DOE/ER/45370--4

DE92 040162

Progress Report for DOE Grant DE-FG02-88ER45370

MORPHOLOGICAL ANALYSIS OF IONOMERS

August 1, 1987 - December 31, 1991

I. ASAXS from Amorphous and Semi-Crystalline Ionomers

Our recent investigations using anomalous small-angle x-ray scattering (ASAXS) are presented in detail in two manuscripts which have appeared in *Macromolecules*. In one set of experiments, nickel-neutralized ionomers with amorphous polymer matrices were examined by ASAXS at the nickel K-edge. In a series of sulfonated polystyrene ionomers with varying neutralization level, the intensity of the ionomer peak in the difference patterns, formed from SAXS patterns at two different energies, was shown to scale with the real (f') and the fluorescent background with the imaginary part (f"). No change in the shape of the scattering patterns with energy was discernable, and the single-energy and difference patterns were found to be superimposable with appropriate scaling. The same superposability was found for a polyurethane ionomer, which also exhibits a high-q shoulder on the main peak. These observations prove that the peak, the upturn near zero angle, and the shoulder are due to an inhomogeneous distribution of ionic repeat units throughout the material, and not to precipitated neutralizing agent or microvoids. Debye plots of the intensity near zero angle were concave downward in all cases, contrary to the prediction of core-shell models of ionomer morphology and to the Debye-Bueche description of this large-scale heterogeneity.

In a second series of experiments, ionomers with semicrystalline matrices were investigated. These three-phase materials are more complicated and typically show two SAXS reflections. All observed features of the scattering pattern are consistent with the generally-accepted three-phase model incorporating lamellar crystallites, interlamellar layers of amorphous polymeric material, and ionic aggregates distributed within the interlamellar regions. The ability of ASAXS to determine the sign of the electron density difference between the crystalline and amorphous phases in a nickel-neutralized

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poly(ethylene-co-methacrylic acid) ionomer was demonstrated. The only *a priori* knowledge required is which of the phases causing the reflection has a greater concentration of nickel. The change in the intensity of the low-q "crystallite" reflection was in reasonable agreement with that calculated from experimental values of f' for Ni metal. Also, since ASAXS provides a means to vary the intensity of the two reflections independently, it can separate two reflections by a suitable subtraction and provide data for morphological modelling uncontaminated by other reflections. This was demonstrated for the same poly(ethylene-co-methacrylic acid) ionomer. A nickel-neutralized Nafion perfluorosulfonate ionomer was also studied, but no ionomer peak was visible due to a fortuitous equality of ionic aggregate and amorphous polymer electron densities.

II. Effect of Matrix Polarity and Ambient Aging on the Morphology of Sulfonated Polyurethane Ionomers

Ethylene oxide units were incorporated into the backbone of Na^+ sulfonated polyurethane ionomers in an attempt to induce aggregate dissociation at elevated, but observable, temperatures by reducing the incompatibility between ions and polymer. However, no dissociation could be observed by small-angle x-ray scattering (SAXS) before the onset of degradation, even when the polyol was pure ethylene oxide. At 100°C and above, the SAXS patterns for all samples were quite similar, indicating morphological similarity. However, after annealing for several days at room temperature, two of the specimens appeared to develop a greater degree of microdomain order as evidenced by a narrowing of the main peak at q^* and the development of a shoulder at $2q^*$.

III. SANS of Telechelic and Model Polyurethane Ionomers

We have utilized small-angle neutron scattering (SANS) to determine the influence of ionic aggregation on ionomer chain dimensions in telechelic and model polyurethane ionomers. In the first series of experiments, carboxy-telechelic polystyrenes with degrees of polymerization near seventy were examined in the Na^+ ionomer and methyl ester forms. Small-angle x-ray scattering demonstrated that the ionomers contained ionic aggregates, yet the chain dimensions were found to be identical for the ionomer and the ester. The results support the predictions of one set of theories regarding ionic aggregate but refute those of other theories. Detailed analysis of the data showed that contacts between two isotopic types were random, as intended, in contrast to some previous attempts at SANS analysis of ionomer chain conformation. The data could not be satisfactorily described by a Debye function, but a polydisperse assembly of worm-like chains provided a good representation.

In the next series of experiments, sulfonated polyurethane ionomers bearing various fractions of deuterated soft segments (poly(tetramethylene oxide)) were examined. These ionomers differ from the telechelic polystyrene ionomer discussed above in three important ways. First, the ionic groups are distributed along the chain, roughly separated by the soft segment units, rather than solely at the chain ends. Second, the polyurethane ionomers contain sulfonate rather than carboxylate functionalities. Third, the ion content of the polyurethane ionomers is much greater than that of the telechelics. Analysis of data using a polydisperse worm-like chain model indicated very small chain expansion of the PTMO soft segments upon aggregation. We were unable to synthesize and measure PTMO of high enough molecular weight to meet the DeGennes criteria ($N_{short} >> N_{long}^{1/2}$). Assuming the literature value of the segment length calculated from viscometric studies,[1] the relative increase in R_g^2 is on the order of only 30%.

It is suggested that the results for sulfonated polyurethane ionomers can be reconciled with the absence of chain expansion seen for the telechelics by postulating that a corona of extended chains surrounds the ionic aggregates. Because of the higher ion content in the polyurethane ionomers than in the telechelics, the fraction of chain segments in the corona surrounding the aggregates and their contribution to the overall chain expansion is greater. This theory was tested by varying the PTMO molecular weight from 1000 to 2000. If the corona theory is correct, soft segment chain expansion should be larger in the ionomer based on PTMO-1000. Soft segment chain expansion was larger for the PTMO-1000 material.

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[1] J.M. Evans and M.B. Hughlin, *Makromol Chem*, 129, 141 (1969).

however measurement error does not allow exact quantification of this expansion. The increase in R_g^2 between these two materials was on the order of 10%.

IV. Comparison of Structure-Property Relationships in Carboxylated and Sulfonated Polyurethane Ionomers

Studies have been completed on a series of carboxylated and sulfonated model polyurethane ionomers in order to determine the effect of the pendant ionic group on ionomer structure-property relationships. The mechanical properties of the model ionomers are strongly dependent on anion used, as well as on the backbone and cation combination, with the sulfonated ionomers giving stronger polymers than the carboxylated ionomers. However, Young's moduli for ionomers differing only in the anion type are approximately equivalent. Thermal and dynamic mechanical techniques showed that the degree of phase separation was greater for the sulfonated ionomers and that aggregates persist in sulfonated materials to much higher temperatures than the corresponding carboxylate ionomers. Small-angle x-ray scattering analyses demonstrated the larger aggregate sizes in the carboxylated ionomers. It was postulated that ionic aggregation causes the formation of chain entanglements in ionomers, which also act as effective crosslinks. Since the aggregates in the carboxylated ionomers are larger, the number of entanglements formed are greater which gave rise to higher initial moduli than aggregate density effects alone would predict.

Extended x-ray absorption fine structure spectroscopy (EXAFS) was used to study the cation local environment in the sulfonated and carboxylated polyurethane ionomers in order to elucidate the degree of short-range order in the ionomers. A correlation between the degree of local ordering and the tensile properties of the ionomers was observed, with ionomers containing the more ordered local environments also exhibiting the higher tensile properties. Ionomers based on poly(tetramethylene oxide), poly(propylene oxide), and poly(ethylene oxide) soft segments were studied. Soft segment type was seen to have little or no influence on the local environment of the cation in the ionomers. Anion type also appeared to have no effect on the local environment of the cations. The method of sample preparation, however, affected both the local environment and the ultimate properties of the samples, for both carboxylated and sulfonated ionomers.

One final and potentially very attractive feature of the carboxylated materials compared to the sulfonated materials was the carboxylate ionomers insolubility in many solvents. In order to combine the favorable mechanical properties of sulfonate ionomers with the insolubility of carboxylate ionomers, mixed anion ionomers were synthesized and tested. All the properties of the mixed ionomers changed monotonically as the sulfonate to carboxylate ratio varied, except the tensile modulus. The behavior of the tensile modulus was very complicated and the reasons are not clear at this time.

Articles Resulting from This Grant

1. R. A. Register, M. Foucart, R. Jerome, Y.S. Ding, and S.L. Cooper, "Structure-Property Relations in Elastomeric Carboxy-Telechelic Polyisoprene Ionomers", **Macromolecules 21**, 1009 (1988).

2. D.C. Lee, R.A. Register, C.Z. Yang, and S.L. Cooper, "MDI-Based Polyurethane Ionomers. I. New Small-Angle X-Ray Scattering Model", **Macromolecules 21**, 998 (1988).

3. D.C. Lee, R.A. Register, C.Z. Yang, and S.L. Cooper, "MDI-Based Polyurethane Ionomers. II. Structure-Property Relationships", **Macromolecules 21**, 1005 (1988).

4. R.A. Register, A. Sen, R.A. Weiss, and S.L. Cooper, "Effect of Thermal Treatment on Cation Local Structure in Manganese Sulfonated Polystyrene", **Macromolecules 22**, 2224 (1989).

5. Y.S. Ding, R.A. Register, C.Z. Yang, and S.L. Cooper, "Synthesis and Characterization of TDI-Based Polyurethane Ionoemrs", **Polymer 30**, 1204 (1989).

6. Y.S. Ding, R.A. Register, C.Z. Yang, and S.L. Cooper, "Small-Angle X-Ray Scattering from TDI-Based Sulfonated Polyurethane Ionomers", **Polymer 30**, 1213 (1989).

7. Y.S. Ding, R.A. Register, C.Z. Yang, and S.L. Cooper, "Effect of Cation Local Structure on the Physical Properties of Model Polyurethane Ionomers", **Polymer 30**, 1221 (1989).

8. R.A. Register, A. Sen, R.A. Weiss, and S.L. Cooper, "Morphology and Cation Local Structure in a Blend of Copper-Neutralized Carboxy-Polybutadiene and Poly(Styrene-co-4 Vinyl Pyridine)", **J. Polym. Sci.: Polym. Phys. Ed. 27**, 1227 (1989).

9. C. Li, R.A. Register, and S.L. Cooper, "Direct Observation of Ionic Aggregates in Sulfonated Polystyrene Ionomers", **Polymer 30**, 1227 (1989).

10. R.A. Register, Y.S. Ding, M. Foucart, R. Jerome, S.R. Hubbard, K.O. Hodgson, and S.L. Cooper, "Recent Advances in X-Ray Analysis of Ionomers", L.A. Utracki and R.A. Weiss, eds., **ACS Advances in Chemistry**, Series 395, pp. 420-438 (1989).

11. R.A. Register and S.L. Cooper, "Anomalous Small-Angle Scattering from Nickel-Neutralized Ionomers: 1. Amorphous Polymer Matrices", **Macromolecules 23**, 310 (1990).

12. R.A. Register and S.L. Cooper, "Anomalous Small-Angle Scattering from Nickel-Neutralized Ionomers: 2. Semicrystalline Polymer Matrices", **Macromolecules 23**, 318 (1990).

13. R.A. Register, P. Thiyagarajan, S. Chakrapani, R. Jerome, and S.L. Cooper, "Effect of Ionic Aggregation on Ionomer Chain Dimensions: 1. Telechelic Polystyrenes", **Macromolecules 23**, 2978 (1990).

14. R.A. Register, G. Pruckmayr, and S.L. Cooper, "Effect of Ionic Aggregation on Ionomer Chain Dimensions: II. Sulfonated Polyurethane Ionomers", **Macromolecules 23**, 3023 (1990).

15. R.A. Register, X.-H. Yu, and S.L. Cooper, "Effects of Matrix Polarity and Ambient Aging on the Morphology of Sulfonated Polyurethane Ionomers", **Polymer Bulletin 22**, 565 (1990).

16. R.A. Register, "Ionomer Morphology Probed by Small-Angle Scattering", Ph.D. thesis, University of Wisconsin - Madison, 1989.

17. S.A. Visser and S.L. Cooper, "Comparison of the Physical Properties of Carboxylated and Sulfonated Model Polyurethane Ionomers", **Macromolecules 24**, 2476 (1991).

18. S.A. Visser and S.L. Cooper, "Analysis of Small-Angle X-ray Scattering Data for Model Polyurethane Ionomers: Evaluation of Hard Sphere Models", **Macromolecules 24**,,2584 (1991).

19. S.A. Visser and S.L. Cooper, "Effect of Neutralizing Cation Type on the Morphology and Properties of Model Polyurethane Ionomers", **Polymer**, in press.

20. S.A. Visser and S.L. Cooper, "EXAFS Analysis of Cation Local Environment in Model Polyurethane Ionomers", **Polymer**, in press.

21. S.A. Visser and S.L. Cooper, "Small-Angle Neutron Scattering Analysis of Model Polyurethane Ionomers", **Macromolecules**, submitted for publication.

22. S.A. Visser and S.L. Cooper, "Morphology and Properties of Mixed Anion Ionomers", **Polymer**, submitted for publication.

23. S.A. Visser and S.L. Cooper, "Two Dimensional Small-Angle X-ray Scattering Investigation of Ionomer Deformation and Evaluations of Models of Ionomer Morphology", **Macromolecules**, submitted for publication

24. S.A. Visser and S.L. Cooper, "Small Angle Neutron Scattering Investigation of the Response of Model Polyurethane Ionomers to Uniaxial Deformation," **Polymer**, submitted for publication.

25. S.A. Visser and S.L. Cooper, "Small Angle X-ray Scattering Investigation of Ionomer Deformation," **Polymer**, submitted for publication.

26. S.A. Visser, "Morphology-Property Correlations in Model Polyurethane Ionomers", Ph.D. thesis, University of Wisconsin - Madison, 1991.

27. X. Yu, B.P. Grady, R.S. Reiner and S.L. Cooper, "Properties of Amic Acid Ionomers," **J. Appl. Polym. Sci.**, submitted for publication.

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10/28/92