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In the ARO project, we have succeeded in characterizing a random copolymer of poly(isobutyl methacrylate-co-tertbutyl aminoethyl methacrylate), abbreviated as poly(iBMA-tBAEMA) in polar and protic solvents by means of laser light scattering (LLS) and viscosimetry. Intra- and intermolecular interactions could be used to explain the aggregation behavior which dominates the rheological properties of a large variety of such polymer solutions, making poly(iBMA-tBAEMA) a useful polymer additive/thickening agent. By adding another polymer which can complex with poly(iBMA-tBAEMA), we have found that the polymer can be used as a viscosity enhancer for the polymer additive, poly(iBMA-tBAEMA). With sulfonated polystyrenes, the enhancement could reach a factor of 20.					
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Light Scattering Characterization of Polymer Additives and
Correlation of Molecular Properties of Polymer Fluids

Final Report

Ben Chu

March 27, 1991

U.S. Army Research Office

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FOREWORD

Polymer additives are used to influence rheological properties of fluids. Non-Newtonian fluid behavior can be created by entanglement of polymer coils in solution. In order to increase the effectiveness in the entanglement of polymer coils based on per unit weight, it is desirable to create an environment in which the polymer coils tend to aggregate to form supra-molecular coils and to increase the coil size by swelling so that the effective value of the overlap concentration decreases. The aims of our projects were:

1. to characterize the polymer additives of interest, e.g., poly(iBMA-tBAEMA),
2. to study polymer dynamics in the semidilute solution regime, and
3. to investigate whether the aggregation effect could be improved by the presence of other forces.

I.1. Characterization of Polymer Additives

Polymer additives tend to form supramolecular systems which are large (perhaps even of the order of thousands of Angstroms) in size. Our prism-cell laser light scattering spectrometer [1] is specifically designed to characterize the conformation and dynamics of large polymer coils in solution. It is capable of measuring both the angular distribution of scattered intensity and of Rayleigh linewidth and can perform small-angle self-beating dynamic light-scattering measurements down to a scattering angle of a few degrees.

The semidilute polymer solution is viscous and often exhibits non-Newtonian fluid behavior. So, we have constructed a magnetic sphere/needle rheometer [4,7] capable of viscosity and viscoelastic measurements in a closed system which offers a unique advantage because of the long-term rheological tests of semidilute polymer solutions with possible volatile solvent components.

I.2. Polymer Dynamics in the Semidilute Solution Regime

Diffusion of polymer in binary and ternary semidilute solutions [5] was carried out by investigating the dynamic properties of polystyrene (PS) in toluene (TOL), PS1/PS2 in TOL and PS1/PMMA2 in TOL where "1" and "2" denote matrix polymer at semidilute concentrations and probe polymer at dilute concentrations, respectively. It

should be noted that poly(methyl methacrylate), PMMA, was isorefractive with the solvent TOL. The polymer chain dynamics revealed a fast mode which could be interpreted as the cooperative diffusion of entangled chains and a slow mode which could be attributed to the coupling of the matrix polymer with the probe polymer. We were not satisfied with the dynamics of the equilibrium conformation. So, we tried to deform the macromolecule (DNA) by applying an electric field and to examine the field-free relaxation time of DNA in the presence of a polymer network (agarose gel) [2].

I.3. Aggregation Behavior

Polymer additives, such as poly(iBMA-tBAEMA), are random copolymers and would have been almost impossible to characterize if it were not for the coincidental fact that the two components (iBMA-tBAEMA) form essentially isorefractive polymer segments. Thus, one can determine the true molecular weight and the size of the aggregates by means of light-scattering [8]. Viscosity measurements [9] confirm a breakup of poly(iBMA-tBAEMA) at extreme dilutions. A combination of the two physical methods of characterization permits us to detect the degree of aggregation.

The aggregation behavior of block copolymers which are better defined than random copolymers, such as poly(iBMA-tBAEMA), were examined in terms of composition heterogeneity [3] and polymer block length of one of the components [6].

In summary, we have constructed unique instrumentation [1,4,7] and have taken advantage of the fact that poly(iBMA-tBAEMA) can be treated as a "homopolymer" as far as laser light scattering (LLS) is concerned. Thus, the aggregation behavior could be investigated under a variety of experimental conditions. It should be noted that LLS represents the only absolute method for molecular weight (or more precisely, molar mass) and size determination of this unique copolymer, poly(iBMA-tBAEMA).

In the process of trying to find out how we can enhance poly(iBMA-tBAEMA) as a polymer additive, we have begun our studies on interacting polymers [10] and interactive polymer mixtures [11] in solution. By adding an ionomer to poly(iBMA-tBAEMA), the viscosity of fluids can be enhanced more effectively up to a factor of 20.

FINAL REPORT

Statement of the Problem

1. Determination of the weight average molecular weight M_w , the radius of gyration R_g , the second virial coefficient A_2 , the translational diffusion coefficient D_T and the polydispersity of poly(iBMA-tBAEMA) in different solvents.
2. Study of the rheological properties of poly(iBMA-tBAEMA) as a function of concentration, temperature and shear rate.
3. Investigation of ion-containing polymers as a complexing agent for poly(iBMA-tBAEMA), which will promote the viscosity of fluids as a thickening agent.

Summary of Most Important Results

1. We have succeeded in characterizing poly(iBMA-tBAEMA), which tends to aggregate at dilute concentrations.
2. A magnetic needle rheometer (MNR) was developed and constructed in order to measure the rheological properties of semidilute and concentrated polymer solutions whose solvents tend to be volatile. The MNR was featured on the front cover of **Polymer News** in the December, 1990 issue. A patent (R-625) has been filed for this invention.
3. We have begun studies of polymer mixtures which interact with each other via hydrogen bond and electrostatic interactions. The resulting aggregates form very large globules making the fluid solvent medium viscous. Viscosity enhancers to the polymer additives, which are used as thickening agents, have been developed. This idea has been communicated to the Research Foundation of the State University of New York for possible patent application.

List of all Publications and Technical Papers Presented Discussed in I.1-3.

- A. Publications with acknowledgement of support by the U.S. Army Research Office

1. Benjamin Chu, Renliang Xu, Tadakazu Maeda and Harbans S. Dhadwal, "A Prism Laser Light Scattering Spectrometer," *Rev. Sci. Instrum.*, **59**, 716 (1988).
2. Benjamin Chu, Renliang Xu and Zhulun Wang, "Low Field Transient Electric Birefringence of DNA in Agarose Gels," *Biopolymers, Communication*, **27**, 2005 (1988).
3. Zukang Zhou and Benjamin Chu, "Anomalous Micellization Behavior and Composition Heterogeneity of a Triblock ABA Copolymer of (A) Ethylene Oxide and (B) Propylene Oxide in Aqueous Solution," *Macromolecules*, **21**, 2548 (1988).
4. Rolf Hilfiker, Benjamin Chu and Jeffrey Shook, "Magnetic Sphere Rheometer," *Rev. Sci. Instrum.*, **60**, 760 (1989).
5. Zhulun Wang, Qin-wei Wang, Lewis Fetters and Benjamin Chu, "Diffusion of Polymer in Binary and Ternary Semidilute Solutions," in *Proceedings of the International Symposium on New Trends in Physics and Physical Chemistry of Polymers Honoring Professor P. G. DeGennes*, (1989) Plenum Publishing, NY, pp. 207-228.
6. R. Hilfiker, B. Chu and Z. Xu, "Micelle Forming Properties of Polystyrene/Polyisoprene AB Block Copolymers," *J. Colloid & Interface Sci.*, **133**, 176 (1989).
7. Benjamin Chu and Rolf Hilfiker, "High Temperature Magnetic Sphere/Needle Rheometer," *Rev. Sci. Instrum.*, Note, **60**, 3828 (1989).
8. Benjamin Chu, Jian Wang and Wendel J. Shuely, "Solution Behavior of a Random Copolymer of Poly(isobutyl methacrylate-*t*-butyl aminoethyl methacrylate). 1. Laser Light Scattering Studies," *Macromolecules*, **23**, 2252 (1990).
9. Benjamin Chu, Jian Wang and Wendel J. Shuely, "Solution Behavior of a Random Copolymer of Poly(isobutyl methacrylate-*t*-butyl aminoethyl methacrylate). 2. Viscosity and Light Scattering Intensity Studies," *Polymer*, **31**, 805 (1990).
10. Jian Wang, Zhulun Wang, Dennis Peiffer, Wendel J. Shuely and Benjamin Chu, "Light Scattering and Small Angle X-Ray Scattering Studies of an Ionomer Poly(styrene-sodium-2-acrylamido-2-methylpropanesulfonate) in Polar Solvents," *Macromolecules*, **24**, 790 (1991).
11. Benjamin Chu, Jian Wang, Dennis G. Peiffer and Wendel J. Shuely, "Effects of an Ionomer Additive on the Rheological Properties of a Random Copolymer

Poly(isobutyl methacrylate-tert-butyl aminoethyl methacrylate)," *Macromolecules, Communication*, **24**, 809 (1991).

B. Papers presented with acknowledgement of support by the U.S. Army Research Office (* denotes abstract or preprint)

1988. 1. Workshop on Measurement of Properties in Bulk Materials, U.S. Army Natick Research, Development and Engineering Center, Natick, MA. Transient Grating and Other Techniques, by Ben Chu. (Invited speaker)
2. * 62nd Colloid and Surface Science Symposium, University Park, PA. Micelle Forming Properties of Polystyrene/Polyisoprene AB Block Copolymers, by R. Hilfiker, Z. Xu and B. Chu. (Invited speaker. Talk presented by R. Hilfiker).
3. NATO ASI on Reactive and Flexible Molecules in Liquids, Nauplia, Greece. "Structure and Dynamics of Branched (Epoxy) Polymers and Kinetics of the Polymerization Process," (2 lectures) by B. Chu and C. Wu. "Transition of Coil-to-Rod Aggregates in a Conducting Polymer (P4BCMU) Solution" by B. Chu. (B. Chu, Invited speaker and session chairman).
4. * 1988 U.S. Army Chemical Research, Development, and Engineering Center Scientific Conference on Chemical Defense Research. Aberdeen Proving Ground, MD. "Magnetic Sphere Rheometer" by B. Chu, R. Hilfiker, J. Shook and J. Wang in Proceedings of 1988 U.S. Army CRDEC Conference on Chemical Defense Research, CRDEC-SP-013, Vol. 1, pp.477-483 (1988). (Paper presented).
1989. 5. * 197th ACS National Meeting, Dallas, Texas. "High Temperature Magnetic Sphere Rheometer," by Ben Chu, Zhulun Wang and Rolf Hilfiker. (Paper presented)
6. * Rolduc Polymer Meeting 4, Limburg, The Netherlands. "Branching Kinetics of Epoxy Polymerization of 1,4-Butanediol Diglycidyl Ether with Cis-1,2-Cyclohexanedicarboxylic Anhydride," by B. Chu and C. Wu. (Paper presented).

7. 1989 U.S. Army Chemical Research, Development and Engineering Center Conference on Chemical Defense Research, Aberdeen Proving Ground, MD. Solution Behavior of a Random Copolymer of Poly(isobutyl methacrylate-*t*-butyl aminoethyl methacrylate). 1. Laser Light Scattering Studies, by Benjamin Chu, Jian Wang and Wendel J. Shuely in Proceedings of the 1989 U.S. Army Chemical Research, Development and Engineering Center Scientific Conference on Chemical Defense, CRDEC-SP-024, pp. 239-245 (1989). (Paper presented).
1990. 8. Gordon Research Conference on Dynamics of Macromolecules and Polyelectrolytes, Oxnard, California. The Solution Behavior of Polystyrene/Polyisoprene AB Block Copolymers in Aniline, by B. Chu and R. Hilfiker. (Poster presented).
9. 33rd IUPAC International Symposium on Macromolecules, Montreal, Canada. Session Chairman, Session 1.3.3, Thermodynamic Properties of Ionic Polymers in Aqueous Solutions. Solution Behavior of Random Copolymers of Styrene with Sodium-2-acrylamido-2-methyl Propane Sulphonate (Na-AMPS), by Z.-L. Wang, J. Wang and B. Chu. (Invited speaker).
10. 1990 U.S. Army Chemical Research, Development and Engineering Center Scientific Conference on Chemical Defense Research, Aberdeen Proving Ground, Maryland. Polymer Additive Enhancer for Effects of an Ionomer Additive on the Rheological Properties of a Random Copolymer Poly-Isobutyl Methacrylate-Tert-Butyl Aminoethyl Methacrylate, by B. Chu and J. Wang. (Paper presented.)

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