Morphological Interpretation of the Dynamic Mechanical Properties of Some $(AB)_n$ Urea-*b*-urethane Copolymers

James L. Work

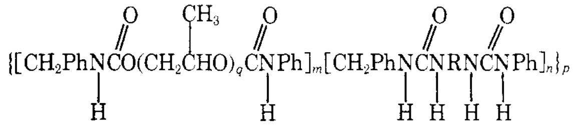
Armstrong Cork Company, Research and Development Center, Lancaster, Pennsylvania 17604. *Received April 14, 1976*

ABSTRACT: The preparation of urea-*b*-urethane block copolymers based on polyether diols, 4,4′-methylenebis(cyclohexyl isocyanate), and three different diamines is described. Decreasing the urethane content of the urethane segments and increasing the molecular weight of the urethane and/or urea segments increases the aggregation of the copolymers into pure urethane and urea domains. The T_g of the pure urethane domains is a function of the urethane content of the urethane segments and can be calculated from one of the equations used to calculate the T_g of random copolymers or miscible polymers. The T_g of the pure urethane domains is not a function of molecular weight. The distribution of molecular weights in the polyether diols and in the urethane segments may result in solubilization of the short urethane segments or urethane segments containing the low molecular weight diols in the urea domains. Modification of the chemical structure of the urea segments results in changes in the degree of solubilization of the segments.

Numerous theories[1–12] have been proposed to explain the phenomenon of domain formation in block copolymers. The most recent of these theories has been proposed by Helfand.[1] All of these theories assume that domains of pure segments are formed and any mixing of the segments occurs in the interphase between the domains. This assumption is probably valid for ionically polymerized block copolymers where the segments are uniform in size. However, this assumption is probably not valid for block copolymers where there are broad distributions in segment size. It is thermodynamically possible that the domains of one segment type will contain segments of the other type. This proposal will be substantiated by data on the dynamic mechanical behavior of polyether based urea-*b*-urethane polymers. This system is presumed to have a large χ parameter between the segments and therefore domain formation will occur at much smaller segment sizes than is normally observed for a copolymer system like styrene-*b*-butadiene.

Experimental Section

The urea-*b*-urethane polymers used in this study have the general formula



$$\{[\mathrm{CH_2Ph}\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O(CH_2}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{HO)}_q\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}\mathrm{Ph}]_m[\mathrm{CH_2Ph}\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}\mathrm{R}\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}\mathrm{Ph}]_n\}_p$$

where R is $PhCH_2Ph$, $(CH_2)_6$, or $(CH_2)_3N(CH_3)(CH_2)_3$. These polymers are prepared by reacting an isocyanate-terminated urethane segment with an amine-terminated urea segment or with water to generate the amine in situ. In some instances, the urea blocks are prepared in situ by first adding 1 equiv of an isocyanate-terminated urethane oligomer to 2 equiv of a diamine in solution. Sufficient amine and diisocyanate are added to the reaction mixture to achieve the desired amount of urea.

The values of m were calculated from the experimentally determined equivalent weight of the isocyanate-terminated urethane oligomer using

$$m = (2E_u - M_I)/M_u \qquad (1)$$

where E_u is the equivalent weight of the urethane oligomer, M_I is the molecular weight of the diisocyanate, and M_u is the molecular weight of the urethane repeat unit. The values of n were calculated from the experimentally determined equivalent weight of the amine-terminated urea oligomer using

$$n = (2E_A + M_I)/M_A \qquad (2)$$

where E_A is the equivalent weight of the urea oligomer, M_I is the molecular weight of the diisocyanate, and M_A is the molecular weight of the urea repeat unit. In cases where the urea blocks were prepared in situ, n could not be calculated. Insolubility of the polymers in readily available solvents precluded the determination of molecular weights. However, it was demonstrated previously[13] that small changes in molecular weight have no effect on the dynamic mechanical properties of these systems.

The urethane and urea segments listed in Table I were prepared using 4,4′-methylenebis(cyclohexyl isocyanate) and various polyether glycols and diamines, respectively. The dynamic mechanical properties of these polymers were determined using a Rheovibron Model DDV-II. Samples were prepared by compression molding at 200 °C for 3 min.

Results

(A) Polymers Based on Segments I and V. The urea segments of these polymers were prepared in situ at three different levels of urea (Table II). These polymers are all aggregated into domains as evidenced by the presence of two distinct relaxation (T_g) regions in their modulus/temperature profiles (Figure 1). T_g's are normally defined in dynamic mechanical measurements as the temperature at which a maximum in loss modulus or tan δ occurs. This definition is adequate for the low-temperature relaxation of these polymers, but there are no clearly defined maxima for the high-temperature relaxation. Therefore, the high-temperature relaxation will be defined arbitrarily as the temperature at which the rate of decrease in modulus with increasing temperature increases significantly. This definition will be adequate for the gross effects observed in these systems.

The low-temperature relaxation region is associated with the urethane domains and within experimental error remains constant as a function of composition. The urea relaxation region (high-temperature relaxation) shifts to higher temperatures when the urea content is increased from 7.8 to 32% but remains constant from 32 to 37% urea. The urea T_g region of polymers IIA and IIIA is approximately 20 °C higher than the T_g region of the corresponding urea homopolymer (Figure 1). This may be a result of the low molecular weight of the homopolymer or the presence of a trace of solvent. On the basis of the observed T_g's, it can be concluded that polymers IIA and IIIA are aggregated into pure domains of urethane and urea. The urea domain of polymer IA probably contains some of the shorter urethane segments which would lower the T_g of the urea.

(B) Polymers Based on Segments II and V. The urea segments of these polymers were prepared in situ at four different levels of urea content (polymers IB to IVB in Table III). These polymers are all aggregated into domains as evidenced by the presence of two distinct T_g regions in their modulus/temperature profiles (Figure 2). The urethane relaxation region (low-temperature relaxation) is constant as a function of composition with the possible exception of polymer IB. The urea relaxation region shifts to higher temperatures as the

Table I
Segments Used to Prepare Copolymers

Segment designation	Glycol or amine
I	Poly(oxyethylene) capped poly(propylene oxide) of 2900 mol wt
II	Poly(oxypropylene) glycol of 840 mol wt
III	Poly(oxypropylene) glycol of 440 mol wt
IV	4,4′-Methylenebis(cyclohexylamine)
V	1,6-Hexanediamine
VI	Bis(3-aminopropyl)methylamine

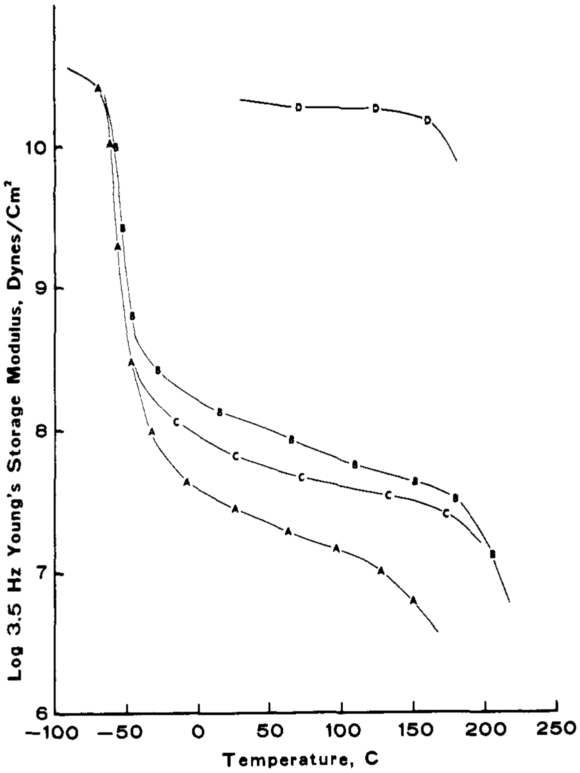


Figure 1. Young's modulus–temperature data for block polymers IA (A), IIA (C), and IIIA (B) and the urea homopolymer (D).

urea content increases. Up to 45 w/w % urea, the urea relaxation region in the block copolymer occurs at a lower temperature than the relaxation region of the corresponding urea homopolymer. On the basis of the observed T_g's, these polymers are aggregated into domains, but the urea domains are not pure.

Polymers VB and VIB (Table III) were prepared by reacting preformed segments. Polymer VIB has urethane and urea segments nearly twice the size of polymer IIB. The increased segment lengths increase the temperature of the urea relaxation region and sharpen the urethane relaxation region (Figure 3). Polymers IIIB and VB differ mainly in the distribution of the urea segment sizes. Polymer IIIB has something approaching a bimodal distribution while polymer VB has a more normal distribution. The normal distribution increases the urea T_g and broadens the urethane relaxation region when compared to the abnormal distribution (Figure 3).

(C) Polymers Based on Segment II with IV, V, or VI. These polymers were prepared by using diamine to extend the purified segment II. The weight percent urea and the urethane segment sizes are nearly constant (Table IV). All three of these polymers are aggregated into domains (Figure 4). The urethane transition region is constant for the three polymers and occurs at the expected temperature. However, the high-temperature relaxation region occurs at considerably lower temperatures than the T_g region of the urea homopolymers (Table IV and Figure 4). Further, the difference between the urea homopolymer T_g and the urea T_g in the block copolymer is not the same for the different ureas. Segment V exhibits the greatest difference and segment VI exhibits the least difference.

(D) Polymers Based on Water-Cured Segments I, II, and III. These polymers were prepared by water curing the purified isocyanate-terminated segments I, II, and III as described previously.[13] In one series the molecular weight of the

Table II
Characteristics of Urea-*b*-urethane Copolymers Based on Segments I and V

Polymer No.	Urea w/w %	m	n	Urethane T_g, °C[a]
IA	8.1	1.38	1.00	−60
IIA	31.8	1.38		−60
IIIA	36.7	1.38		−60

[a] E'' = 3.5 Hz.

Table III
Characteristics of Urea-*b*-urethane Copolymers Based on Segments II and V

Polymer No.	Urea w/w %	m	n	Urethane T_g, °C
IB	11.5	2.65	1.00	−28
IIB	23.4	2.65		−22
IIIB	34.3	2.65		−20
IVB	44.5	2.65		−17
VB	33.5	2.92	4.30	−20
VIB	26.1	6.85	5.61	−23

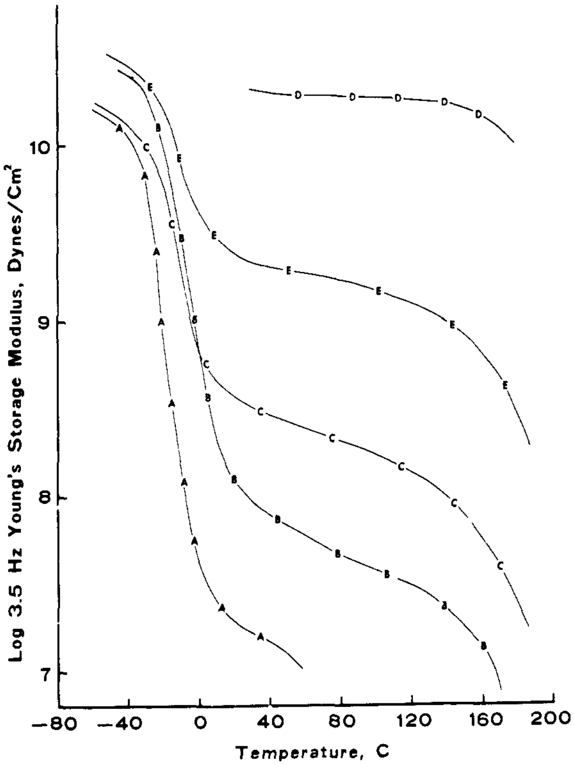


Figure 2. Young's modulus–temperature data for block polymers IB (A), IIB (B), IIIB (C), and IVB (E) and the urea homopolymer (D).

Table IV
Characteristics of Urea-*b*-urethane Copolymers Based on Segment II with Segments IV, V, or VI

Polymer No.	Urea w/w %	*m*	*n*	Segment No.	Urea T_g, °C	Urethane T_g, °C
IB	11.5	2.65	1.00	V	180	−28
IC	13.1	3.03	1.00	IV	212	−18
IIC	11.3	2.92	1.00	VI	163	−21

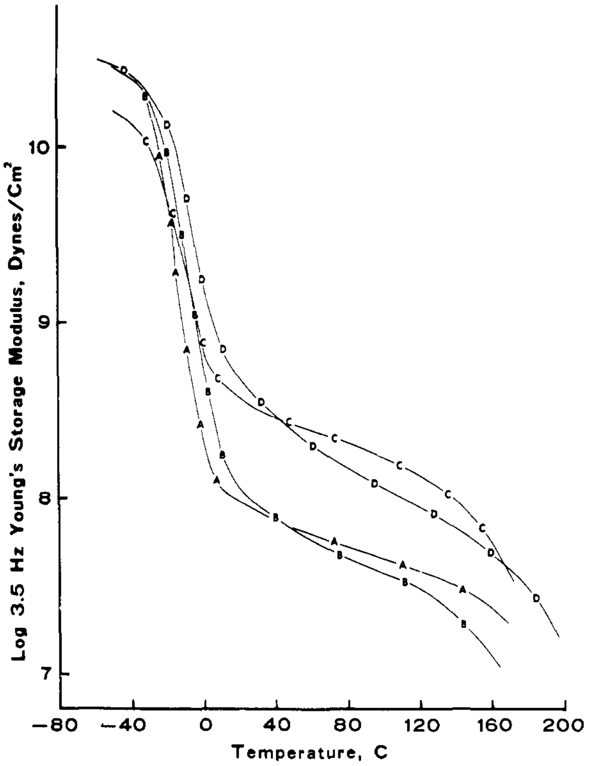


Figure 3. Young's modulus–temperature data for block polymers VIB (A), IIB (B), IIIB (C), and VB (D).

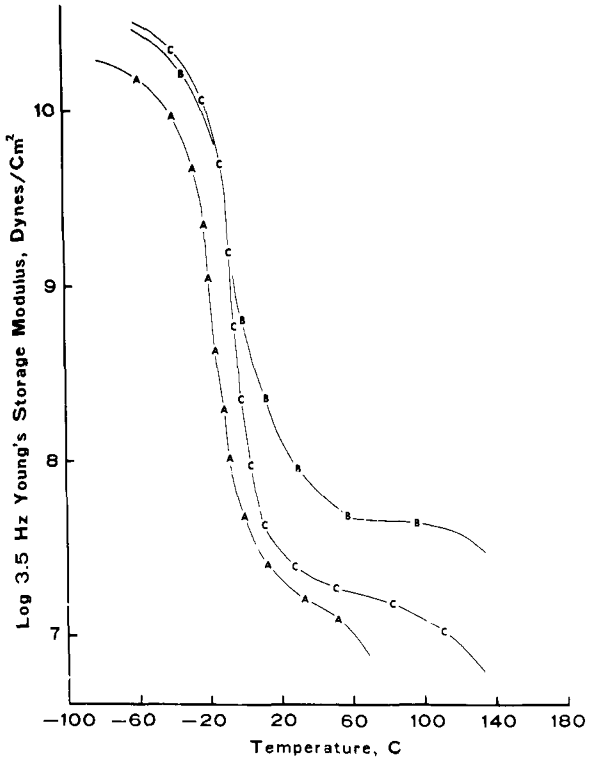


Figure 4. Young's modulus–temperature data for block polymers IB (A), IC (B), and IIC (C).

urethane segments was increased as the glycol molecular weight decreased (Table V). All three of these polymers are aggregated into domains (Figure 5). The urethane T_g's occur at the expected temperatures, but the urea T_g's occur at temperatures well below the expected urea T_g (212 °C). Further, the urea T_g in the block copolymer decreases as the molecular weight of the glycol decreases. The urea T_g in the block copolymer depends not only on the molecular weight of the urethane segment but also on its urethane content.

A series of polymers based on segment II was prepared in which the urea segment size was held constant while the urethane segment size was varied (Table V). Within experimental error, the urethane T_g does not change with segment size. However, only polymer IID shows a clearly defined urea T_g which is considerably lower than the expected urea T_g (Figure 6). The urethane relaxation region increases in breadth as *m* is decreased and the urea content increases. Even at the shortest segment lengths possible, a single, sharp T_g is not observed. This is to be contrasted with data presented previously[13] on water-cured polymers from segment III where a single, sharp T_g was observed for $m = 1.74$ and $n = 0.5$. When *m* is increased to 11 and *n* to 3.23, a system aggregated into domains is obtained with the urethane T_g occurring at the expected temperature and the urea T_g occurring at much lower temperatures than expected.

Discussion

As the theories of Helfand[1] and others[2-12] predict, it is possible to manipulate the block lengths of block copolymers and the χ parameters of the blocks such that the blocks are totally miscible or aggregate into domains of pure segments. Polymers IIA and IIIA based on segments I and V are examples of polymers that are within the limits of detectability of this technique, aggregated into domains of pure segments.

The first detectable departure from aggregation into pure domains appears as a reduction in temperature of the high-temperature T_g. Polymer IA is an example of this behavior. The existence of an interphase with varying composition between the domains of pure material has been proposed theoretically. The nature of the compositional gradient has not been ascertained experimentally but it would appear reasonable to assume a sigmoidal gradient. The interphase, because the compositional gradient exists, would not have a single T_g associated with it, but would have a diffuse transition region extending from the lowest to the highest T_g. In a sigmoidal-type compositional gradient, the volume of material having compositions rich in either component will be greater than the volume of material having nearly equal amounts of each block. This compositional variation in the interphase will cause the low-temperature end of the high-temperature relaxation region to shift to lower temperatures and the high-temperature end of the low-temperature relaxation region to shift to higher temperatures. The amount of the shift will depend upon the interphase volume. Most techniques used to determine T_g define some particular temperature in the transition region as the T_g and this temperature generally is in the lower half of the relaxation region. Therefore, one would expect to find the high-temperature T_g shifting to lower

Table V
Characteristics of Urea-*b*-urethane Copolymers Based on Segments I, II, and III

Polymer No.	Segment No.	Urea w/w %	m	n	Urethane segment mol wt	Urethane T_g, °C
ID	I	5.03	1.38	0.50	4300	−64
IID	II	3.06	6.85	0.50	7500	−28
IIID	III	3.17	11.0	0.50	7750	+6
IVD	II	7.00	3.00	0.50	3290	−21
VD	II	12.2	1.64	0.50	1800	−19
VID	II	22.9	1.00	0.65	1097	−24

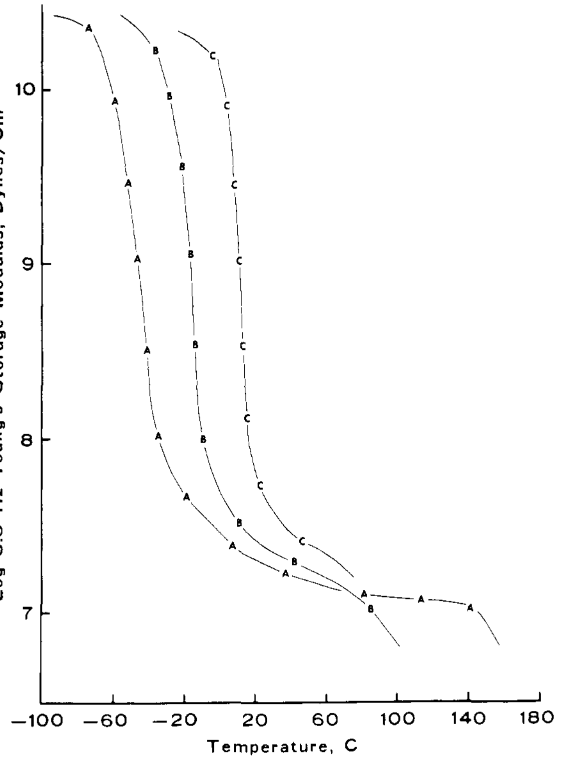


Figure 5. Young's modulus–temperature data for block polymers ID (A), IID (B), and IIID (C).

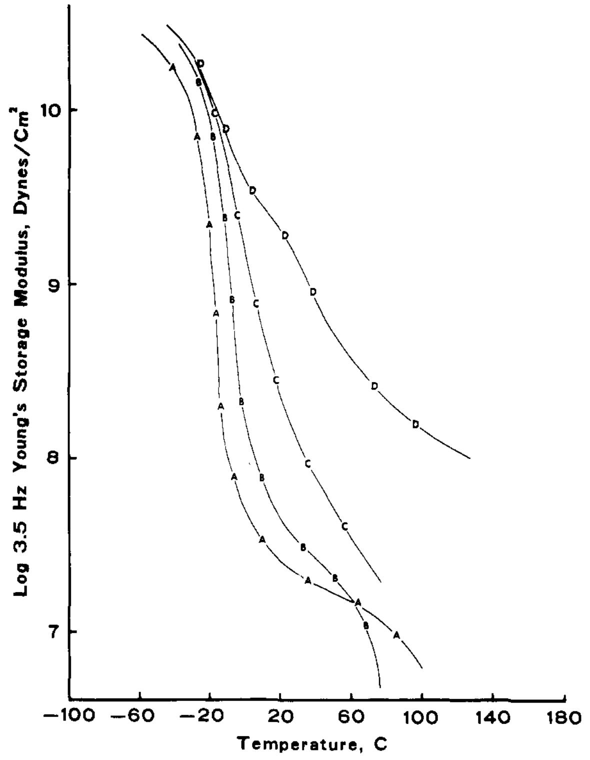


Figure 6. Young's modulus–temperature data for block polymers IID (A), IVD (B), VD (C), and VID (D).

temperatures as the interphase volume increases much sooner than the low-temperature T_g shifting to higher temperatures. The shifts in the low-temperature transition region are occurring in the high-temperature portion of this region, which is generally not used for defining T_g. An example of this type of behavior can be seen by comparing the modulus/temperature profiles of polymers VIB and IIB in Figure 3. The shorter blocks in polymer IIB shift the high-temperature end of the urethane relaxation region to higher temperatures and the low-temperature end of the urea relaxation to lower temperatures. By most techniques of defining T_g, one would conclude that the urethane T_g has not changed but that the urea T_g has decreased, when in fact the changes observed can be equally well explained by changes in concentration gradients in the interphase. These observations would be consistent with the observation of Bares[14] that the decrease in polystyrene T_g increases as the surface-to-volume ratio of the polystyrene domains increases.

In the series of polymers IID, IVD, VD, and VID, the molecular weight of the urethane segments decreases from 7500 to 1100. The urethane T_g throughout this series varies only 9 °C. Even the urethane segment consisting only of urethane-capped polyether (polymer VID) has the same urethane T_g as the higher molecular weight segments. The T_g's of these segments can be calculated from the relationship developed in ref 13, which assumes that the urethane segments can be treated as a copolymer of polyether and urethane. This assumption is further supported by comparing the urethane T_g's of polymers ID, IID, and IIID, which have similar urethane-segment molecular weights but widely different urethane contents in the segments. The urethane T_g is a function of the composition of the urethane segment but not of its molecular weight.

The ether diols and urethane segments have distributions in molecular weight. It is probable that urethane segments containing low molecular weight diols will have a different solubility parameter than those containing high molecular weight diols. Those segments containing low molecular weight diols will be more soluble in the urea domains than the segments containing the high molecular weight diols. The shorter urethane segments will also be most soluble in the urea domains. It is likely, therefore, that within the same block copolymer some urethane segments will dissolve in the urea domains while others will not. Polymers ID, IID, and IIID in Figure 4 all have the same urea molecular weight and similar urethane molecular weights. The urea T_g decreases as the urethane content of the urethane segments increases. Increasing the urethane content of the urethane segments will lead to a reduced χ parameter between the segments and, therefore, greater solubility. These changes cannot be explained by changes in urea molecular weight since this is constant. The copolymer with the highest urea T_g has the lowest urethane-segment molecular weight and the lowest urethane content in the urethane segment.

Modifications of the chemical structure of the urea segments influences the χ parameter between the urea and urethane segments. Polymers IB, IC, and IIC have the same urethane segments but chemically different urea segments. The deviation of the urea relaxation region in the block copolymer from the urea homopolymer relaxation region can be rationalized in terms of differences in χ parameters. The χ parameters were not measured, but from these data it would be surmised that the urea based on 1,6-hexamethylenediamine has the lowest χ parameter and the urea based on bis(3-aminopropyl)methylamine has the highest χ parameter.

Conclusions

It can be concluded that decreasing the urethane content of the urethane segments and increasing the molecular weight of the urethane and/or urea segments increases the aggregation of urea-*b*-urethane copolymers into pure urethane and urea domains. The T_g of the pure urethane domains is a function of the urethane content of the urethane segments and can be calculated from one of the equations used to calculate the T_g of random copolymers or miscible polymers. The T_g of the pure urethane domains is not a function of molecular weight. The distribution of molecular weights in the polyether diols and in the urethane segments may result in solubilization of the short urethane segments or urethane segments containing the low molecular weight diols in the urea domains.

The chemical structure of the urethane and urea segments determines the χ parameter between the segments. Modification of the chemical structure of either the urea or urethane segments will result in changes in the χ parameter and therefore the degree of solubilization of the segments.

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Effects of Pressure on the Equilibrium Properties of Glass-Forming Polymers

Edmund A. DiMarzio,*[1a] Julian H. Gibbs,[1b,c] Paul D. Fleming, III,[1c] and Isaac C. Sanchez[1d,e]

Polymers Division, Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234; Chemistry Department, Brown University, Providence, Rhode Island 02912; and Polymer Science and Engineering and Materials Research Laboratory, University of Massachusetts, Amherst, Massachusetts 01002.

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ABSTRACT: The entropy theory (Gibbs–DiMarzio theory) of the glass transition is extended to incorporate the effects of pressure. The second order transition temperature T_2 increases with increasing pressure but approaches a finite asymptote at very high pressure (>10 kbars). This conclusion is unlike that of an isofree volume theory, according to which the transition temperature should increase without bound. The variation of T_2 with pressure is shown to satisfy the Ehrenfest relations $\mathrm{d}T_2/\mathrm{d}P = TV\Delta\alpha/\Delta C_p = \Delta\beta/\Delta\alpha$, even though the theory appears, at first sight, to be a double order parameter theory of the transition. The point is that the apparent order parameters are not independent. A useful classification of order parameters is presented. The theory also predicts that the volume decreases along the transition line as pressure increases, in contradistinction to an isofree volume theory. This volume decrease is in accord with known experimental data and can also be used to explain the densification of glasses. Finally, it is suggested how the relevant kinetic parameters associated with this theory can be determined experimentally.

I. Introduction

In previous papers[2] Gibbs and DiMarzio characterized the equilibrium properties of amorphous polymers by using a statistical mechanical theory (hereafter referred to as GD theory). In the approximation represented by use of the counting procedures of Flory or Huggins on the Meyer lattice, the polymer liquid was shown to traverse an Ehrenfest[3] second-order phase transition at a temperature T_2. The decrease of the configurational entropy to very small values as the putative transition temperature T_2 is approached from higher temperatures was identified as the underlying cause of the increasing sluggishness of transport properties that is manifest in the intervention of the glass transition at a temperature T_g (where $T_g > T_2$).

Whether this decrease in configurational entropy on (infinitely slow) cooling would be found in an exact (equilibrium) theory to terminate abruptly (Figure 1a) at a true second-order transition (i.e., with a discontinuity in slope) at the temperature T_2, as in the approximate GD theory, or whether it would be found to terminate somewhat more gradually