sol fraction. An increase in scattering intensity at low angles occurred in the cable which was exposed to a high level of thermoelectrical stress during service and had deteriorated. This obvious consequence of the field aging process indicates the formation of voids in the size range 500 to 1000 Å. It is, however, also possible that this increase in SAXS intensity at the lower angles is caused by "tree" formation which was observed by optical microscopy using a staining technique. Ongoing research is attempting to quantify the void size and shape distribution using subtraction methods and fractal analysis.

Another apparent difference in morphological features between cables lies in the size of the crystalline layer. Thicknesses of the crystalline layer were calculated from the Bragg angle and crystallinity values obtained from the WAXD technique. In general, the outer layers of the cable insulation have relatively higher values of long periodicity and crystal thickness than the inner layers. The crystal thicknesses of thermally aged cables are relatively larger than those of the unaged counterparts. The crystal and amorphous thicknesses of field aged cable show essentially similar values to those of unaged cable, indicating that application of annealing procedures does not improve the crystallinity significantly. Despite the facts that extractable levels increased and molecular weight of the extractables decreased, demonstrating partial molecular breakdown in the matrix, the overall crystalline and amorphous phase distribution was found to be unchanged.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 10-M SAXS

Title The Influence of Thermal History on the Small-Angle X-Ray Scattering of
Sulphonated Polystyrene Ionomers

Research Sponsor University of ConnecticutGrant or Contact No. _____

Participants and NCSASR Collaborator(s)

R. A. Weiss

J. A. Lefelar

J. S. Lin

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

The influence of thermal history on the small-angle X-ray scattering of the sodium and zinc salts of lightly sulphonated polystyrene (SPS) ionomers is described. Increasing temperature above T_g promotes phase mixing in ZnSPS and increased phase separation in NaSPS. The effect of annealing at elevated temperatures on the microstructure of ZnSPS is reversible, but dependent on the cooling rate. Changes in the microstructure of NaSPS on annealing are irreversible.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASRInstrument(s) ORNL 10-m SAXS SystemTitle Polymer Crystallinity and Morphology in Polysiloxanes.Research Sponsor National Science Foundation Grant or Contact No. DMR 811-3089 and Alexander von Humboldt Foundation of West Germany.

Participants and NCSASR Collaborator(s)

To Be Completed by ORNLJ. H. Magill, University of Pittsburgh Date Received _____J. S. Lin, Oak Ridge National Laboratory Proposal No. _____

_____ Date of Experiment(s) _____

Report

**Polymer crystallinity and morphology in polysiloxanes.
Poly(tetramethyl-*p*-silphenylenesiloxane) and
poly(tetramethyl-*p*-silphenylene/dimethylsiloxane) copolymers**

Joseph H. Magill

School of Engineering, University of Pittsburgh, 841 Benedum Hall,
Pittsburgh, PA 15261, U.S.A.

(Date of receipt: May 2, 1985)

SUMMARY:

The crystallinities of polysiloxane homo- and copolymers, measured by DSC and checked by X-ray measurements, are presented. A wide range of crystallization conditions and molecular weight fractions were investigated. The morphological implications of crystallinity changes as a function of molecular weight are discussed in regard to other physical parameters. It is concluded that the dependence of crystallinity and X-ray long period on molecular weight is in accord with a defect interface created via chain entanglements primarily, which are trapped during crystallization. The morphology of the specimens directly reflects their preparative history and molecular weight.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) SAXS, SANS

Title Melting and Crystallization of UHMWPE Gels:
I. Melt Structure of UHMWPE.

Research Sponsor NSF Grant or Contact No. MSM-85 19906

Participants and NCSASR Collaborator(s)

Thein Kyu

Kenichi Fujita

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Date Received _____

Proposal No. _____

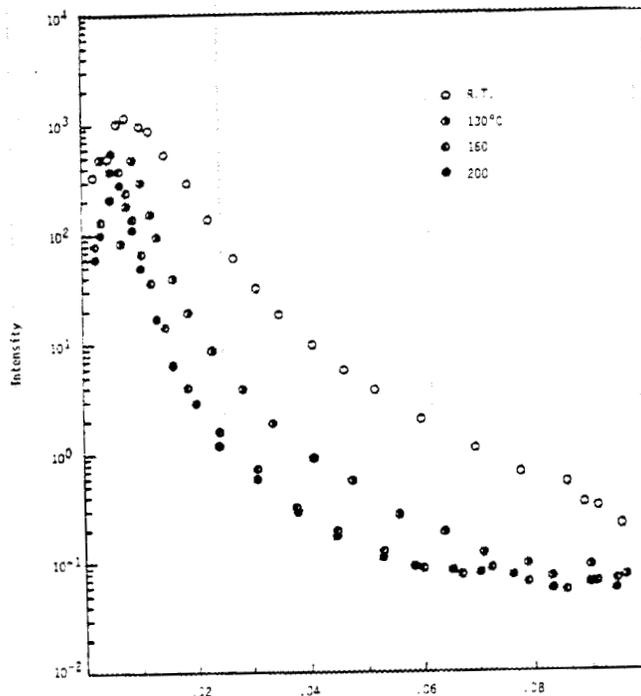
Date of Experiment(s) _____

Report

In an effort to examine the miscibility between ultra-high molecular weight polyethylene (UHMWPE) and conventional polyethylenes, a preliminary small-angle neutron scattering (SANS) experiment on blends of UHMWPE with deuterated linear low density polyethylene (D-LLDPE) was undertaken in the melt state. The increase in SANS intensity was noticed during isothermal runs at 160°C, 180°C and 200°C. It was suspected at the beginning that, the phenomenon may be associated with thermal-induced phase separation which is occasionally observed in amorphous polymer blends. This behavior was further pursued by Ree and Stein who concluded that it may be an artifact. The detail is expected to be reported by the Stein's group.

Meanwhile, the investigation on the melt behavior of UHMWPE was in progress in our laboratory using small-angle light scattering (SALS) and wide-angle x-ray diffraction (WAXD). It was found that SALS scattering indeed persists in the UHMWPE melts. WAXD studies, however, show the disappearance of (110) and (200) crystal planes above the T_m (140°C) of UHMWPE, implying that light scattering from the UHMWPE melts is not relevant to crystal orientation fluctuation. SAXS studies at ORNL also support the above observation in that SAXS intensity persists up to 200°C (Fig. 1). It seems that the melt viscosity of UHMWPE, associated with extremely high molecular weight, is so high so much so that their melts remain heterogeneous even in the melt state.

In summary, the increase of SANS intensity of UHMWPE/D-LLDPE with increasing temperature above their T_m is not necessarily due to thermal induced phase separation. Scattering can occur from heterogeneity of UHMWPE melts; ordered structure is likely to exist in the melt state.



References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASRInstrument(s) 10 m SAXSTitle Dynamic or In situ SAXS Crystallization of PolymersResearch Sponsor ORAU, NSF, DOE Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

J. M. Schultz, Univ. of DelawareJ. S. Lin, NCSASR**To Be Completed by ORNL**

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report Several presentations at the Amer. Phy. Soc. and Amer. Chem. Soc. Meetings were presented on this research. There were other lectures (invited and contributed) dealing with SAXS results obtained at Oak Ridge. Published papers are enclosed with this report.

Dynamic crystallization experiments using poly(TMPS) fractions were made with a sample cell designed and constructed at the University of Pittsburgh (it was patterned after an earlier Oak Ridge model of Schultz et al). All crystallization measurements were made in real time using the 6 K watt Rigaku generator which aborted on many long runs invalidating the experiments. The New 12 K watt facility has not yet been used for in situ SAXS kinetics, but it is hoped to activate it soon for this purpose.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

See attached sheet

Report of Measurements Carried Out at the NCSASRInstrument(s) 10 meter SAXS cameraTitle SAXS Studies of the Microdomain Structure in Copolyester-ether ElastomersResearch Sponsor University of Tennessee, Knoxville Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

Galen C. RichesonDr. J. E. Spruiell**To Be Completed by ORNL**

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

EFFECT OF COMPOSITION AND PROCESSING CONDITIONS
ON THE STRUCTURE AND PROPERTIES OF ELASTIC FILAMENTS
MELT SPUN FROM COPOLYESTER-ETHERS

Elastic filaments have been produced by melt spinning poly(tetramethylene terephthalate)/poly(tetramethylene ether glycol)-terephthalate (PTMT/MTMEG-T) copolymers of various hard segment contents (HSC). The microstructure and mechanical properties were found to be strongly dependent on the composition and processing conditions.

The crystallization behavior depends primarily on HSC and the crystallization temperature. Small angle X-ray scattering studies (SAXS) show that the degree of phase separation in as-spun filaments decreases as HSC increases. Annealing produces a significant increase in the degree of phase separation in filaments having a high HSC, but has little effect on those low in HSC. Thus, the shorter hard segment sequences are able to crystallize at the quench temperature, whereas the

longer sequences require higher temperatures for crystallization.

Wide angle X-ray diffraction studies show the orientation of the crystalline hard segments increases greatly in all compositions as the spin draw ratio is increased. The two-point SAXS patterns indicate a lamellar structure with some degree of preferred orientation in all samples. As the spin draw ratio is increased, the lamellae become increasingly aligned with their long axis perpendicular to the fiber axis. Wide angle line broadening experiments show that the crystallite thickness is relatively independent of HSC, while SAXS shows a decrease in the long period as HSC increases. Thus, the thickness of the amorphous phase decreases with increasing HSC due to there being a greater number of lamellae stacked in the axial direction.

Upon annealing, the crystallites grow primarily by the addition of new chain stems to their lateral surfaces, although some crystallite thickening appears to occur in filaments having a high HSC. The increase in crystallite thickness, however, is not enough to account for the large increase observed in the long period. Thus, the thickness of the amorphous phase must increase as annealing temperature goes up. It is believed that the smaller crystallites melt at the annealing temperature. This, in effect, increases the axial distance between the larger crystallites.

The tensile properties were determined so that structure-property relationships could be established. The modulus and drawing stress were found to depend primarily on the HSC and the degree of phase separation. The tenacity seems to depend more on the initial degree of orientation than on the degree of phase separation in a particular sample. Both the amount of hard segment drawing and soft segment elasticity play a role in determining the ultimate elongation.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

"Effect of Composition and Processing Conditions on the Structure and Properties of Elastic Filaments Melt Spun from Copolyester-Ethers," presented at the Society of Plastics Engineers 45th Annual Technical Conference, Los Angeles, Calif., May 4 - May 7, 1987. Paper published in Conference Proceedings.

Report of Measurements Carried Out at the NCSASRInstrument(s) ORNL 10 meter SAXS system with 2 dimensional detectorTitle Small-Angle X-ray Scattering Studies of Solution-Cast Perfluorosulfonate Ionomer FilmsResearch Sponsor Dow Chemical CompanyGrant or Contact No. RF 5379

Participants and NCSASR Collaborator(s)

Dr. Charles R. Martin (TAMU)Robert B. Moore III (TAMU)Dr. J. S. Lin (NCSASR)

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Small-angle x-ray scattering experiments were conducted to detect and measure the microdomains present in perfluorosulfonate ionomers (PFSI's). Three forms of 1100 EW Nafion (E.I. duPont Company) were analyzed. The first form was the as-received polymer membrane which has been well characterized by previous SAXS studies (1-4). The other two forms of the PFSI, termed solution-processed and recast, were prepared by completely evaporating a solution of the polymer at different temperatures. The recast PFSI was prepared by room temperature evaporation of a Nafion solution in ethanol and water. The solution-processed PFSI was prepared by evaporation of a Nafion solution in DMSO at 185°C. These solution-cast forms of the PFSI have not been previously characterized.

Figure 1a shows SAXS data from as-received 1100 EW Nafion. In agreement with previous studies, a large scattering peak at $k = 0.12$ (Bragg spacing of ca. 50Å) is observed. This peak has been attributed to scattering from ionic clusters present in this PFSI (1,2).

Figures 1b and c show SAXS data from solution-processed and recast Nafion, respectively. The prominent scattering peaks suggest that ionic clusters are also present in both solution-cast forms of the polymer. Furthermore, because the k values are approximately the same, the Bragg Spacing in all three forms of this PFSI are equivalent.

The SAXS data also reveal information about the extent of crystallinity in these polymers. The shoulder at ca. $k = 0.04$ (Bragg spacing = 160\AA) in the as-received polymer has been attributed to scattering from the PFSI crystallites (2-4). Note that only as-received and solution-processed Nafion produce this shoulder. No evidence for crystallinity exists for the recast Nafion. Thus, the solution-processing procedure apparently regenerates crystalline regions similar to those found in the as-received polymer.

References

- 1.) Gierke, T.D.; Munn, G.E.; Wilson, F.C. J. Polym. Sci. Polym. Phys. Ed. 1981, 19, 1687.
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- 3.) Fujimura, M.; Hashimoto, T.; Kawai, H. Macromolecules 1981, 14, 1309.
- 4.) Roche, E.J.; Pineri, M.; Duplessix, R.; Levelut, A.M. J. Polym. Sci. Polym. Phys. Ed. 1981, 19, 1.

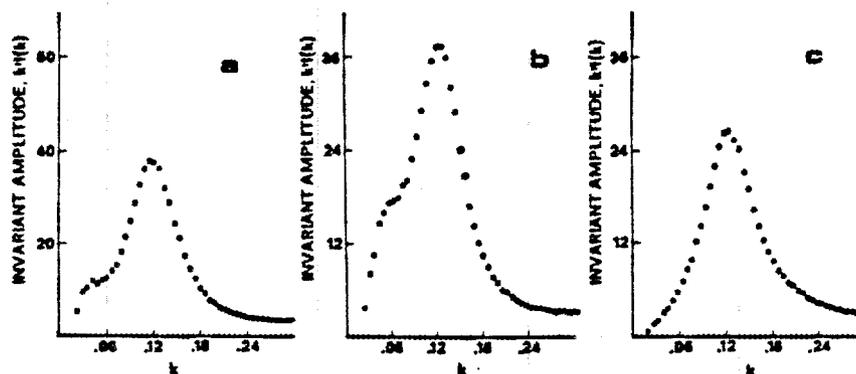


Figure 1. SAXS data for 1100 EW Nafion.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Submitted to Macromolecules.

Report of Measurements Carried Out at the NCSASRInstrument(s) SAXSTitle Search for Ion Aggregation in Doped PolyanilineResearch Sponsor U. S. Department of Energy Grant or Contact No. DE-AC05-84OR24100
KC 02 03 02 0

Participants and NCSASR Collaborator(s)

Brian K. AnnisStephen Spooner**To Be Completed by ORNL**

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

The SAXS and SANS scattering patterns for a number of ion containing polymers have been found to contain peaks which correspond to Bragg spacings in the range 20 to 60 Å. These peaks are normally attributed to the formation of ion clusters.

As a part of a study of the structural aspects of the conducting polymer-doped polyaniline, SAXS measurements on the emeraldine and emeraldine hydrobromide forms of polyaniline were carried out. The conducting form, emeraldine hydrobromide, contained the maximum possible doping level of Br which corresponds to a Br/N atom ratio of 0.52. Both samples were provided by A. G. MacDiarmid and A. F. Richter of The University of Pennsylvania and were in powder form. The SAXS measurements were made on compressed pellets of the materials and covered a range of momentum transfer of 0.02-0.04 Å⁻¹. In this range, no peaks were observed which could be attributed to clustering of the bromine.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASRInstrument(s) ORNL 10-m SAXS CameraTitle Small-Angle X-Ray Scattering of Doubly Oriented Polymers.Research Sponsor Oak Ridge Associated University Grant or Contact No. _____Potential NSF or Army Research Office

Participants and NCSASR Collaborator(s)

J. H. Magill, University of PittsburghM. J. Shankernarayan, University of PittsburghJ. S. Lin, NCSASR, Oak Ridge National Laboratory**To Be Completed by ORNL**

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Doubly-oriented commercial plastics polyolefins, polyamides and polyesters especially have been prepared with very high moduli and strengths, high transparency, low shrinkage and creep properties using a one step compressive rolling operation with substantial "take-off" tension applied to the workpiece simultaneously. Quality polymers of moderate molecular weight with well organized "amorphous" and crystalline regions displaying pseudo "single-crystal-like" morphologies have been investigated using SAXS and other techniques. Oak Ridge SAXS demonstrated that well oriented polymers exhibit triaxial disposition of crystallites showing several orders of reflection along the orientation direction, parallel and perpendicular to the rolling plane. There is also substantial crystallite order transverse to the draw (machine) direction. A low index crystallographic plane always lies parallel to the roll plane in these well defined specimens which have numerous technological applications.

Small-Angle X-ray Scattering from Rolltruded Polyolefins. J. H. Magill and M. J. Shankernarayanan, University of Pittsburgh, and J. S. Lin, NCSASR, Oak Ridge. Superior doubly oriented polymers of high modulus, strength and transparency amongst other properties have been investigated by many techniques including small-angle X-ray scattering. Commercial polyethylene and polypropylene have been studied using the Oak Ridge 10 meter small angle scattering equipment to provide unique results on morphology-property correlations over a wide range of draw ratios and processing conditions. These rolltruded specimens, of reproducible quality, are comprised of well organized triaxially oriented crystallites associated with a variously oriented amorphous matrix of controllable dimensions. Some of the implications and correlations derived from these processed samples will be correlated and discussed in regard to processing conditions.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Amer. Phy. Soc. Reprints (DHPP) Abst. 32 #3, OV6
p. 837, March 16-20 New York (1987)

Report of Measurements Carried Out at the NCSASR

Instrument(s) SAXS

Title Characterization of Surface Modified Carbon Fibers and Their Epoxy Composites
by Small Angle X-Ray Scattering

Research Sponsor Fulbright Commission (BS) Grant or Contact No. _____

Participants and NCSASR Collaborator(s)
J. S. Lin

To Be Completed by ORNL
Date Received _____
Proposal No. _____
Date of Experiment(s) _____

Report

CHARACTERIZATION OF SURFACE MODIFIED CARBON FIBERS AND THEIR
EPOXY COMPOSITES BY SMALL ANGLE X-RAY SCATTERING

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ABSTRACT

This paper correlates the interlaminar shear strength of 7 different carbon fiber/epoxy composite with structural characteristics determined by Small Angle X-ray Scattering (SAXS) measurements. The carbon fibers were all of the same type but had different surface treatments. The SAXS patterns of the fibers and of the composites showed a highly nonlinear Guinier region which could not be approximated by traditional linear regression. A new approach to the Guinier approximation was developed to treat this nonlinear curve using a polynomial of second order. The radius of gyration (RG) of the fibers, as determined by this new method, correlated clearly with both the extent of the surface treatment and the interlaminar shear strength of the composite. Also the difference in scattering between a dry fiber and a glycerine soaked fiber provides a way to characterize the changes obtained by surface treatments. These methods provide new ways to estimate the efficiency of a surface treatment and its effect on the interlaminar shear strength by analyzing the SAXS patterns of the fibers.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Bernhard Stoll, J. F. Fellers and J. S. Lin, "Characterization of Surface Modified Carbon Fibers and Their Epoxy Composites by Small Angle X-Ray Scattering," Presented at MRS Symposium For Scattering, Deformation and Fracture in Polymers, Dec. 1-4, 1986, Boston, MA.

Report of Measurements Carried Out at the NCSASRInstrument(s) 10 meter SAXS unitTitle Small Angle X-ray Diffraction from Nylon StrappingResearch Sponsor University of Tennessee Grant or Contact No. none

Participants and NCSASR Collaborator(s)

Dr. Edward S. ClarkMr. Y. Shinoharawith J. S. Lin NCSASR**To Be Completed by ORNL**

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Research had been conducted at an earlier date at NCSASR on polyethylene sheeting which was highly oriented uniaxially but showed a strong tendency to delaminate under tearing stress rather than split. This unexpected combination of properties was explained in terms of a new interpretation of morphological structure. Of particular importance in the hypothesis was the nature of SAXS data recorded in three dimensions using a goniometer on the 10m SAXS system. In certain directions, a four-point diagram is found; in other directions, a two-point diagram is seen.

Another sample, a commercial nylon strapping, was found which had similar properties of uniaxial orientation and lack of splitting with delamination under tearing stress. In support of preparing a proposal for further experimentation in support of the hypothesized morphology, SAXS data were recorded in three dimensions on the strapping. Similar two-point and four-point diagrams were observed supporting the proposal that the morphology is a generic type and not specific to polyethylene.

Publication is planned when suitable additional experiments and interpretation are complete.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) SAXS

Title X-Ray Scattering Studies of Graphite Fibers

Research Sponsor _____ Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

J. S. Lin

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

X-ray scattering studies of graphite fibers

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(Received 4 November 1985; accepted for publication 1 April 1986)

The structural features of three different graphite fibers were studied via small- and wide-angle x-ray techniques. The experimental evidence is consistent with a sheath/core fiber morphology. Graphitization, degree of orientation, crystallite size, and microporosity were analyzed. Samples included low (AS4) and high (HMS) modulus poly(acrylonitrile) (PAN) and melt-spun pitch-based (VSB-16) fibers. By wide-angle x-ray diffraction (WAXD) VSB-16 was found to have the highest degree of graphitization, the highest degree of orientation, and the largest crystallite regions, and AS4 the poorest graphitized structure. The void system in these graphite fibers was investigated by small-angle x-ray scattering (SAXS). SAXS from glycerin-soaked fibers indicates the scattering at very small angles ($2\theta < 10$ mrad) is dominated by total reflection of x rays at the fiber surface. The pores in HMS and VSB-16 fibers are inaccessible to glycerin and the pores in AS4 fiber are partially accessible. The pores in PAN-based HMS and AS4 fibers are of needlelike shape and those in VSB-16 are ellipsoidal. The porosity is 12.6%, 8.4%, and 4.5% in HMS, AS4, and VSB-16 fibers, respectively. Deviations from Porod's law were observed at large angles and attributed to scattering from fractal aggregates of carbon atoms in the graphite crystallites and/or fractal boundaries of pores. The fractal dimension of the aggregates is 2.3 ± 0.1 , 2.8 ± 0.2 , and 3.0 ± 0.2 for AS4, HMS, and VSB-16 fibers, respectively. Speculations about the fractal nature of aggregation may stimulate some new insight to the graphitization process, paracrystallinity, and the strength of graphite fibers.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Ming-Ya Tang, G. G. Rice, John F. Fellers and J. S. Lin, "X-ray Scattering Studies of Graphite Fibers," *J. Appl. Phys.* 60(2), 15 July, 1986.

Report of Measurements Carried Out at the NCSASR

Instrument(s) SAXS

Title A Dynamic Small Angle X-ray Scattering Study of Stressed Kevlar 49/Epoxy Composites

Research Sponsor Lawrence Livermore Nat. Lab. Grant or Contact No. 4502810

Participants and NCSASR Collaborator(s)

J. S. Lin

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

A Dynamic Small Angle X-Ray Scattering Study of Stressed Kevlar® 49/Epoxy Composites

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(Received May 1984)

ABSTRACT

The failure mechanisms of Kevlar® 49 fibers, epoxy resin and uniaxial Kevlar® 49 fiber reinforced epoxy composites under tensile loads have been studied using small angle x-ray scattering (SAXS) and scanning electron microscopy (SEM). The behavior of specimens of uniaxial Kevlar® 49 fiber reinforced epoxy with various angles between the fiber direction and the tensile load axis was examined using an Instron Mechanical Tester. SAXS showed the Kevlar® 49 fibers fail due to increases in the volume fraction of microvoids and enlargement of larger microvoids along the fiber axis direction. These changes in microvoids arise from the effect of Poisson's ratio being less than 0.5. Hydrolytic degradation of Kevlar® 49 fibers leads to roughening of the surfaces and decreases in the mass densities. The epoxies and the composites failed in a catastrophic dynamic process, the crack originating from surface flaws or air bubbles entrapped in the epoxies during the curing process. The SEM investigations on the failed composites revealed fiber-splits and fiber-pullouts. The results of mechanical tests showed the composite moduli, the composite ultimate strengths and the elongations at break decrease as the angle between the fibers and loading axis increase. The maximum work theory provides a good fit with the experimental ultimate strength results of the composites.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

J. S. Lee, J. F. Fellers, M. Y. Tang and J. S. Lin, "A Dynamic Small Angle X-Ray Scattering Study of Stressed Kevlar 49/Epoxy Composites," *Journal of Composite Materials*, Vol. 19, March 1985.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 10-m SAXS Facility

Title Thorium Nitrate Hydrous Polymer Solutions (#2)

Research Sponsor DOE-BES-Chemical Sciences Grant or Contact No. FTFA No. 68
KC 03 02 02 0

Participants and NCSASR Collaborator(s)
L. M. Toth
J. S. Lin
L. K. Felker

To Be Completed by ORNL
Date Received _____
Proposal No. _____
Date of Experiment(s) _____

Report

Small angle x-ray scattering measurements (SAXS) on thorium polymers grown with and without uranyl ion present were performed. Samples with 0.05M Th(IV) and 0.05M Th(IV)-0.25M UO_2^{2+} were adjusted to pH 3.5 and aged at 90°C to form hydrous polymers. Comparisons of the polymer particle sizes of these samples with previous data and with a sample to which UO_2^{2+} was added to an aged Th(IV) polymer sample are being made. An additional scouting test using a thorium chloride sample was also measured to compare particle sizes in a different matrix. Analysis of the data from all of these runs is in progress and a report on the thorium system is forthcoming.

At this stage of the analysis, it is not possible to demonstrate that uranyl ion decreases the size of the Th(IV) polymer through a chain termination reaction using the SAXS technique. The problem, however, lies more with the $\text{UO}_2^{2+}/\text{Th}^{4+}$ system since both ions tend to hydrolyze in the same pH region, namely pH= 3-4 and UO_2^{2+} precipitates. It should be realized that the significant chain inhibition reaction was noted with the $\text{UO}_2^{2+}/\text{Pu}^{4+}$ system in which Pu^{4+} begins to hydrolyze in the pH= 1-2 region. (We hope to demonstrate the UO_2^{2+} inhibition effect on Pu^{4+} this fall with neutron scattering.)

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) ORNL 10-m SAXS System

Title In Situ SAXS Investigations of Isothermal Crystallization in
Poly(TMPS) Fractions

Research Sponsor National Science Foundation Grant or Contact No. DMR 811 3089
and NSF CPE 830 40 58

Participants and NCSASR Collaborator(s)

J. H. Magill, University of Pittsburgh

J. M. Schultz, University of Delaware

J. S. Lin, Oak Ridge National Laboratory

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

In situ SAXS investigations of isothermal crystallization in poly(TMPS) fractions*

J. H. Magill¹), J. M. Schultz²), and J. S. Lin³)

¹) Department of Materials, Science and Engineering, University of Pittsburgh, Pittsburgh, U.S.A.,

²) Department of Chemical Engineering, University of Delaware, Newark, U.S.A., and

³) Center for Small-Angle Scattering, Oak Ridge National Laboratory, Oak Ridge, U.S.A.

Abstract: The isothermal crystallization kinetics of poly(TMPS) has been measured by ISSAXS and results obtained for a molecular weight fraction (21,000) below the critical entanglement molecular weight (25,000) and another one above it (371,000). The SAXS intensity vs. time curves suggest that a single transformation mechanism exists. The SAXS long period is independent of crystallization time for both poly(TMPS) fractions. However the interlamellar thickness contribution to the long period is dependent upon molecular weight and crystallization temperature, increasing with temperature and molecular weight. The crystallite contribution also increases over the range studied. Both fractions exhibit a significant, but reversible decrease in thickness on cooling the sample from the crystallization temperature to room temperature and recycling again. The change is more pronounced for 371,000 specimen in keeping with its lower crystallinity. The path dependence of lamellar dimensions has significant implications in the morphological characterization of polymers annealed or crystallized at one temperature and then measured at another one.

Key words: Poly(TMPS), *in situ*, SAXS, crystallization, kinetics.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 10-M/30-M Instruments

Title Absolute Calibration of Small-Angle Neutron Scattering Data

Research Sponsor _____ Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

G. D. Wignall

F. S. Bates

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Absolute calibration forms a valuable diagnostic tool in small-angle neutron scattering experiments, and allows the parameters of a given model to be restricted to the set which reproduces the observed intensity. Discrepancies between the observed and calculated intensities may arise from potential artifacts or even new physical processes and absolute calibration methods are useful in delineating these circumstances. General methods which are available for absolute scaling are discussed along with estimates of the degree of internal consistency which may be achieved between the various standards. In order to minimize the time devoted to calibration in a given experimental program, emphasis is placed on developing a set of precalibrated strongly scattering standards which may be run in the chosen experimental geometry. Comparison of such a set developed at the National Center for Small-Angle Scattering Research (Oak Ridge), and independent determinations by SANS users indicates consistency to within +5%.

References

Give references if the work has been published or submitted to conferences, symposia, etc.
J. Appl. Cryst. 20, 28 (1987).

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30-M (October 6-9, 1986)

Title Long Range Static Correlation in Molten ZnCl₂ Near the Melting Point

Research Sponsor _____ Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

Roberto Triolo

E. Caponetti

P. Migliardo

C. Vasi

G. P. Smith

To Be Completed by ORNL

Date Received _____

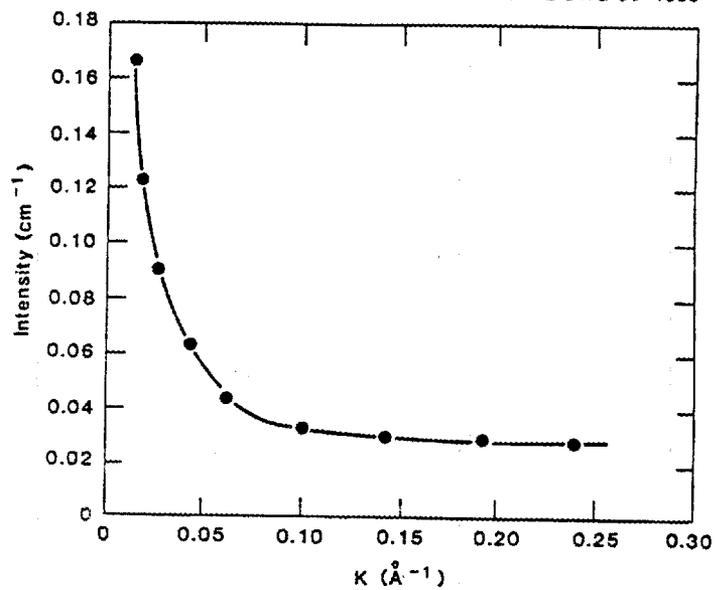
Proposal No. _____

Date of Experiment(s) _____

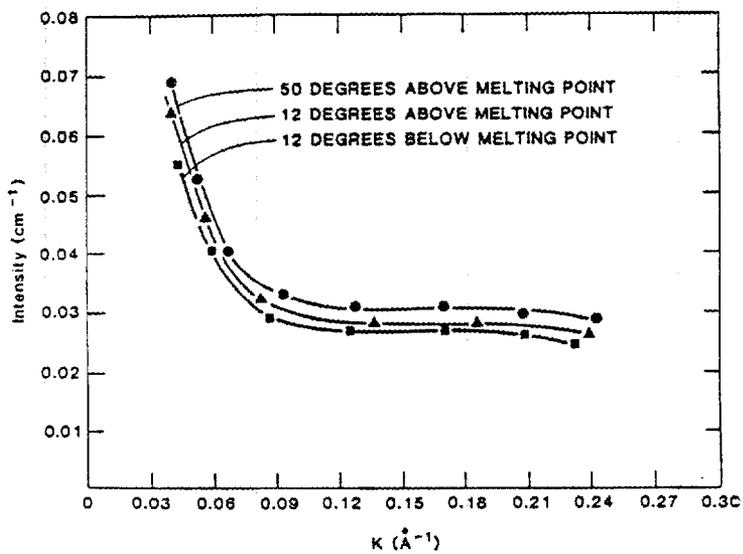
Report

Liquid ZnCl₂ has been studied at 50 and 12 degrees C above the melting point as well as at 12 degrees below the melting point (supercooled liquid). Scattering data have been obtained in the range of momentum transfer k $0.01 < k < 0.25 \text{ \AA}^{-1}$. Due to the low counting rate we have been unable to collect data in the full range of k at all the temperatures. However, the noticeable increase of intensity at small values of k (Fig. 1 and Fig. 2) is a clear indication of long range correlations which seem to extend further than we anticipated. The behavior found explains some peculiar results of literature and correlates well, from a qualitative point of view, with Rawan, Rayleigh wing and quasielastic light scattering experiments by us performed. While analyzing these data we also plan to perform depolarized Brillouin scattering experiments on the same samples.

ORNL DWG 86-1033

ZnCl₂ AT 373°C

ORNL DWG 86-1034

MOLTEN ZnCl₂

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30-meter SANS

Title Investigation of the Flux-Line Lattice in Superconducting Niobium BiCrystals

Research Sponsor DOE Grant or Contact No. _____

Participants and NCSASR Collaborator(s)
D. K. Christen

To Be Completed by ORNL
Date Received _____
Proposal No. _____
Date of Experiment(s) _____

Report

FLUX-LINE PINNING BY THE GRAIN BOUNDARY IN NIOBIUM BICRYSTALS

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Flux-line pinning by the grain boundary in niobium bicrystals was investigated by making four-terminal measurements of the critical current and neutron diffraction measurements of the flux-line bending. The elementary pinning interaction is estimated from the critical current data by using an approximate theory of the current distribution on the grain boundary. The data reported here are mainly for a sample in which the applied magnetic field is parallel to the [111] and the [001] crystal directions in the two grains when it is in the plane of the boundary and perpendicular to the current direction. Evidence is seen of grain boundary faceting and of a flux-flow rectification effect that peaks as a function of temperature below 3 K. The scale of the grain-boundary pinning is consistent with the quasiparticle-scattering theory.

*Research sponsored by the Division of Materials Sciences, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. †Research sponsored by the National Science Foundation under Grant DMR79-15799.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

"Proceedings of the International Symposium on Flux Pinning and Electromagnetic Properties in Superconductors" 11-14 November, 1985, ed. K. Yamafuji and F. Irie. Matsukuma Press, Fukuoka. p.38.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30 M SANS

Title Structure of Porous Vycor Glass.

Research Sponsor AT&T Bell Labs; ORNL

Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

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To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Structure of porous Vycor glass

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Small-angle neutron scattering experiments investigating the structure of porous Vycor glass are reported. The long-wave-length behavior ($0.004 \text{ \AA}^{-1} \leq q \leq 0.025 \text{ \AA}^{-1}$) of the measured structure factor $S(q)$ is in good agreement with Cahn's prediction for spinodal decomposition. The high- q data do not conclusively establish whether the internal surfaces are fractally rough over the length scales probed. Experiments on Vycor contrasted with protonated and deuterated cyclohexane reveal local composition gradients within the glass.

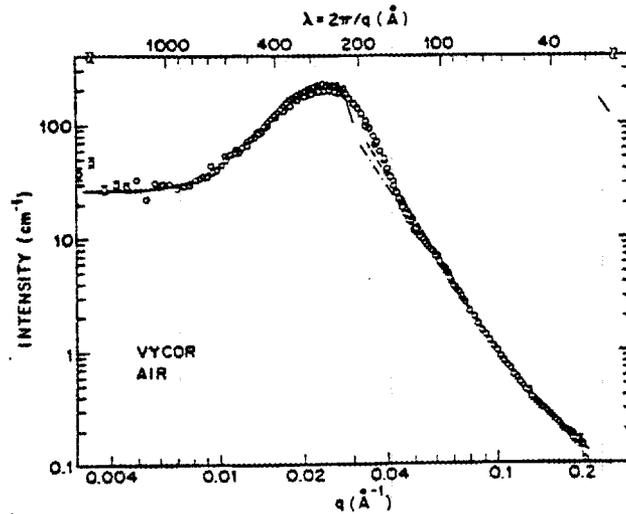


FIG. 1. Intensity of neutrons scattered by dry Vycor as a function of momentum transfer q . Three data sets obtained for various detector settings are spliced together. Statistical error bars are smaller than the symbol if not indicated. The solid line is a fit to the Cahn prediction Eq. (1). The dashed and dashed-dotted lines are fits to Eq. (2) (see text).

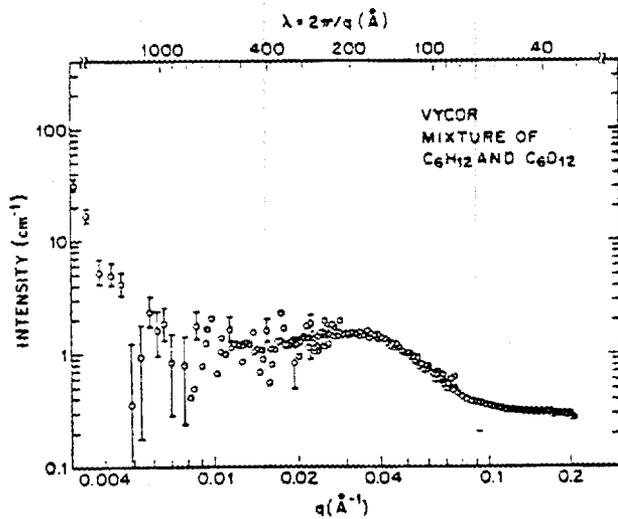


FIG. 2. Intensity of neutrons scattered by Vycor imbibed with a 50/50 mixture by volume of C_6H_{12} and C_6D_{12} .

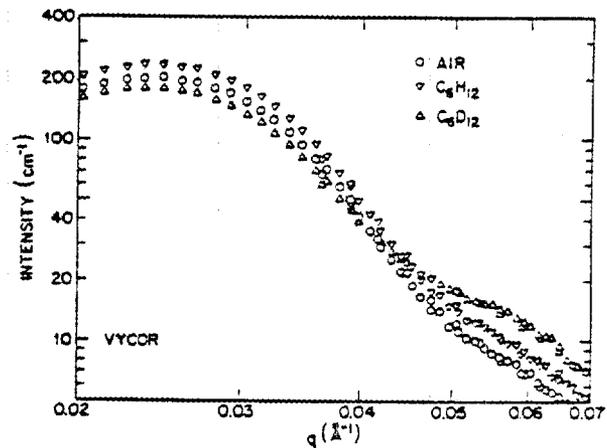


FIG. 3. Intensity of neutrons scattered by Vycor contrasted with air, protonated and deuterated cyclohexane.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Physical Review A (1987), 36, 000.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30-m SANS System

Title Studying Fractal Geometry on Submicron Length Scales
By Small-Angle Scattering

Research Sponsor Schlumberger-Doll Research Center Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

Po-Zen Wong, Schlumberger-Doll

J. S. Lin , Oak Ridge National Laboratory

To Be Completed by ORNL

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Proposal No. _____

Date of Experiment(s) _____

Report

Studying Fractal Geometry on Submicron Length Scales by Small-Angle Scattering

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and

Jar-shyong Lin

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ABSTRACT

Recent studies have shown that the internal surfaces of porous geological materials, such as rocks and lignite coals, can be described by fractals down to atomic length scales. In this paper, we review the basic properties of self-similar and self-affine fractals and discuss how the fractal dimensions can be measured by small-angle scattering experiments.

** Abstract of a paper to appear in *Mathematical Geology* (in press, 1987)

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30 m SANS, Double Crystal SANS, 10 m SAXS

Title STRUCTURE OF POROUS MATERIALS

Research Sponsor DOE

Grant or Contact No. DE-AC-04-76DP00789

Participants and NCSASR Collaborator(s)
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J. H. Aubert, and D. Christen

To Be Completed by ORNL
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Proposal No. _____
Date of Experiment(s) _____

Report

We have studied the structure of a variety of porous materials using Small-Angle Neutron Scattering. Samples included silica aerogels, porous silicas prepared by a vapor-phase growth process, and foams prepared by a gelation process. In the case of the porous silicas, we have used fractal analysis of the scattering curves to interpret the structure. In addition, the observed structures were traced to chemical and physical growth processes that occur in the precursor solution phases to these materials.

We also studied the structure of porous silica prepared by a vapor-phase growth process such as that used to prepare optical fibers. In this case, the scattering curves were basically featureless demonstrating a porosity length scale of about $1\mu\text{m}$ and smooth surfaces on shorter length scales. By doing an index-matching experiment with a saturating mixture of D_2O and H_2O , we demonstrated that the porosity was completely connected.

We also studied the structure of foams prepared by gelation of crystalline polymers in solution followed by freeze drying. In this case, we observed a very interesting fractal growth process during the gelation part of the preparative sequence. At the present time, we interpret the growth of fractal aggregates as a feature of the growth of crystalline polymers, although other interpretations in terms of phase separation cannot be ruled out.

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Give references if the work has been published or submitted to conferences, symposia, etc.

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D. W. Schaefer, J. P. Wilcoxon, K. D. Keefer, and B. C. Bunker, Physics of Chemistry of Porous Media II, edited by J. R. Banavar, J. Koplik, and K. W. Winkler (American Institute of Physics, New York, 1987).

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30-m SANS Camera

Title Small-Angle Scattering Study of Sedimentary Rocks.

Research Sponsor Schlumberger-Doll Research Center Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

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Dr. James Howard, Schlumberger-Doll

To Be Completed by ORNL

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Proposal No. _____

Date of Experiment(s) _____

Report

Surface Roughening and the Fractal Nature of Rocks

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(Received 12 February 1986)

The microstructure of sedimentary rocks is studied by small-angle neutron scattering for length scales between 5 and 500 Å. In limestones and dolomites, we find that the pore surfaces are effectively smooth above 50 Å, but there is evidence for roughening on shorter length scales. In sandstones and shales, the pore surfaces show fractal character due to the presence of clay. The fractal dimension is nonuniversal. We attribute these observations to impurity effects, which can lower the surface tension and maximize the surface area.

Abstract of the paper, *Physical Review Letters*, Vol.57, 637 (1986)

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 10-M SAXS, 10-M SANS, 30-M SANS

Title Intercalibration of Small-Angle X-Ray and Neutron Scattering Data

Research Sponsor IBM/NSF/DOE Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

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J. S. Lin

S. Spooner

G. D. Wignall

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Absolute calibration forms a valuable diagnostic tool in small-angle scattering experiments, and allows the parameters of a given model to be restricted to the set which reproduces the observed intensity. General methods which are available for absolute scaling of small-angle x-ray scattering (SAXS) data are reviewed along with estimates of the degree of internal consistency which may be achieved between the various standards. In order to minimize the time devoted to calibration in a given experimental program, emphasis is placed on developing a set of precalibrated strongly scattering standards for the SAXS facilities of the National Center for Small-Angle Scattering Research (Oak Ridge). Similar standards have been developed previously for calibration of small-angle neutron scattering (SANS) data. Particular attention is given to standards which can be used for either SAXS or SANS experiments, where each sample has been independently calibrated for both types of radiation. These calibrations have been cross-checked via the theoretical relationships between the two cross sections.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

To be presented at the International Conference on Small-Angle Scattering, Argonne, Illinois, October 26-29, 1987.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 10 meter SAXS

Title Fractal Character of Electro-deposited Manganese

Research Sponsor _____ Grant or Contact No. _____

Participants and NCSASR Collaborator(s) _____ To Be Completed by ORNL
John Bates, Solid State Division _____ Date Received _____

S. Spooner _____ Proposal No. _____

_____ Date of Experiment(s) _____

Report

SAX and SANS measurements of the scattering from electrodeposited manganese were made with the object of establishing the fractal character of the structure of these materials. Although the scattering in both neutron and x-ray measurements was very strong, the behavior of the scattering in the Porod region did not show a ~~strong~~ measureable deviation from the k^{-4} behavior. In fact an effective particle size distribution could be calculated which resulted in a log-normal size distribution. It is concluded that fractal character, while evident in the optical microscope, is not seen in the size range of 1 to 100 nm. Only a measurement made in the optical SAS range would be expected to show fractal geometry effects.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 30-m SANS Camera

Title Fractal Surface in Porous Media

Research Sponsor Schlumberger-Doll Research Center Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

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PO-Zen Wong, Schlumberger-Doll Research

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

FRACTAL SURFACES IN POROUS MEDIA

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ABSTRACT

Recent studies have shown that porous materials often have fractal internal surfaces. In the article, we give a brief review of what fractal surfaces are, how they are observed experimentally, why they form, and how they affect the a.c. electrical transport properties through the media. Theoretical results are compared to real systems such as sedimentary rocks and rough/porous electrodes.

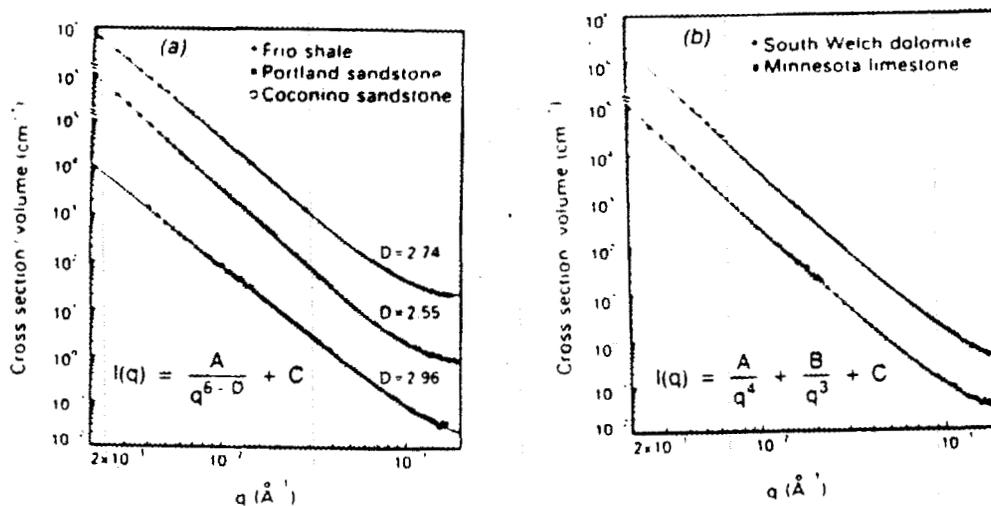


Fig. 3. (a) Small-angle neutron scattering data on sandstones and shales are described by a $1/q^{6-D}$ behavior plus an incoherent scattering background, consistent with having fractal surface. (b) The data on carbonate rocks are well fitted by Eq. (3.9) for self-affine surfaces.

** From "Physics and Chemistry of Porous Media", American Institute of

Physics Conference Proceedings, Volume 154, edited by J. Banavar, J. Koplik,

References

and K. W. Winkler (AIP, New York 1987)

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) ORNL 10-m SAXS

Title Small-Angle X-Ray Scattering Study of Silica Sols and Gels

Research Sponsor AFOSR Grant or Contact No. _____

#F49620-83-C-0072

Participants and NCSASR Collaborator(s)

Dr. J. S. Lin, Coll.

Dr. Robert W. Gould

Dr. Gerry Orzel

Dr. L. L. Hench

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

SAXS STUDY OF SILICA SOLS AND GELS

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Gainesville, Florida 32611

ABSTRACT

Small angle X-ray scattering was used to characterize the structure of sols and gels in the $\text{TMOS-MeOH-H}_2\text{O-CHONH}_2$ system. The scattering curves were analyzed in both the Porod and Guinier regions. A fractal analysis shows that the structure evolves with time and temperature from a linear type polymer to a more highly branched polymer and then towards a "particle". However, these structural units disappear when the temperature increases above a critical value.

Abstract of a paper published in Materials Research Society Symposium Proceedings, Vol. 73, p.289, (1986), Materials Research Society, Pittsburgh, Pennsylvania.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) SAXS

Title _____

Research Sponsor AFORS Grant or Contact No. _____

F 49620-83-C-0072

Participants and NCSASR Collaborator(s)

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Dr. R. W. Gould

Dr. J.S. Lin NCSASR

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Proposal No. _____

Date of Experiment(s) _____

Report

The purpose of these experiments was twofold:

- 1) determination of the structural characteristics of silica sols and gels for different reaction times and temperatures.
- 2) Assess the influence of formamide as a drying control chemical additive on the structure of these sols and gels.

An analysis of the Porod and Guinier domains of the scattering curves shows that for the different sols the Guinier radius of gyration increases with the reaction time. It reaches a value of about 60Å at the gelation point. The corresponding gels have a Guinier radius of gyration of about 20-25Å.

The fractal dimension of the particles, determined from the Porod plots, is insensitive to dilution, showing the validity of the assumptions. A value of 2.2 - 2.3 is measured near the gelation point. This was interpreted as possible growth mechanisms: diffusion limited aggregate or cluster aggregate .

Addition of formamide to the sols leads to higher Guinier radii of gyration as well as higher scattering exponents.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 10 meter SAXS

Title ~~XXXX~~

Measurements of the small angle x-ray scattering from Ludox
sphere sols.

Research Sponsor _____ Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

S. Spooner

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Ludox sphere sols have been used by a ~~number~~ number of investigators for the purpose of establishing scattering standards and calibrations for small angle scattering. Following the ~~the~~ procedure used by Russell in a recent study of Ludox spheres, a series of sols were prepared at 5 different dilutions. The solids content of the sols were was determined by evaporation of the several sols to driness. Integration of the scattered intensity to obtain the scattering invariant, Q_0 , was used ~~as~~ as the basis of calibration. By this measurement an absolute intensity factor was establish and then used to obtain a secondary calibration of a polyethelene sample. The peak in the polyethelene curve was ~~measured~~ measured to be $40. \text{ cm}^{-1}$. Recent work suggests that the determination is too high by 60%.

References

Give references if the work has been published or submitted to conferences, symposia, etc.

Report of Measurements Carried Out at the NCSASR

Instrument(s) 10 meter SAXS

Title Exploration of the Scattering from Gold Sols as a Scattering
Calibration Method

Research Sponsor _____ Grant or Contact No. _____

Participants and NCSASR Collaborator(s)

S. Spooner

To Be Completed by ORNL

Date Received _____

Proposal No. _____

Date of Experiment(s) _____

Report

Gold sol prepared by controlled precipitation from NaAuCl_4 solution (pyridine addition) was used as a scattering sample in SAXS measurements for the purpose of establishing an absolute scattering standard. The basis for establishing the standard is the use of the integrated or invariant intensity with a known concentration of gold colloid in the sol. Measurements made at the 5 m and 2 m setting were combined and the integration of the combined data were integrated to obtain Q_0 . Using the colloid concentration as 0.05 mg/100 ml an absolute intensity factor of 5.5 was found (with a monitor divide factor of 10) so that the PPH peak appeared to be 40 cm^{-1} . Although the right order of magnitude was obtained, ~~for the possibility of aggregation~~ the possibility of aggregation so to reduce the amount of free colloid has to be considered. At the low concentrations which are likely to minimize aggregation the scattering intensity is low but easily measured. The quantitative determination of gold colloid in the scattering sample may be the principal limit in the calibration procedure.

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Give references if the work has been published or submitted to conferences, symposia, etc.

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Thomas G. Consler, Gerard J. Bunick, and James C. Lee, "Small-Angle Neutron Studies of Rabbit Muscle Pyruvate Kinase"

1986 Gordon Conference on Dynamics of Macromolecular and Polyelectrolyte Solutions, Santa Barbara, CA, February 17-21, 1986

L. J. Magid, "Solutions of Rodlike Micelles at Rest and Under Shear: LS and SANS Studies"

TMS-AIME Annual Meeting, New Orleans, LA, March 2-6, 1986

Stephen Spooner, M. K. Miller, and L. L. Horton, "A Multiple-Technique Examination of Spinodal Decomposition in Fe-28.6 wt.% Cr-10.6%"

S. Spooner, D. B. Williams, and C. M. Sung, "Evidence of the Metastable Miscibility Gap in Al-Li from Small-Angle X-Ray Scattering"

First Annual Meeting of the Center for Materials Processing, Knoxville, Tenn, March 24-25, 1986

J. S. Lin, L. D. Hulett, J. M. Dale, T. M. Rosseel, D. Warner, B. Stoll, and J. F. Fellers, "X-Ray Scattering and Positron Annihilation Studies of Graphite Fibers and their Epoxy Composites"

American Physical Society, Las Vegas, Nevada, March 31-April 4, 1986

F. S. Bates, and G. D. Wignall, "The Isotope Effect in Mixtures of Deuterated and Normal Polymers"

K. P. McAlea, J. M. Schultz, G. D. Wignall, and K. H. Gardner, "Small-Angle Neutron Scattering Studies of Polyethylene Terephthalate"

X. Quan, I. Gancarz, J. T. Koberstein, and G. D. Wignall, "Morphological Characterization of Triblock Copolymers-Homopolymer Blends"

T. P. Russell, H. Ito, and G. D. Wignall, "Interactions in Mixtures of Poly(ethylene oxide) and Poly(methyl methacrylate)"

G. D. Wignall, F. S. Bates, and S. B. Dierker, "Phase Behavior of Amorphous Binary Mixtures of Normal and Perdeuterated 1,4-Polybutadienes"

Polyblends '86, Montreal, Canada, April 1-4, 1986

J.-M. Lefebvre, Roger S. Porter, and G. D. Wignall, "On the Deformation of Poly(methyl methacrylate)-Poly(ethylene oxide) Blends: A Molecular Characterization by Small-Angle Neutron Scattering"

American Chemical Society, New York, New York, April 13-18, 1986

M. A. Linne, A. Klein, L. H. Sperling, and G. D. Wignall, "Preliminary Estimate of the Diffusion Constant of Polystyrene During Film Formation from the Latex"

American Society of Plastics Engineers, Boston, Massachusetts, April 28-May 2, 1986

J.-M. Lefebvre, R. S. Porter, and G. D. Wignall, "Small-Angle Neutron Scattering Study on a Polymer Blend: Characterization of the Deformation Behavior"

Workshop on Phase Transitions and Critical Phenomena in Micellar and Microemulsion Systems, MIT, May 6-7, 1986

L. J. Magid, "SANS Studies of Nonionic Micellar Solutions"

60th Colloid and Surface Science Symposium, Atlanta, Ga, June 15-18, 1986

L. J. Magid, "Elucidation of Micellar Structure Using Small-Angle Neutron Scattering for Double-Tailed Surfactants"

L. J. Magid, "Small-Angle Neutron Scattering Studies of Water-in-Oil Microemulsions Containing Solubilized Biopolymers"

Thirteenth International Symposium on Effects of Radiation on Materials, Seattle, Washington, June 23-25, 1986

J. E. Epperson, J. S. Lin, and S. Spooner, "The Fine Scale Microstructure in Cast and Aged Duplex Stainless Steels Investigated by Small-Angle Neutron Scattering"

Gordon Conference on Polymer Physics, New London, New Hampshire, July 14-18, 1986

X. Quan, I. Gancarz, J. T. Koberstein, and G. D. Wignall, "Morphological Characterization of Block Copolymer/Homopolymer Blends"

T. P. Russell, H. Ito, and G. D. Wignall, "Small-Angle Neutron Scattering Studies of Polymer Mixtures"

44th Annual Meeting of the Electron Microscopy Society of America,
Albuquerque, New Mexico, August 10-15, 1986

L. L. Horton, M. K. Miller, and S. Spooner, "Characterization of Spinodally Decomposed Fe-30.1% Cr-9.9% Co: Part I"

S. Spooner, L. L. Horton, and M. K. Miller, "Characterization of Spinodally Decomposed Fe-30.1% Cr-9.9% Co: Part "

American Chemical Society 192nd National Meeting, Anaheim, California, September 7-12, 1986

J. H. An, A. M. Fernandez, and L. H. Sperling, "Development of Multiphase Morphology in Poly(cross-butadiene)-inter-poly(cross--styrene) Interpenetrating Polymer Networks by SANS"

Hoe Hin Chuah, J. S. Lin, and Roger S. Porter, "Deformation of Polyethylene"

J. J. Fitzgerald, and R. A. Weiss, "Effect of Plasticizers on the Morphology of Ionomers"

C. W. Lantman, W. J. Macknight, R. D. Lundberg, D. G. Peiffer, and S. K. Sinha, "Associative Phenomena in Ionomer Solutions"

J. S. Lin, L. D. Hulett, J. M. Dale, T. M. Rosseel, D. Warner, B. Stoll, and J. F. Fellers, "Structural Investigations of Graphite/-Epoxy Composites via Small-Angle X-ray Scattering (SAXS) and Positron Annihilation Spectroscopy (PAS)"

G. D. Wignall, "Neutron Scattering from Polymers"

First European Colloid Society Meeting, Como, Italy, October 1-3, 1986

K. A. Payne, L. J. Magid, and D. F. Evans, "Structural Changes in Anionic Micelles Induced by Counterion Complexation with a Macrocyclic Ligand: Double- vs. Single-Chain Amphiphiles"

The Materials Research Society Meeting, Boston, MA, December 1-6, 1986

F. S. Bates, S. B. Dierker, W. C. Koehler, and G. D. Wignall, "The Isotope Effect and Phase Behavior in Mixtures of Deuterated and Normal Polymers"

F. S. Bates, W. C. Koehler, G. D. Wignall, and L. J. Fetters, "Impact of Isotope Effects on the SANS Analysis of Amorphous Polymers"

C. V. Berney, P. Cheng, P. Kofinas, and R. E. Cohen, "SANS Studies of the Configurations of Single Chains in Heterogeneous Block Copolymers"

- J. B. Hayter, "Neutron Scattering from Charged Polymer Latices"
- J.-M. Lefebvre, Roger S. Porter, and G. D. Wignall, "A Deformation Induced Phase Separation in the Solid State"
- Raymond J. Lo, Alyson Hill, Roger S. Porter, and Richard S. Stein, "The Study of the Orientation of Polyethylene Films Using Small-Angle Neutron Scattering"
- K. P. McAlea, J. M. Schultz, G. D. Wignall, and K. H. Gardner, "Small-Angle Neutron Scattering Studies of Polyethylene Terephthalate"
- X. Quan, I. Gancarz, J. T. Koberstein, G. D. Wignall, and F. C. Wilson, "Morphological Characterization of Block Copolymer/Homopolymer Blends"
- Xina Quan, John Owens, Wen-Li Wu, and J. T. Koberstein, "Small-Angle Neutron Scattering from Mixtures Containing Block Copolymers"
- T. P. Russell, H. Ito, and G. D. Wignall, "Scattering Studies on Mixtures of Poly(Ethylene Oxide) with Poly(Methyl Methacrylate)"
- R. F. Saraf, J. M. Lefebvre, R. S. Porter, and G. D. Wignall, "A Double-Tilt Small Angle Neutron Scattering Experiment on Deformed Polymer Systems"
- Dale W. Schaefer, "Small-Angle Scattering from Disordered Systems"
- J. M. Schultz, "Scattering Studies of Crystallization in Highly Oriented Polymers"
- L. B. Shih, M. H. Luccas, S. H. Chen, and T. L. Lin, "Small-Angle Neutron Scattering Study of Micellization of a Charged Copolymer in Aqueous Solutions"
- S. Spooner, S. Iida, and B. C. Larson, "Diffraction Studies of Cobalt Precipitates in a Cu-0.95 at.% Co Alloy"
- Richard S. Stein, "The Use of Small-Angle Neutron Scattering for the Study of Polymer Miscibility and Deformation"
- Bernhard Stoll, J. F. Fellers, and J. S. Lin, "Characterization of Surface Modified Carbon Fibers and Their Epoxy Composites by Small Angle X-ray Scattering"
- Robert Ullman, "Polymer Chain Deformation in Stretched and Swollen Elastomers"
- R. A. Weiss, J. A. Lefelar, and J. J. Fitzgerald, "Temperature Dependence of the Structure of Sulfonated Polystyrene Ionomers"

G. D. Wignall, "The Physics of Photons and Neutrons with Applications of Deuterium Labeling Methods to Polymers"

Hsinjin Yang, and J. M. O'Reilly, "Small Angle Neutron Scattering Studies on Miscibility of Polystyrene and Tetramethyl-Bisphenol A-Polycarbonate Blends"

Gordon Research Conference on Polymers, Santa Barbara, California, January 5-9, 1987

T. P. Russell, H. Ito, and G. D. Wignall, "Small Angle Neutron and X-ray Scattering Studies on Semicrystalline Mixtures of Poly(ethylene oxide) and Poly(methyl methacrylate)"

Biophysical Society Thirty-First Annual Meeting, New Orleans, Louisiana, February 16-22, 1987

G. J. Bunick, J. B. Hayter, E. C. Uberbacher, and G. D. Wignall, "Oriented Scatter from Biomolecules using the NCSASR Shear Cell"

E. C. Uberbacher, J. M. Harp, and G. J. Bunick, "Unified Nucleosome Theory and Histone Organization"

Annual Meeting of the Metallurgical Society (AIME), Denver, Colorado, February 23-27, 1987

S. Spooner, Bruce D. Gaulin, Yukio Morii, and John Vitek, "Elevated Temperature Measurements of Phase Separation Kinetics in Mn-20% Cu with Small-Angle Neutron Scattering (SANS) and Wide-Angle Neutron Diffraction Scattering (WANDS)"

S. Spooner, "Kinetics of Decomposition in Aluminum-Lithium Alloys"

Po-zen Wong, and J. S. Lin, "Fractal Nature of Sedimentary Rocks" [invited]

J. L. Zarestky, and S. Spooner, "Lattice Dynamics of Gamma-Fe"

American Physical Society, New York, New York, March 16-20, 1987

S. Amelar, K. C. Hermann, T. P. Lodge, and E. D. Von Meerwall, "Static and Dynamic Properties of Short Chain Polystyrenes" [Bull. Am. Phys. Soc. 32, 665 (1987)]

J. E. Anderson, J.-H. Jou, G. C. Summerfield, and R. Ullman, "Small Angle Neutron Scattering Diffusion Studies in Bulk Polymers" [Bull. Am. Phys. Soc. 32, 664 (1987)]

F. S. Bates, "Isotope Effects on Polymer Phase Behavior" [Bull. Am. Phys. Soc. 32, 534 (1987)]

W. W. Graessley, "Viscoelasticity and Diffusion in Polymer Melts" [Bull. Am. Phys. Soc. 32, 873 (1987)]

W. Herman, and R. S. Stein, "SANS Studies of the Morphology of Crystallized Poly(vinylidene fluoride)/Poly(methyl methacrylate) Blends" [Bull. Am. Phys. Soc. 32, 876 (1987)]

A. Hoehr, P. W. Schmidt, H. B. Neumann, H. Kaiser, and J. S. Lin, "Small-Angle X-Ray and Neutron Scattering Studies of Fractal Porosity of Silicas and other Materials" [Bull. Am. Phys. Soc. 32, 752 (1987)]

A. J. Hurd, D. W. Schaefer, J. E. Martin, and W. L. Flower, "Fractal Clusters and Surfaces in Fumed Silica" [Bull. Am. Phys. Soc. 32, 753 (1987)]

T. Kyu, K. Fujita, and M. H. Cho, "Biaxial Stretching of UHMWPE Gel Films" [Bull. Am. Phys. Soc. 32, (1987)]

J. H. Magill, M. J. Shankernarayanan, and J. S. Lin, "Small-Angle X-Ray Scattering from Rolltruded Polyolefins" [Bull. Am. Phys. Soc. 32, 837 (1987)]

Ravi F. Saraf, and Roger S. Porter, "Deformation-Induced Phase Transition In Semicrystalline Polymers: Isotactic Polypropylene" [Bull. Am. Phys. Soc. 32, 739 (1987)]

R. S. Stein, "Studies of the Effect of Orientation, Mobility and Miscibility on the Properties of Solid Polymers" [Bull. Am. Phys. Soc. 32, 534 (1987)]

G. D. Wignall, F. S. Bates, and L. J. Fetters, "SANS Evaluation of RPA Theory for Homopolymer Mixtures" [Bull. Am. Phys. Soc. 32, 876 (1987)]

P. Wiltzius, F. S. Bates, S. B. Dierker, and G. D. Wignall, "The Structure of Porous Vycor Glass" [Bull. Am. Phys. Soc. 32, 753 (1987)]

NATO ASI, Norway, Mar 29, 1987

B. D. Gaulin, S. Spooner, and Y. Morii, "A Neutron Scattering Study of the Kinetics of Phase Separation in Mn_{1-x}Cu_x"

UCLA Symposium: Protein Structure and Design, Los Angeles, California, April 4, 1987

D. Voet, G. Bunick, J. -H. Jih, J. Koepka, K. Ogawa, A. Secco, P. Swaminathan, and E. Uberbacher, "Structure of Yeast Inorganic Pyrophosphatase: A Progress Report"

The American Chemical Society, Denver Colorado, April 5-10, 1987

J. H. An, A. M. Fernandez, G. D. Wignall, and L. H. Sperling, "Development of Multiphase Morphology in Poly(Cross-Butadiene)-Inter-Polymer Networks by SANS"

Mathematical Geologists of the United States, Redwood City, California, April 13-15, 1987

J. S. Lin, and Po-zen Wong, "Small-Angle Neutron Scattering Study of the Fractal Character of Some Geological Materials" [invited]

Materials Research Society, Spring Meeting, Palo Alto, California, April 15-19, 1987

K. A. Hardman-Rhyne, T. D. Coyle, E. P. Lewis, and S. Spooner, "Kinetic Investigations of Alkoxysilane Sol-Gel Processing"

American Ceramic Society, Pittsburgh, Pennsylvania, April 26-30, 1987

R. A. Page, S. Spooner, W. B. Sanderson, and D. L. Johnson, "Pore Evolution during Glow Discharge Sintering of Alumina"

Society of Plastics Engineers 45th Annual Technical Conference, Los Angeles, Calif., May 4-7, 1987

G. C. Richeson, and J. E. Spruiell, "Effect of Composition and Processing Conditions on the Structure and Properties of Elastic Filaments Melt Spun from Copolyester-Ethers"

Euchem Conference on Microaggregates in Homogeneous Solution, Reactivity and Structure, June 1987, Assis (Italy)

W. L. Griffith, R. Triolo, and A. Compere, "Analytical Structure Function of a Polydisperse Percus-Yevick Fluid with Schulz (gamma) Distributed Diameters"

W. L. Griffith, R. Triolo, and A. Compere, "Analytical Scattering Function of a Polydisperse Percus-Yevick Fluid with Schulz (gamma) Distributed Diameters"

Fifth Conversation in the Discipline Biomolecular Stereodynamics, State University of New York at Albany, Albany, New York, June 2-6, 1987

Edward C. Uberbacher, Joel M. Harp, and Gerard J. Bunick, "Structure of the Nucleosome Core Particle at 8 A Resolution"

61st Colloid and Surface Science Symposium, Ann Arbor, MI, June 22-24, 1987

L. J. Magid, "Scattering Studies on Microemulsions"

J. P. Wilcoxon, D. W. Schaefer, and E. W. Kaler, "Equilibrium and Non-Equilibrium Aggregate Structures Near Critical Points in Micellar Solutions"

The Institute of Metals, Cambridge, England, July 6-10, 1987

S. Spooner, B. D. Gaulin, and Yukio Morii, "An In Situ Study of Decomposition in Magnanese-Rich Copper-Manganese Alloys with Neutron Scattering"

1987 Prague Meetings on Macromolecules - 10th Discussion Conf., Small-Angle Scattering and Related Methods, Prague, Czechoslovakiz, July 13-16, 1987

G. D. Wignall, and F. S. Bates, "Applications of Deuterium Labeling Methods to Neutron Scattering Studies of Polymers" [invited]

Gordon Conference, New London, New Hampshire, August 3-8, 1987

C. F. Wu, S. H. Chen, L. B. Shih, and J. S. Lin, "A Direct Measurement of Counterion Condensation around Cylindrical Micelles"

36th Annual Denver X-Ray Conference, Denver, Colorado, August 3-7, 1987

J. S. Lin, "Polymer Investigations at the National Center for Small-Angle Scattering Research"

