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13. ABSTRACT *(Maximum 200 words)*

The effect of the introduction of mesogenic groups on the properties and structure of segmented polyurethanes was investigated. The objectives were to determine to what extent the phase behavior of such polyurethanes is controlled by the phase behavior of the mesogen and the effect of structural considerations such as hydrogen bonding and asymmetric placement of methyl groups on the phase behavior. A summary of the most important results appears in the final report.

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SYNTHESIS, STRUCTURE AND PROPERTIES OF SEGMENTED POLYURETHANES

FINAL REPORT

WILLIAM J. MACKNIGHT

OCTOBER 31, 1990

U.S. ARMY RESEARCH OFFICE
CONTRACT DAAL 03-87-K0075

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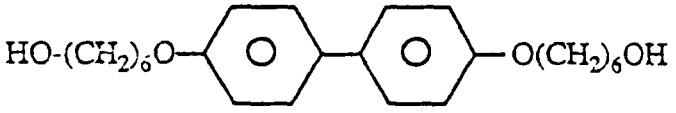
A. Statement of the Problem

The effect of the introduction of mesogenic groups on the properties and structure of segmented polyurethanes was investigated. The objectives were to determine to what extent the phase behavior of such polyurethanes is controlled by the phase behavior of the mesogen and the effect of structural considerations such as hydrogen bonding and asymmetric placement of methyl groups on the phase behavior.

B. Summary of the Most Important Results

A series of polyurethanes containing the mesogenic diol, BHHBP, was synthesized

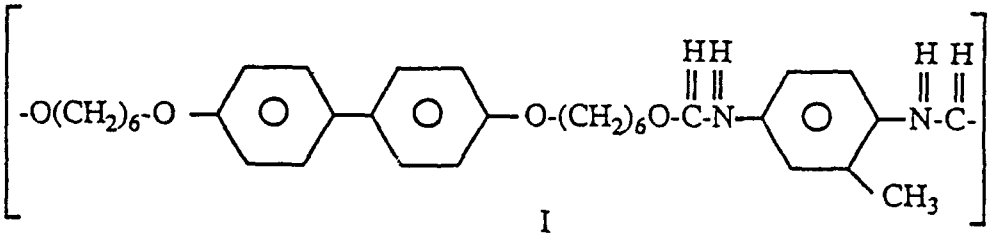


BHHBP

BHHBP was itself characterized with regard to its thermal and morphological behavior. The major findings of this research may be summarized as follows:

(1) BHHBP forms a crystal phase which melts to produce a highly ordered smectic phase in which the molecules are tilted at 45°-55° in the smectic layers.

(2) A polyurethane synthesized from 2,4 toluene diisocyanate and BHHBP having the repeat unit



I

exhibited no thermodynamically stable mesophase. An evanescent mesophase can be produced on cooling from the isotropic melt. Its morphology can then be preserved by quick quenching the polymer below its glass transition temperature. On the basis of X-ray analysis, this mesophase is also of the smectic type with the molecules tilted in the smectic layers in a similar fashion to BHHBP itself. Polyurethane I forms a stable three dimensional crystalline phase.

(3) A polyurethane identical in structure to I, but with the N-H groups replaced by N-CH_3 groups, exhibits a stable smectic mesophase, again similar in structure to that in BHHBP. This polymer does not crystallize under any experimental conditions.

(4) A series of segmented polyurethanes with poly(tetramethylene oxide) soft segments and hard segments built up from BHHBP and either 2,4 toluene diisocyanate or "Hylene W", (dicyclohexane methane diisocyanate) was prepared. Preliminary results indicate that their mechanical properties are determined by the ability of the soft segment to crystallize under extension and their overall molecular weights. Only preliminary data are available concerning the morphology of the hard segment pnase.

(5) The kinetics of microphase separation in model segmented polyurethanes based on poly(tetramethylene oxide) and diphenylmethane diisocyanate with butane diol as a chain extender could be followed by observing spectral changes in the carbonyl stretching vibration region by Fourier Transform Infrared Spectroscopy. A model for this process based on the concepts of nucleation and growth analyzed by the method of Avrami was put forward.

C. List of Publications

1. Thermal and Rheological Properties of a Liquid-Crystalline Polyurethane
Macromolecules 1989 22, 1467.

2. Infrared and X-Ray Diffraction Studies of a Semi-Rigid Polyurethane
Macromolecules 1989 22, 551.

3. Spectroscopic Analysis of Phase Separation Kinetics in Model Polyurethanes
Macromolecules 1988 21, 270.

4. Development of Crystallinity in a Polyurethane Containing Mesogenic Units.
1. Morphology and Mechanisms
Macromolecules 1990 23, 3389.

5. Microstructure and Dynamics of a Mesogenic Diol
Liquid Crystals 1990 7, 838.

6. A Novel Synthesis of Mesogenic N-Methyl Polyurethanes and Demonstration of the Effect of Hydrogen Bonding on Liquid Crystalline Properties
Polymer Preprints 1990 31, 486.

D. List of All Participating Scientific Personnel and Degrees Awarded

Personnel	Degree
Professor Shaw Ling Hsu	-
Professor Richard J. Farris	-
Professor William J. MacKnight	-
Doctor Enrique Valles	-
L. Anderson	Ph.D., Chemical Engineering
K. Antolin	-
Chen Ho Chen	-
Elliot Douglas	M.A.
Chris Haak	M.A.
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F. Papadimitrakopoulos	-
B. Reekmans	-
D.Y. Shi	-
K. Tung	-
D.Waldman	Ph.D.
Q. Wang	M.A.