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13. ABSTRACT (Maximum 200 words) In the ARO project, several aspects of polymer rheology and microstructures were investigated by using a variety of physical techniques, including the development of a new magnet-enhanced optical falling needle/sphere rheometer. From studies of rheological properties and association behavior of mixtures of poly(isobutyl methacrylate-tert-butyl aminoethyl methacrylate) and an ionomer in solution, and of random copolymers of styrene with sodium-2-acrylamido-2-methylpropane sulphonate, it becomes clear that structures of associative polymers can best be approached by using well-defined block copolymers. Furthermore, the ionic interactions deserve special examination in view of ion cluster formation and long-range inhomogeneities which are present often because of processing procedures. A series of studies of block copolymers, including lightly sulfonated polystyrene-b-poly(tert butylstyrene) and triblock poly(oxyethylene-oxypropylene-oxyethylene) in nonpolar (xylene), polar (water) and water/o-xylene mixtures. The size, shape and aggregation number were determined by using laser light scattering, small angle x-ray scattering and transient electric birefringence techniques.			
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Macromolecular Characterization and Solution Behavior
of Polymer Additives

Final Report

Ben Chu

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U.S. Army Research Office

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Chemistry Department
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FOREWORD

Polymer additives are used to influence rheological properties of fluids. In order to increase the effectiveness of polymer additives, one needs to take advantage of intermolecular interactions so as to enhance the supramolecular formation of polymer additives. The aims of our projects were

1. to devise new methods for the characterization of polymer additives
2. to determine the structure of interactive polymer systems, and
3. to understand the factors which govern supramolecular formation.

1. New Method for Polymer Additives Characterization.

Polymer additives tend to form supramolecules which effectively change the fluid viscosity. A magnet enhanced optical falling needle/sphere rheometer [3] was developed to study the viscosity of highly viscous fluids [10] in the presence of polymer additives.

2. Structure of Interactive Polymer Systems

From rheological studies on the association behavior of mixtures of poly(isobutyl methacrylate-tert-butylaminoethyl methacrylate) and an ionomer in solution [1] and of random copolymers of styrene with sodium-2-acrylamido-2-methylpropane sulphonate [2], it became clear that ill-defined polymers could never yield sufficiently detailed information on the pertinent factors governing the supramolecular formation in a quantitative manner. Thus, well-defined block copolymers were chosen to further the studies.

For interacting polymers, the phase diagram could be complex [4]. Even the polymer in the melt state could have microstructures [8], in the presence of long range inhomogeneities [5]. Time-resolved SAXS was used to study the crystallization kinetics of poly(aryl ether ether ketone) [6].

3. Factors Governing Supramolecular Formation

For diblock copolymers of styrene and tert-butyl styrene in N,N-dimethyl acetamide [7], micelle formation could be induced by temperature changes. The essential factors could be separated to chain length, chain ratio, chain architecture and solvent quality. By changing the temperature [7] or by changing the solvent quality [15] from addition of a nonsolvent, to one of the two blocks [11],[13], polymer micelles are formed in order to minimize the free energy [16]. Like polymer additives, the supramolecular formation can be controlled from a combination of these factors. Unfortunately, only limited theoretical

development and computer simulation have been attempted to address this complex problem.

FINAL REPORT

Statement of the Problem

1. To use transient electric birefringence in order to study the shape of model polymer additives.
2. To combine rheology with optical and scattering techniques to study the structure and dynamics of supramolecules.
3. To study polymer interactions by varying functional groups.
4. To study the temperature dependence of polymer aggregation behavior.

Summary of Most Important Results

1. We have developed a magnet enhanced optical falling needle/sphere rheometer. Together with the magnetic needle/sphere rheometer, the viscosity and shear thinning properties of complex polymer fluids can be investigated in a closed system and at high temperatures.

2. New methodology have been developed to investigate the aggregation number, the molar mass, the size and the shape of supramolecules formed by well-defined block copolymers. In anticipation for larger size aggregates, an ultrasmall angle x-ray scattering apparatus was developed. The instrument should be ideal for structural studies of colloidal systems.

List of all Publications Acknowledging Support by the U.S. Army Research Office

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15. Zukang Zhou and Benjamin Chu, "Phase Behavior and Association Properties of Poly(oxypropylene)-Poly(oxyethylene)-Poly(oxypropylene) Triblock Copolymer in

Aqueous Solution," *Macromolecules*, **27**, 2025 (1994).

16. Benjamin Chu, Zukang Zhou and Guangwei Wu, "Structure and Dynamics of Polymeric Micelles in Solution," *J. Non-Cryst. Solids*, in press.

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