Structure and morphology of segmented polyurethanes: 1. Influence of incompatability on hard-segment sequence length

M. Xu*, W. J. MacKnight, C. H. Y. Chen and E. L. Thomas
Department of Polymer Science and Engineering and Materials Research Laboratory, University of Massachusetts, Amherst, Massachusetts 01003, *USA*

(*Received* 27 *September* 1982)

Separation of three polybutadiene/toluene diisocyanate/butane diol segmented polyurethanes by means of solvent extraction and the characterization of their fractions indicate that the molecules of the original polyurethanes are quite dissimilar in chemical composition and average hard-segment length. These polyurethanes are just blends of two fractions of segmented copolymer with very different average hard-segment content and average hard-segment length. For these polyurethanes, in addition to the segregation of the hard and soft segments, as expected usually for segmented copolymers, the segregation of macromolecules as a whole according to their composition should be considered in the interpretation of their morphology and properties and has been proved to be the origin of the existence of two hard-segment T_g's. This ind of compositional non-uniformity is the result of the poor compatibility between the components of the system. It should be a common phenomenon for segmented copolymers, but is especially obvious in the case of polybutadiene-containing polyurethanes owing to the extremely poor compatibility between their components.

Keywords Segmented polyurethane; compositional heterogeneity; incompatibility; glass transition temperature; infra-red; differential scanning calorimetry

INTRODUCTION

Polybutadiene-containing polyurethanes are a special kind of segmented polyurethane which offer the advantage of low moisture permeability. They have been the subject of several studies aimed at exploiting this property for adhesives and electrical potting compounds[1-3]. These polyurethanes are also of interest as a model system in which there is no possibility of hydrogen bonding between the hard and soft segments, in contrast to the more familiar polyester or polyether polyurethanes.

The segregation of hard and soft segments and the formation of domain structure are expected for these kinds of polymers. Their morphological features and transition behaviour have been examined as a function of chemical structure, composition and processing conditions. Lagasse[4] first observed the individual glass transitions of the hard-segment and soft-segment regions of polybutadiene-containing (PBD) polyurethanes. Schneider and Matton[5] studied the thermal transition behaviour of PBD-containing polyurethanes by means of d.s.c. techniques. The hydroxy-terminated polybutadiene (HTPBD) was Arco R45M which has a number average molecular weight of 2800, an average functionality between 2.1 and 2.3 hydroxyls per molecule and mixed chain microstructure consiting of 60% *trans*, 20% *cis* and 20% vinyl units. The diisocyanates used were 4,4′-diphenyl methane diisocyanate (MDI) and 2,4-toluene diisocyanate (2,4-TDI) and extenders were bis(2-hydroxypropylaniline) (HPA) or 1,4-butane diol (BDO). They found that the glass transition temperature (T_g) of the soft-segment regions is independent of the hard-segment content and is very close to (only 4°–8°C higher than) that of the original HTPBD. These results are accepted as evidence for very nearly complete phase segregation in the PBD-containing polyurethanes. The unusual transition behaviour observed at higher temperatures is related to the hard-segment regions. Two hard-segment T_g's have been observed, the T_1 transition at about 40°C and the T_2 transition at about 103°C for HTPBD/2,4-TDI/HPA samples and at about 72°–89°C for HTPBD/2,4-TDI/BDO and HTPBD/MDI/BDO samples. These transitions have been attributed by the authors to phase-segregated structures made up of shorter hard-segment units and longer hard-segment units, respectively. Schneider *et al.*[6] and Brunette *et al.*[7] confirmed these results using d.s.c., dynamic mechanical measurements and thermal mechanical analysis. In these papers a series of 2,4-TDI/BDO polyurethanes with hydrogenated polybutadiene as soft segment is also included. In the recent studies of Brunette *et al.*[8], an anionically polymerized hydroxy-terminated polybutadiene made by Japanese Synthetic Rubber Co. (JSR HTPBD) of $M_n = 2200$ is used as the soft segment. This macroglycol has an average hydroxyl functionality of 1.97, which avoids crosslinking through the soft-segment phase. It contains 55% vinyl butadiene, 35% *trans*-1,4- and 10% *cis*-1,4-butadiene units. In polyurethanes based on the JSR material an almost composition-independent soft-segment T_g was found only 8°C higher than that for the pure hydroxy-terminated JSR HTPBD. Two hard-segment T_g's at ~20°–40°C and 55°–80°C were observed depending upon hard-segment content.

---

* Permanent address: Institute of Chemistry, Academia Sinica, Beijing, China

0032-3861/83/101327-06$03.00

It appears that the presence of two hard-segment T_g's is a characteristic feature of polybutadiene-containing polyurethanes and is explained as transitions in domains of different hard-segment lengths. However, it remains unclear why there is a distinct bimodal distribution of hard-segment length within these samples and what is the driving force for the separation or fractionation of the hard segments in the amorphous state according to their length.

In the study of the crystallization of polyester–polyether segmented copolymers, Xu *et al.*[9] have found that, in the case of poor compatibility between the components, the segmented macromolecules can vary greatly in their chemical composition and average segment length, and the segregation of these macromolecules as a whole may strongly affect the morphology and transition behaviour of the samples. In this paper the compositional non-uniformity of macromolecules of polybutadiene-containing polyurethanes and its influence on their transitions are discussed.

EXPERIMENTAL

The synthesis of the segmented polyurethane was carried out by a two-step method involving endcapping the hydroxy-terminated polybutadiene with the diisocyanate followed by reaction with the chain extender. The details of this procedure have been described previously[8]. Both 2,4-TDI and 2,6-TDI were used as diisocyanate with BDO as the chain extender, and the same JSR HTPBD as in ref. 8 was utilized as the prepolymer. Three samples were investigated and their overall compositions are given in *Table 1*.

Differential scanning calorimetry (d.s.c) was carried out in a temperature range from 170 to 450 K using a Perkin–Elmer DSC-2, purged with helium and chilled with liquid nitrogen. Runs were conducted on polymer samples of about 15 mg at a heating range of 20°C min^{-1} and an attenuation of 5 mcal s^{-1}. Cyclohexane (crystal–crystal transformation at 186K) and indium (melting point at 429.8K) were used as thermal standards for temperature calibration. The glass transition temperature was taken to be the temperature corresponding to one-half the increase in heat capacity accompanying the transition. Infra-red spectra (4000–400 cm^{-1}) were obtained with a Perkin–Elmer 283 i.r. spectrophotometer. The resolution used was 3 cm^{-1}. Data were usually taken using KBr pellets containing 1% sample by weight.

RESULTS

Fractionation of the samples

If macromolecules have different hard-/soft-segment compositions, they should also differ in their solubility behaviour. Fractionation was carried out by the solvent extraction method using DMF. It was found that after several days at 70°C all samples separated into a sol fraction and a gel fraction. The gel fractions became soluble in DMF if higher temperatures were used. Fractions were cast on a glass plate at 70°C for 3–4 h, then dried in a vacuum oven at the same temperature. The relative amounts of these fractions are listed in the second column of *Table 2*. The composition and transition behaviour of these fractions were determined by i.r. and d.s.c. measurements.

Table 1 Overall compositions of the samples

Sample	Diisocyanate	Molar composition, PBD/TDI/BDO	Hard-segment content (wt %)
4T4	2,4-TDI	1/4.2/3	31.3
4T10	2,4-TDI	1/10.5/9	54.5
6T4	2,6-TDI	1/4.2/3	31.3

Table 2 Hard-segment content of sol and gel fractions

Sample	Percentage of fractions (wt %)	Hard-segment content (wt %)	Hard-segment content of original sample	
			Data of fractions	Synthesis condition
4T4-S	56	41.7	30.8	31.3
4T4-G	44	17.0		
4T10-S	80	67.5	56.1	54.5
4T10-G	20	10.5		
6T4-S	54	35.0	25.8	31.3
6T4-G	46	15.0		

Infra-red measurements

The assignments of spectra of polybutadiene and polybutadiene-containing segmented polyurethanes have been reported by many authors[7,10–14]. Very strong bands characteristic for the hard segment are 3310–3440 cm^{-1} (NH stretching), 1710–1735 cm^{-1} (C=O stretching), 1535 cm^{-1} (NH bending and CN stretching), and 1230 cm^{-1} (NH bending and CN stretching). Characteristic bands for the soft segment are those related to the double bond at 995 cm^{-1} (*cis*-1,4), 965 cm^{-1} (*trans*-1,4) and 910 cm^{-1} (vinyl). The spectra of the two fractions of each polyurethane show that their compositions are quite different. *Figure 1* is a comparison of 4T4-S and 4T4-G (sol fraction of sample 4T4, and gel fraction of sample 4T4). Bands of 910, 965 and 995 cm^{-1} have relatively much higher absorbance for the gel fraction than for the sol fraction. It implies that the sol fraction is relatively hard-segment-rich and the gel fraction is soft-segment-rich. A similar situation is found for 6T4 fractions, and much greater compositional differences are observed for 4T10-S and 4T10-G (*Figure 2*).

A quantitative analysis of the i.r. measurements has been carried out to determine the composition of these fractions. The 1710 cm^{-1} (hard-segment) and 910 cm^{-1} (soft-segment) bands were used. The 910 cm^{-1} band is due only to the vinyl group of the polybutadiene. The fact that the absorbance ratio A_{965}/A_{910} remains nearly constant for all the fractions and very close to that of the pure polybutadiene indicates that the proportions of the *cis*, *trans* and vinyl isomers of the soft segment do not change during the separation into fractions. The carbonyl stretching band can be influenced by hydrogen bonding, so that the absorbance value at the peak position is not only a function of the hard-segment content but also of the degree of hydrogen bonding of the C=O groups. Senich and MacKnight[15] have shown that for 2,6-TDI polyurethane the ratio of the hydrogen-bonded to the free extinction coefficient is equal to 1.05 for the carbonyl stretching vibration. This means that the area of the C=O stretching band can be used to characterize the amount of hard segment within the sample without considering the

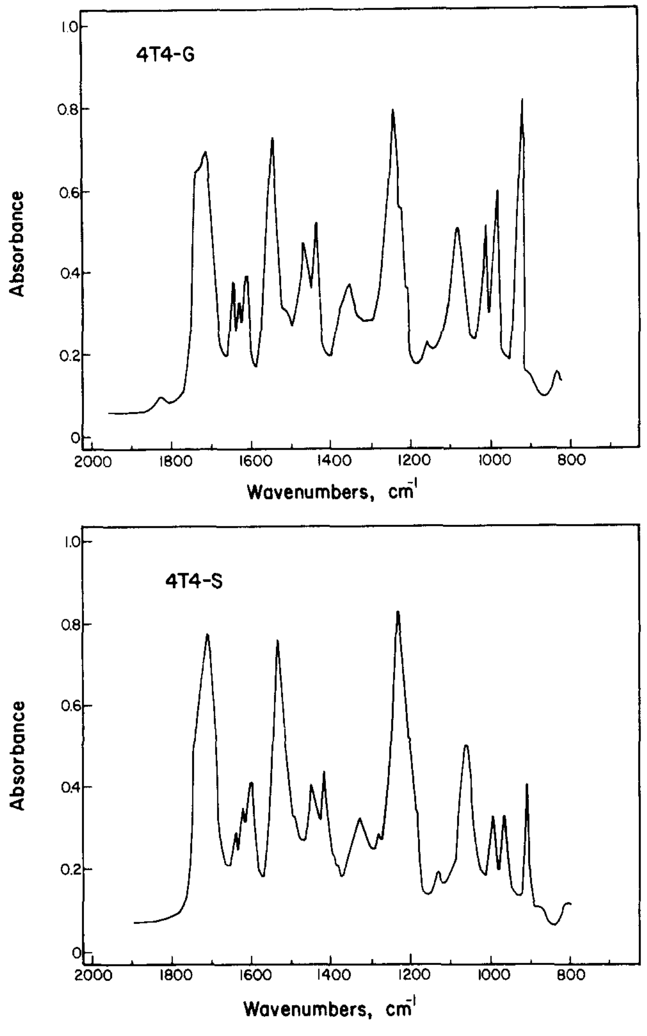

Figure 1 I.r. spectra of 4T4-S and 4T4-G

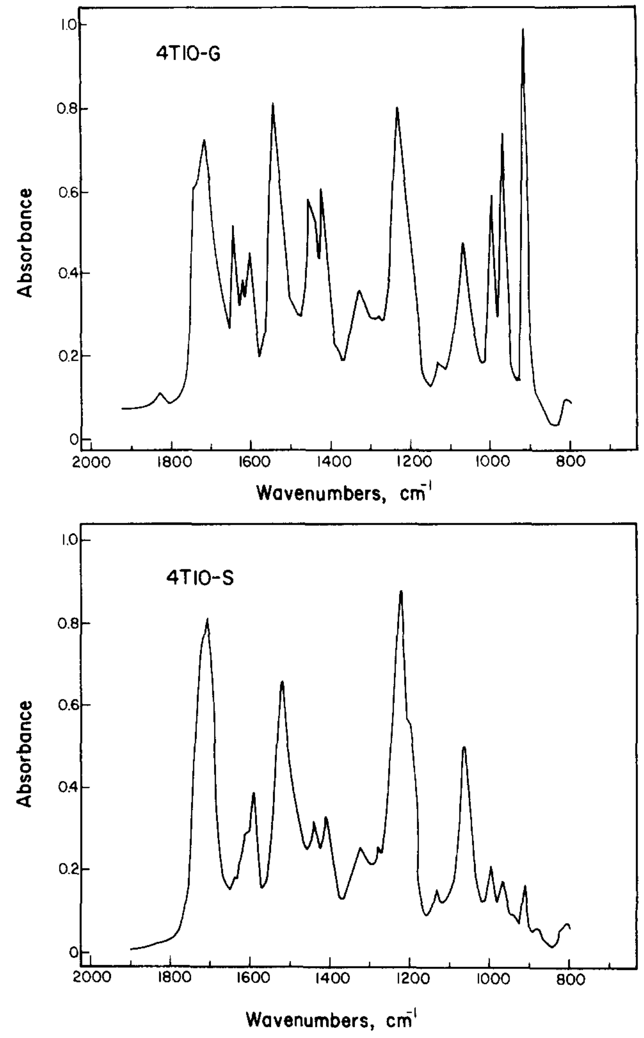

Figure 2 I.r. spectra of 4T10-S and 4T10-G

degree of hydrogen bonding. Blends of pure hard- and pure soft-segment homopolymers and copolymers of known composition are used to establish the calibration curve. The compositions of all the six fractions determined by this method are given in *Table 2*. The hard-segment content of the sol fraction is about 2.5 times as high as that of the gel fraction in the case of 4T4 and 6T4, but about 6 times higher for 4T10 fractions. Good agreement is obtained between the hard-segment content of the original samples (*Table 2*) calculated from the hard-/soft-segment composition of the fractions and the stoichiometric value. This indicates that the i.r. method to determine the hard-/soft-segment composition is valid.

Differential scanning calorimetry measurements

The d.s.c. curves of the original samples and their fractions obtained by solvent extraction are given in *Figures 3–5*, and their glass transition temperatures are summarized in *Table 3*. The soft-segment glass transition T_g is found to be at about −57°C for all the samples. Two hard-segment glass transitions T_1 and T_2 are observed for 4T4 and 6T4. The sol fractions of these two samples also show two hard-segment T_g's located at almost the same temperatures as the T_1's and T_2's of the original samples, but their gel fractions only show the T_1 transitions. Sample 4T10 has a single hard-segment T_g which is at higher temperature than that of 4T4 and 6T4. The transition behaviour of 4T10-S is similar to that of 4T10, but 4T10-G shows a hard-segment transition at −8°C. Measurements for HTPBD and HTPBD extended by 2,4-TDI indicate that they have the same glass transition temperature at −65°C, which is 8°C lower than that of the soft-segment transition of the polyurethanes. No other transitions have been observed for HTPBD/2,4-TDI. The

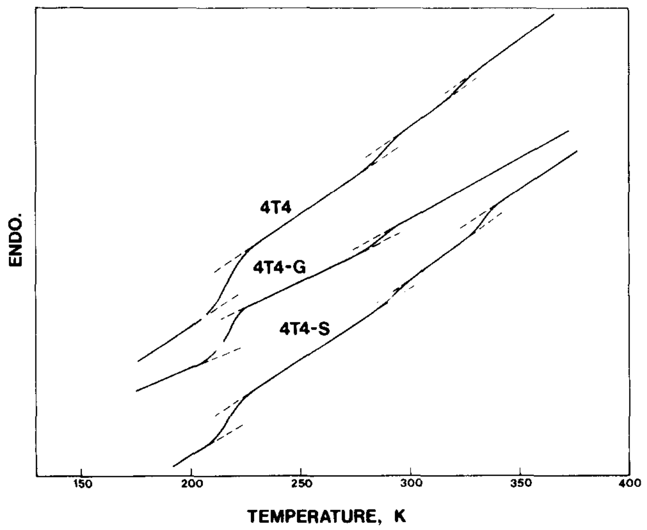

Figure 3 D.s.c. scans of 4T4 and its fractions

relative heat capacity changes at the transitions are also given in *Table 3*.

DISCUSSION

The T_g for the soft-segment region is found to be independent of the hard-segment content and the kind of isocyanate. These results are consistent with those of the previous studies[5-8]. Our results indicate the polybutadiene soft segments are so incompatible with the urethane hard segments that they are completely phase-separated no matter what may be the sample preparation technique (i.e. compression moulding or solvent casting).

Segmented polyurethanes are usually considered to be products of the random copolymerization of diisocyanates, macromolecular diisocyanates and extenders. If this were the case the macromolecules would all have the same average chemical composition and average hard-segment length and therefore would be statistically identical. The microphase separation of hard and soft segments is postulated to explain their morphological features and properties.

Our results show that as in the case of polyester–polyether segmented copolymers, macromolecules of the segmented polyurethanes can be quite non-uniform in chemical composition and average segment length and they can be separated according to their differences in solubility. Since the hard-segment glass transitions T_1 and T_2 remain almost unchanged during solvent extraction, one may approximately consider these samples as mixtures of two fractions (fractions 1 and 2) of segmented copolymers which have distinctly different average chemical composition and average hard-segment length. The transitions T_1 and T_2 are then assigned to the T_g's of domains composed of fractions 1 and 2, respectively. In addition to the segregation of the hard and soft segments, the poor compatibility and the great differences in solubility cause the segregation of macromolecules as a whole according to their composition during moulding or subsequent solution casting of the dissolved material and hence the separation of hard segments of different lengths.

The existence of two hard-segment T_g's for 4T4-S and 6T4-S means that the separation by solvent extraction under the experimental conditions is not complete, and only the gel fractions are relatively uniform, as a single hard-segment transition is observed in their case. The relative heat capacity changes give an indication of the separation efficiency. The content of hard segments of

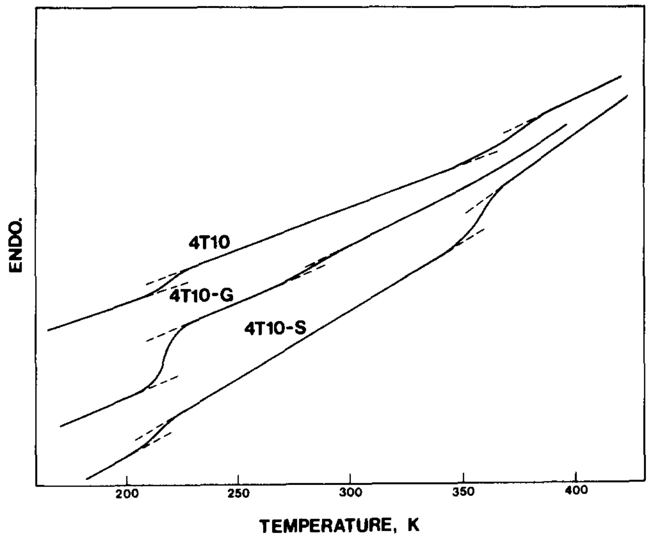

Figure 4 D.s.c. scans of 4T10 and its fractions

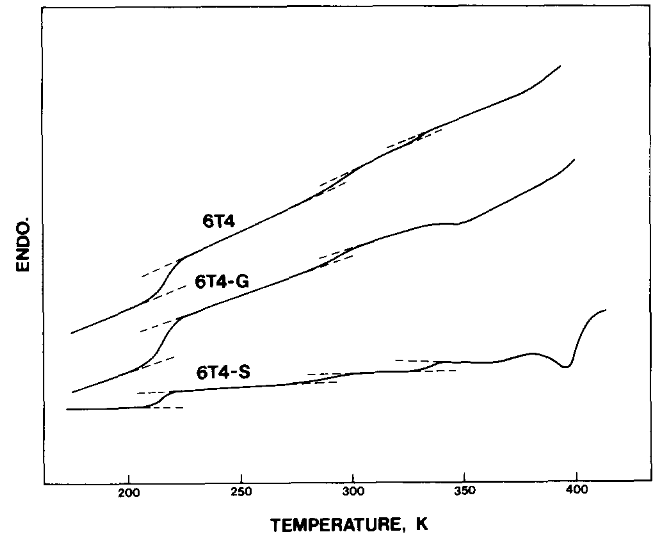

Figure 5 D.s.c. scans of 6T4 and its fractions

Table 3 Data of d.s.c. measurements

Sample	T_g (°C)	T_1 (°C)	T_2 (°C)	$(\Delta C_p)_2/(\Delta C_p)_g$	$\frac{(\Delta C_p)_1}{(\Delta C_p)_1 + (\Delta C_p)_2}$
4T4	–58	17	48	0.19	0.62
4T4-S	–56	21	60	0.54	0.45
4T4-G	–57	17	–	0	1
4T10	–57	–	93	0.93	0
4t10-S	–59	–	84	2.08	0
4t10-G	–57	–8	–	0	1
6T4	–57	22	67	0.12	0.62
6T4-S	–58	15	61	0.54	0.46
6T4-G	–57	17	–	0	1
HTPBD	–65	–	–	–	–
HTPBD/2,4-TDI	–65	–	–	–	–
2,4-TDI/BDO	86	–	–	–	–

short sequence lengths which is related to transition T_1 is too low (~2%) in the sample 4T10, so T_1 cannot be detected except where molecules of short hard-segment sequence lengths are present in high concentration as in the case of 4T10-G.

From the hard-segment content of the sol and gel fractions and the original samples determined by the i.r. technique and the ratio of

$$(\Delta C_p)_1/[(\Delta C_p)_1+(\Delta C_p)_2]$$

it is possible to estimate the contents of fractions 1 and 2 and their compositions for the three original samples (*Table 4*). These data show how far the compositions of the fractions may deviate from that expected stoichiometrically. The mole ratio of TDI/PBD for the soft-segment-rich fractions (fraction 1) is as low as 1.3–2.0. This means that those polybutadiene segments are TDI-endcapped and extended on average by one butane diol molecule or even only connected with each other through a single TDI molecule.

Using the relative amounts and the average sequence length of hard segments in fractions 1 and 2, a rough estimate of the bimodal weight distribution of hard-segment length for sample 4T4 can be made (see *Figure 6*). It is assumed that both fractions have a Gaussian distribution with $M_w/M_n=1.5$. Under ideal conditions, i.e. random reaction and equal reactivity of both ends of units, the sequence length distribution of hard segments follows the most probable distribution[16,17], which is also given in the figure for comparison.

Using the sequence lengths of fractions 1 and 2 determined in the manner described, the dependence of the glass transition temperature of the hard segment upon the average hard-segment length is found to be inversely proportional to the mole ratio R of TDI/BDO (see *Figure 7*). This relation is of the form

$$T_g=T_g^{\infty}-R/M_n \qquad (1)$$

which may be derived from free volume considerations. We may take T_g^{∞} to be the T_g of the 'pure hard-segment' (2,4-TDI/BDO) polymer and M_n is simply related to R.

Domain structures of several micrometres dimensions in solution-cast 4T4 films have been observed by electron microscopy. These domains cannot be the result of the segregation of hard and soft segments alone because of their large size compared to the dimensions of the segments. This phenomenon can be understood if the segregation of macromolecules of different compositions is considered and will be discussed in a subsequent paper. It is very interesting to note that the relative amounts of the soft-segment-rich or hard-segment-rich fractions estimated from stereological analysis of the electron micrographs are in good agreement with those given in *Table 4*.

Table 4 Heterogeneity of the segmented polyurethanes

Sample	Percentage of fractions (wt %)	Hard-segment content (wt %)	Mole composition, TDI/PBD
4T4		31.3	4
4T4-1	62	17.0	2
4T4-2	38	53.0	9.3
4T10		54.5	10
4T10-1	20	10.5	1.3
4T10-2	80	67.5	17
6T4		31.3	4
6T4-1	62	15.0	1.7
6T4-2	38	43.0	6.4

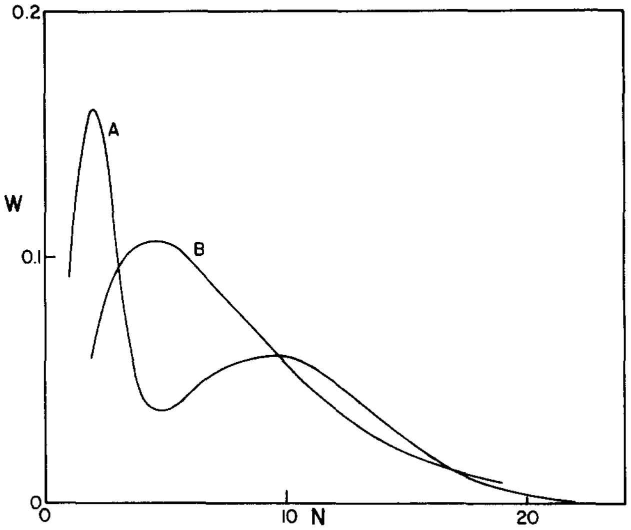

Figure 6 A schematic weight distribution of hard-segment length for sample 4T4. *N* is the number of TDI units in a hard segment. Curve A, calculated as a blend of fractions 1 and 2; curve B, most probable distribution

It has been proposed[9] that a bimodal distribution of molecules in chemical composition and hard-segment sequence length can result from the heterogeneity of the reactants themselves. This means in the present system that both the isocyanate groups of the endcapped polybutadiene and those of the free TDI are not distributed uniformly throughout the reaction mixture.

Reactions in free-TDI-rich regions will result in hard segments of longer length, and in the endcapped-polybutadiene-rich regions reactions will result in hard segments of shorter length including a large amount of segments with only two TDI units. A schematic model of the heterogeneous reaction mixture and its influence on the subsequent sequence distribution of the polyurethane hard segments is discussed in detail in an accompanying paper[18].

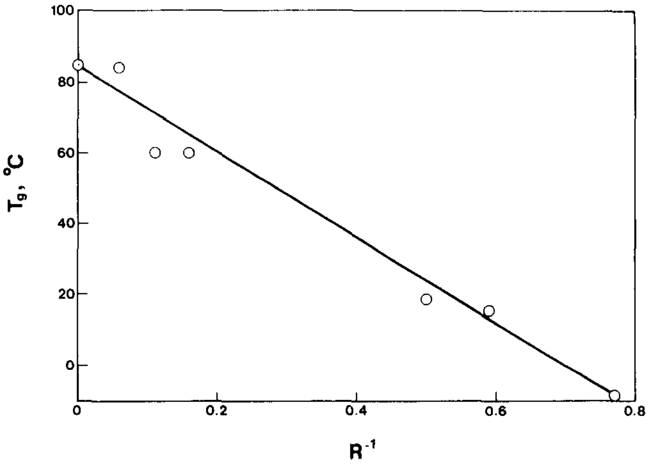

Figure 7 Dependence of hard-segment T_g on the segment length. R = mole ratio of TDI/PBD

In most cases the reactants used to form a copolymer are not compatible or at least not completely compatible, so the non-uniformity in chemical composition and average segment length should be a common phenomenon for segmented copolymers. The extremely poor compatibility between the reactants of polybutadiene-containing polyurethanes makes them good examples to demonstrate this hypothesis.

CONCLUSIONS

Segmented polyurethanes prepared by reacting isocyanate-endcapped butadiene oligomers with a chain extender such as BDO are heterogeneous with respect to hard-segment sequence length.

The heterogeneity leads to phase separation in the bulk of macromolecules containing shorter and longer hard segments, and is the origin of the two hard-segment T_g's observed.

The heterogeneity results from the incompatibility of the reactants.

ACKNOWLEDGEMENTS

We are grateful to the Army Research Office, Durham, under Grant No. DAAG 29 80 C 0054, and the National Science Foundation, Grant CPE-8118232, Chemical and Process Engineering Program, for partial support of this research.

REFERENCES

1 Arnold, C., Jr *J. Elastomers Plastics* 1974, **6**, 238
2 Elmore, R. D. 'Use of EN-7 to Encapsulate Analyzer Assemblies', September 1974, PDO 6989189 USAEC Contract AT(29-1)-613
3 Wood, G. B. 'Evaluation of Conformal Coatings of Microelectronic Circuitry in Fuse Applications', March 1977, HDL-TR-1777
4 Lagasse, R. R. *J. Appl. Polym. Sci.* 1977, **33**, 2489
5 Schneider, N. S. and Matton, R. W. *Polym. Eng. Sci.* 1979, **19**, 1122
6 Schneider, N. S., Brunette, C. M., Hsu, S. L. and MacKnight, W. J. 'Advances in Polyurethane Science and Technology' Frisch, K. C. and Klempner, D. Eds. Techoromic, Westport, CT, 1981, p. 49
7 Brunette, C. M., Hsu, S. L., MacKnight, W. J. and Schneider, N. S. *Polym. Eng. Sci.* 1981, **21**, 163
8 Brunette, C. M., Hsu, S. L., Rossman, M., MacKnight, W. J. and Schneider, N. S. *Polym. Eng. Sci.* 1981, **21**, 668
9 Xu, M., Hu, S., Meiyan, W., Chuanfu, C. and Yongze, J. *Polym. Commun.* 1982, No. 1, 27
10 Binder, J. L. *J. Polym. Sci. A* 1965, **3**, 1587
11 Neto, N. and diLauro, C. *Eur. Polym. J.* 1967, **3**, 645
12 Cornell, S. W. and Koenig, J. L. *Macromolecules* 1969, **2**, 540
13 Hsu, S. L., Moore, W. H. and Krimm, S. *J. Appl. Phys.* 1975, **46**, 4185
14 Paik Sung, C. S. and Schneider, N. S. *Macromolecules* 1975, **8**, 68
15 Senich, G. A. and MacKnight, W. J. in 'Multiphase Polymers', *Adv. Chem. Ser.* No. 176, American Chemical Society, New York, 1979, p. 97
16 Peebles, L. H., Jr *Macromolecules* 1974, **7**, 872
17 Peebles, L. H., Jr *Macromolecules* 1976, **9**, 58
18 Chen, C. H. Y., Briber, R. M., Thomas, E. L., Xu, M. and MacKnight, W. J. *Polymer* 1983, in press