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FINAL PROJECT REPORT

for

ONR Contract N00014-83-K0423

Synthesis and Interfacial Properties of New Generation

Polyurethane Systems

Stuart L. Cooper Department of Chemical Engineering University of Wisconsin Madison, WI 53706

Time Period of This Report: June 1, 1987 to May 31, 1989

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I. Project Summary

Synthesis and Interfacial Properties of New Generation Polyurethane Systems

Polyurethanes based on non-polar soft segments exhibit improved environmental stability relative to the conventional polyether or polyester containing polyurethanes, but at the expense of mechanical strength due to low molecular weight, compositional heterogeneity, and extreme segmental incompatibility. Stress concentrations in the sharp interfacial zones of materials with very high segmental incompatibility markedly decrease mechanical properties. There are also an increasing number of applications for polyurethanes that have been modified by blending, cross-linking, incorporation of ionic groups, or grafting of side chains.

The thrust of this research has been to synthesize and study the structure-property relationships of several families of modified polyurethanes in three main areas. First, we have attempted to improve the mechanical properties of environmentally stable polyurethanes by inserting polar groups into non-polar soft segments and by using blends of the conventional (polar) and non-polar work examined the effect on segmental soft-segments. Early compatibility of introducing polar (cyanomethylethyl) groups into a non-polar (siloxane) soft segment (Tech. Rep. #13). Blends of polar poly(tetramethylene oxide) (PTMO) and non-polar poly(dimethylsiloxane) (PDMS) were later used in soft segments in an effort to reduce polyurethane moisture sensitivity while retaining good mechanical properties. (Tech. Rep. #19). Similar studies were out blends carried more recently for of PTMO and poly(perfluoroalkylether) (PFEG) used as soft segment materials. These studies demonstrated that the desirable surface properties of non-polar soft segment materials may be imparted to the block-copolymer as a whole at low levels of PFEG incorporation due to surface enrichment of the low surface energy material (Tech. Rep. #21). The morphological contrasts between polyurethanes based on polar (PTMO) and non-polar (polybutadiene) soft segments were closely examined via high voltage electron microscopy (Tech. Rep. 14, 15, and 16). The importance of maintaining some minimum of segmental compatibilty in order to achieve qood mechanical properties was prominent among the recurring conclusions of our studies involving non-polar soft segment materials.

 $^{
m a}$ Second, we have studied the incorporation of novel pendant structures (UV-curable groups and ionic groups) in segmented and the material properties of the resulting polyurethanes, polymers. A liquid urethane methacrylate prepolymer and various monomers form semimethacrylate were used to and networks full-interpenetrating (IPNs). The structures and properties of these materials were examined using a variety of techniques, particularly the unique damping behavior characteristic IPNs (Tech. Rep. #22). Polyurethanes provide a unique of

opportunity for the study of ion-containing polymers (ionomers) in that pendant ion groups may be regularly spaced along the chain backbone. Ion containing polyurethanes have been synthesized by the addition of sulfonate and carboxylate pendant groups at the urethane linkage followed by neutralization with various metal cations. These polymers have been used to probe ionic aggregate structure (Tech. Rep. #17), as well as the effects of ion content, cation type (Tech. Rep. #18), and of anion type (Tech. Rep. #20) on material properties.

Third, because molecular characterization is a critical tool in the interpretation of strucuture-property relationships for these materials, we have investigated the analysis of polyurethane molecular weight distributions and their relationship to synthesis conditions. Most of this work was completed under the first three-year cylce of this ONR grant,; however, work has continued on the upgrading of our molecular weight characterization facilities. In addition, a series of polyurethanes with hydrolyzable soft segment to hard segment linkages has been synthesized. These materials will be hydrolyzed and the molecular weight distributions of the hard segments analyzed to relate the polymer structure to synthesis conditions.

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II. Technical Reports

- Number 13: Synthesis and Properties of Poly(cyanoethylmethyl siloxane) Polyurethanes; Study of Segmental Compatibility
- 2. Number 14: Characterization of Polyurethane Morphology
- 3. Number 15: The Morphology of Segmented Polybutadiene Polyurethane Elastomer
- 4. Number 16: Surface and Bulk Morphology of Segmented Polyurethanes
- 5. Number 17: MDI-Based Polyurethane Ionomers: I. New SAXS Model
- 6. Number 18: MDI-Based Polyurethane Ionomers: II. Structure-Property Relationships
- 7. Number 19: Structure-Property Relationships and Moisture Sensitivity of PDMS/PTMO Mixed Soft Segment Urethane Elasotmers
- 8. Number 20: Comparison of Carboxylated and Sulfonated Model Polyurethane Ionomers

9. Number 21: Synthesis and Properties of

Poly(perfluoroalkylether)urethanes

- 10. Number 22: UV-Curable Polyurethane-Methacrylate Co-Networks and Interpenetrating Networks
- III. Published Journal Articles
 - J.A. Miller, T.A. Speckhard, J.G. Homan, and S.L. Cooper, <u>Polyer</u>, 28, 758 (1987).
 - T.A Speckhard, J.G. Homan, J.A. Miller, and S.L. Cooper, <u>Polymer</u>, 28, 768 (1987).
 - C. Li, R.M. Nagarajan, C.C. Chiang, and S.L. Cooper, <u>Polym. Eng. Sci., Vol.</u> 26, 20 (1987).
 - 4. C. Li, X. Yu, T.A. Speckhard, and S.L. Cooper, <u>J.</u> <u>Polym. Sci., Polym. Phys. Ed., 26</u>, 315 (1988).
 - D.C. Lee, R.A. Register, C.Z. Yang, and S.L. Cooper, <u>Macromol.</u>, <u>21</u>, 998 (1988).
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 - C. Li, S.L. Goodman, R.M. Albrecht, and S.L. Cooper, <u>Macromol.</u>, <u>21</u>, 2361-2375 (1988).
- IV. Participating Personnel
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8/87 through 12/87

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