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| 19. ABSTRACT (Continue on reverse if necessary and identify by block number)<br>The relationships between microdomain structure and properties in segmented polyurethane elastomers have been elucidated by application of a number of sophisticated characterization techniques. Solid state deuterium NMR spectroscopy was used to explore the degree of phase separation in elastomers based upon 4,4'-diphenylmethane diisocyanate (MDI), butane diol(deuterium labelled)(BDO), and oxyethylene end-capped polyoxypropylene; and to study molecular motions in model hard segments of MDI/BDO and 2,4-toluene diisocyanate/BDO. The influence of morphological transitions on hydrogen bonding in the elastomers was examined by performing Fourier transform infrared spectroscopy simultaneously with a Differential Scanning Calorimeter (DSC) experiment. The origins of multiple endotherms in crystallizable polyurethanes were probed by performing simultaneous Small-Angle X-Ray Scattering (SAXS)/DSC and Wide-Angle X-Ray Diffraction (WAXD)/DSC experiments. Real-time SAXS and WAXD experiments have also been accomplished in order to characterize the kinetics of crystallization and microphase separation. |       |                                             |                                                                                                                 |                         |
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| 22a. NAME OF RESPONSIBLE INDIVIDUAL<br>Jeffrey T. Koberstein                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |       |                                             | 22b. TELEPHONE (Include Area Code)<br>203-486-4716                                                              | 22c. OFFICE SYMBOL      |

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These experimental results have furnished an initial understanding of the relationship between the thermal properties and microdomain structure of polyurethane elastomers.

OFFICE OF NAVAL RESEARCH

FINAL TECHNICAL REPORT

FOR

Period 07-01-84 to 06-30-86

Contract N00014-84-K-0534

STRUCTURE-PROPERTY CHARACTERIZATION IN SEGMENTED  
POLYURETHANE BLOCK COPOLYMERS

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This final project report describes reasearch that was performed during the past two years at Princeton University. The principal investigator is presently completing the original proposed research at the University of Connecticut in the Institute of Materials Science. For this reason the report is limited to describing the first two years of initial program results.

The project addresses the development of quantitative structure-property relationships for segmented polyurethane elastomers. To this end, a number of sophisticated characterization techniques have been applied. The first two papers that appeared in print<sup>1,2</sup>, discussed the use of solid state deuterium NMR spectroscopy to probe for the extent of microphase mixing in polyurethane elastomers, and to characterize the motions in pure hard segment materials. For materials prepared from 4,4'-diphenyl methane diisocyanate, butanediol, and polyoxyethylene end-capped polyoxypropylene soft segments, the following conclusions were reached: (1) the motions of the core of hard segment microdomains are identical to those of the pure hard segment material; (2) the amount of interfacial material quantified by NMR is in good agreement with that estimated from small angle x-ray scattering(SAXS); (3) the motions of interfacial hard segments are rapid and isotropic, suggesting that interurethane hydrogen bonds are

short-lived in the interfacial regions.

NMR was also applied to compare the motional behavior of crystalline and non-crystalline polyurethane hard segments. In the semicrystalline material, two clean components are discernable in the distribution of relaxation times, while only a single broad distribution is observed for the non-crystalline hard segment. The results also demonstrated that the predominant motion of the alkyl chain extender is a gauche-trans conformational hop, consistent with the existence of kinked rather than extended conformations in the chain extender.

In a third manuscript, Fourier transform infrared spectroscopy (FTIR) was used to examine the influence of morphological transitions on hydrogen bonding<sup>3</sup>. In previous publications we had used differential scanning calorimetry (DSC) and simultaneous SAXS/DSC experiments to demonstrate the existence of order-disorder transitions at temperatures in the range of 170-190C<sup>4,5</sup>. The FTIR experiments were novel in that they were the first simultaneous FTIR/DSC experiments to be performed. The results clearly reflected the onset of the order-disorder transition seen in earlier measurements as a decrease in the hydrogen bonding index. The technique also revealed that chemical changes occur during a DSC thermogram as evidenced by the emergence of an isocyanate band at high temperatures. The band appears due to the reversibility of



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the urethane reaction.

Several manuscripts are currently being prepared based upon recent work. In particular, real-time diffraction and SAXS experiments have been performed to study the kinetics of crystallization and phase separation; simultaneous SAXS/DSC and WAXD/DSC experiments have elucidated the origins of multiple endotherms; comparison of these results with measurements of thermo-mechanical properties have furnished an understanding of the factors that control softening behavior; and finally a method for the estimation of phase compositions has been developed based on the combination of information garnered from SAXS and DSC analysis.

#### References

1. J.J. Dumais, L. Jelinski, L. Leung, I. Gancarz, A. Galambos, and J.T. Koberstein, *Macromolecules*, 18, 116, 1985.
2. A. Kintanar, L. Jelinski, I. Gancarz, and J.T. Koberstein, *Macromolecules*, 19, 1876, 1986.
3. J.T. Koberstein, I. Gancarz, and T. Clarke, *J. Polym. Sci. Polym. Phys. Ed.*, in press.
4. L. Leung and J. Koberstein, *Macromolecules*, 19, 706, 1986.
5. J. Koberstein and T. Russell, *Macromolecules*, 19, 714, 1986.

### Student Support

To date, the contract has provided support for two graduate students: Mr. A. Galambos, who is scheduled to complete his PhD degree during the next year, and Mr. W. Stockton, who is currently completing a Masters degree.