

Structure–Property Relationships in Thermoplastic Elastomers. IV. Dynamic Mechanical Relaxations in Polydioxolane, Polybutyltrioxocane, and Poly(propylene Oxide) Polyurethanes

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Synopsis

Dynamic mechanical measurements had been made on polyurethanes of a range of hard segment content (HSC) obtained from α,ω -dihydroxy derivatives of polydioxolane, polybutyltrioxocane, and poly(propylene oxide) of 2000–12,000 MW coupled with MDI and TDI with hydroxyethyl phthalamide chain extenders. *N*-methylated chain extender was used to investigate the effect of hydrogen bonding. A broad γ transition was observed between -100 and -115°C attributable to the local motion of methylene sequences with a distribution of relaxations. The β -transition between -55 and -72°C is influenced by the degree of hydration; the α -transition occurs at nearly the same temperatures for all the TPEs, independent of HSC and thermal history. The magnitude of the loss tangent peak is nearly proportional to the soft segment content; the peak corresponds to the glass transition. An α -transition at higher temperature is sensitive to the structure of soft segment, HSC, and thermal history. It is probably associated with the melting of some weakly ordered regions in the soft domain. The hard domain counterpart was observed at the next higher temperature as the ϵ -relaxation. The final large loss of storage modulus occurs at temperatures much below the melting transition.

INTRODUCTION

Segmented urethane block copolymers have found a wide range of applications by virtue of their morphology and viscoelastic properties which can be fine tuned by the proper choice of the structures and amounts of the component diisocyanate, soft segment polymer, and chain extender. To promote the molecular designing of thermoplastic elastomers (TPE), we have undertaken a systematic study of structure property relationships. The X-ray, thermogravimetric, and differential calorimetric results of polyether polyurethanes and polyacetal polyurethanes have already been reported.^{1–3}

The relaxation behavior of thermoplastic elastomers are the determining factors for their mechanical properties which is the reason for the extensive dynamical mechanical measurements on them.^{4–14} Relaxations of pendant groups and of main chain segments as well as low temperature crystal–crystal transitions have been reported.⁵ Two phase structures¹⁰ and hydrogen bonding effects^{11,12} had been observed. The glass transition temperature T_g of the soft segment is said to be independent of the hard segment content (HSC).¹³ In the case of polyether polyester TPEs the compatibility of segments is found to depend on the segmental lengths.¹⁴

The central purpose of this work is to measure the dynamic mechanical relaxations of polyurethanes containing polydioxolane (PDO), polybutyltrioxocane (PBOT), and poly(propylene oxide) (PPO), soft segments. By using symmetric and unsymmetric diisocyanates, methylation of amide group in the chain extender, and variation of HSC, we were able to deduce the probable mechanisms of six types of relaxation processes.

EXPERIMENTAL

Materials

The soft segments are the α,ω -dihydroxy terminated polymers, PPO MW 2000, was obtained from Polysciences. Poly(2-butyl-1,3,6-trioxocane) was obtained by the condensation polymerization of valeraldehyde and diethylene glycol³ to \bar{M}_n of 1850 ± 50 . Poly(1,3-dioxolane) was obtained by cationic polymerization of 4-methyl-1,3-dioxolane with an \bar{M}_n of 12,000. The \bar{M}_n values were determined by VPO and GPC.

The coupling agents used are 4,4'-diphenyl methane diisocyanate (MDI) from Mobay Chemicals and 2,4-toluene diisocyanate (TDI) from Aldrich Chemicals. They were vacuum-distilled immediately before use.

The chain extenders were *N,N'*-bis(2-hydroxy ethyl) isophthalamide (BI), *N,N'*-bis(2-hydroxyethyl)-*N,N'*-dimethyl isophthalamide [BI(M)], and *N,N'*-bis(2-hydroxy ethyl)terephthalamide (BT). BI and BT were synthesized by aminolysis of the corresponding phthalate esters using 2 aminoethanol. BI(M) was synthesized by the reaction of BI with methyl bromide in pyridine.

Synthesis

Segmented block copolymers were synthesized by a previously described two-stage process.^{1,3} The copolymers were designated by the abbreviated names of the constituents and by three numbers in parenthesis denoting their molar ratios. For instance, PBOT-TDI-BT (1-3-2) corresponds to the copolymers prepared from 1 mol PBOT, 3 mol TDI, and 2 mol BT, etc. The schematic structures are shown in Figure 1. The intrinsic viscosities, MWs, HSC, and DSC of the copolymers have been given earlier.^{1,3} The HSC contents of the copolymers are summarized in Table I to facilitate discussion. Film samples for dynamic mechanical measurements were cast from DMF solutions of the TPE onto a glass surface by slow evaporation of the solvent at 40–45°C. The TPE films were vacuum-dried at ambient temperature for four days.

In some studies the TPE film was annealed between Teflon plates in vacuum oven at 110°C for 2 h followed by very slow cooling to room temperature. These samples were also quenched by quick transfer from the oven into a dry ice box.

Dynamic Mechanical Properties

A Polymer Laboratory DMTA instrument was used to make dynamic mechanical measurements from -140 to 200°C at a heating rate between 1 and 1.5°C min⁻¹ under dry nitrogen at 0.1, 1, and 10 Hz frequencies.

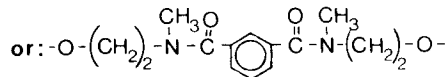
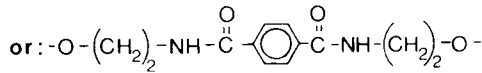
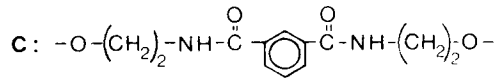
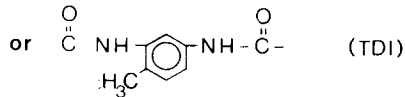
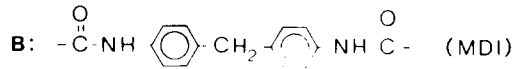
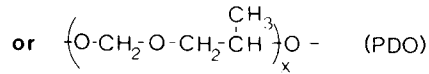
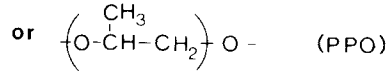
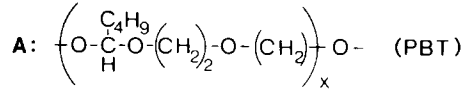
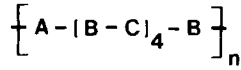


Fig. 1. Schematic structures for polyurethane TPEs.

TABLE I
Hard Segment Contents of TPE

Sample	HSC (%)
PBOT-M-BI (1-2-1)	28
PBOT-M-BI (1-3-2)	40
PBOT-M-BI (1-4-3)	48
PBOT-M-BI (1-6-5)	59
PBOT-T-BT (1-2-1)	25
PBOT-T-BT (1-3-2)	36
PBOT-T-BT (1-4-3)	45
PPO-M-BI (1-2-1)	27
PPO-M-BI(M) (2-5-3)	34
PPO-M-BI(M) (1-4-3)	48
PDO-M-BI (1-5-4)	15
PDO-M-BI (1-7-6)	20
PDO-M-BI (1-9-8)	25
PDO-M-BI (1-11-10)	35

RESULTS

Polybutyltrioxocane Polyurethanes (PBOT-PU)

PBOT-PU copolymers of 28–59% HSC were obtained with MDI and BI. Their dynamic mechanical behaviors are shown in Figure 2. In the order of increasing temperature for the loss tangent peaks the lowest temperature peak is designated the γ relaxations. It is a very weak relaxation, the transition temperature (T_γ) of which is at $-112 \pm 2^\circ\text{C}$. The intensity of the loss tangent peak decreases monotonically with the increase of HSC without discernible shift of T_γ .

A weak β -relaxation was observed for the PBOT-M-BI (1-2-1) copolymer at $T_\beta \sim -64^\circ\text{C}$. Copolymers with higher HSC have no distinct loss peak, which vanishes for the (1-6-5) sample with the highest HSC. Furthermore, samples of PBOT-M-BI (1-4-3) which have been either annealed or quenched exhibit no loss.

Between 0 and -50°C there are significant relaxations which diminished markedly when HSC increases from 48 to 59%. The α -relaxations can be seen at T_α of -30 and -40°C in the (1-2-1) and (1-6-5) copolymers, respectively.

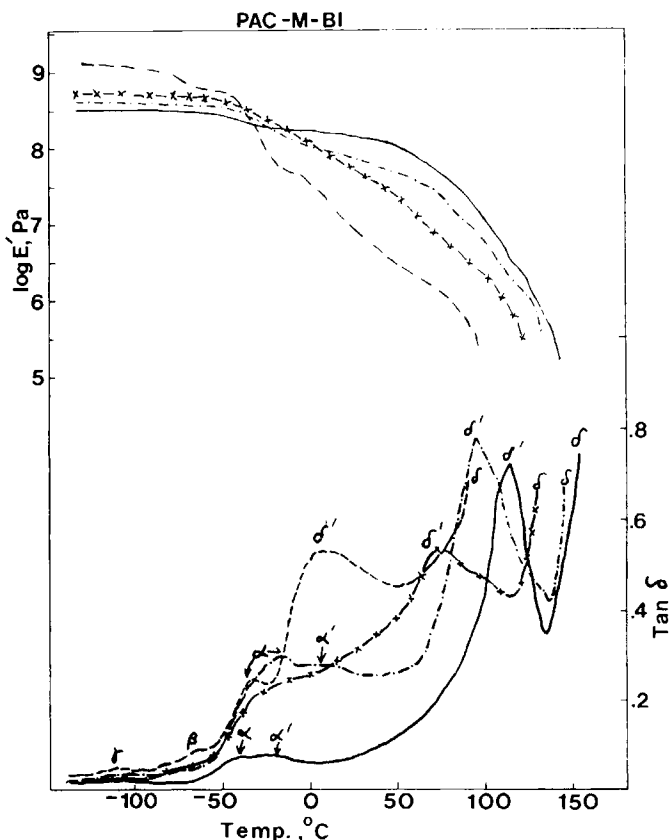


Fig. 2. Dynamic mechanical properties of PBOT-M-BI copolymers at 1 Hz: (---) (1-2-1); (-×-) (1-3-2); (···) (1-4-3); (—) (1-6-5).

There is no discernible corresponding peaks in samples with intermediate HSC, but the magnitude of loss seems to decrease with increasing HSC. It was observed in some polyacetal materials but not in the PPO samples that there is an additional process denoted as α' . The $T_{\alpha'}$ are found at -15 and -20°C , respectively, in the (1-3-2) and (1-6-5) materials.

An intense ϵ loss peak was seen in all the samples whose transition temperature (T_{ϵ}) increases markedly with increasing HSC. The values are 15, 58, 94, and 113°C for the (1-2-1), (1-3-2), (1-4-3), and (1-6-5) samples, respectively. In the same order, the loss tangent values exceeded 0.7 at 83, 130, 147, and 162°C . This is associated with sharp decreases in moduli which will be referred to as the δ process, though an actual loss tangent peak for it is seldomly observed.

The dynamic properties of the PBOT-PU's chain-extended with TDI and BI, shown in Figure 3, are similar to those above. The γ - and β -relaxations are discernible for the (1-2-1) copolymer at -115 and -80°C , respectively, but not for materials of other compositions. The higher HSC copolymers (1-3-2) and (1-4-3) showed T_{α} at -36 and -39°C , respectively, with T_{ϵ} at 62 and 95°C . However, the two relaxations merged as a single peak at -9°C in the

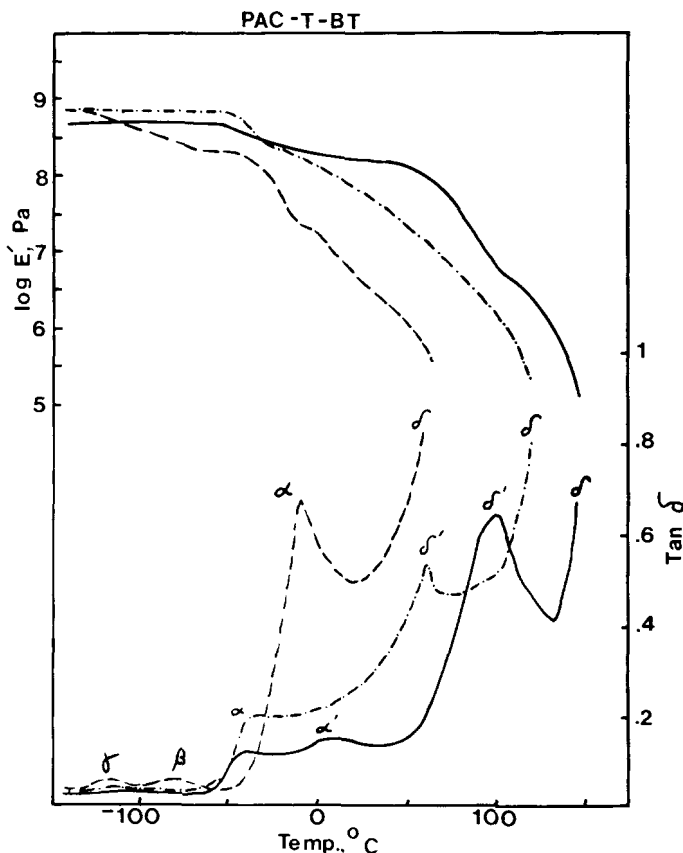


Fig. 3. Dynamic mechanical properties of PBOT-T-BT copolymers at 1 Hz: (---) (1-2-1); (-·-) (1-3-2); (—) (1-4-3).

case of the (1-2-1) copolymer. Onset of the δ -relaxation appeared at 60, 123, and 157°C for the (1-2-1), (1-3-2), and (1-4-3) samples, respectively.

Poly(propylene Oxide) Polyurethanes (PPO-PU)

The effect of annealing and quenching as well as methylation of the amide group were investigated for the PPO-PU copolymers. Figure 4 contains the dynamic mechanical data for the PPO-M-BI(M) (2-5-3) material with HSC of 34%. Relaxations for the γ , β , α , and ϵ processes are resolved at -105, -61, -25, and 25°C, respectively, with onset of δ -transition at 85°C. In the (1-4-3) copolymer the reduced magnitudes of the γ - and β -transitions are consonant with the increase of HSC as noted above in the PBOT-PU copolymers. Unlike the latter systems, the β processes were virtually eliminated by annealing, this did not happen for the present case. The difference may be attributed to the effect of *N*-methylation of the amide group. In support of this attribution, the annealed TPE of PPO-M-BI (1-2-1) has no resolved β loss peak (Fig. 5). The α loss peak occurs at the same temperature for the annealed and quenched TPEs. On the other hand,

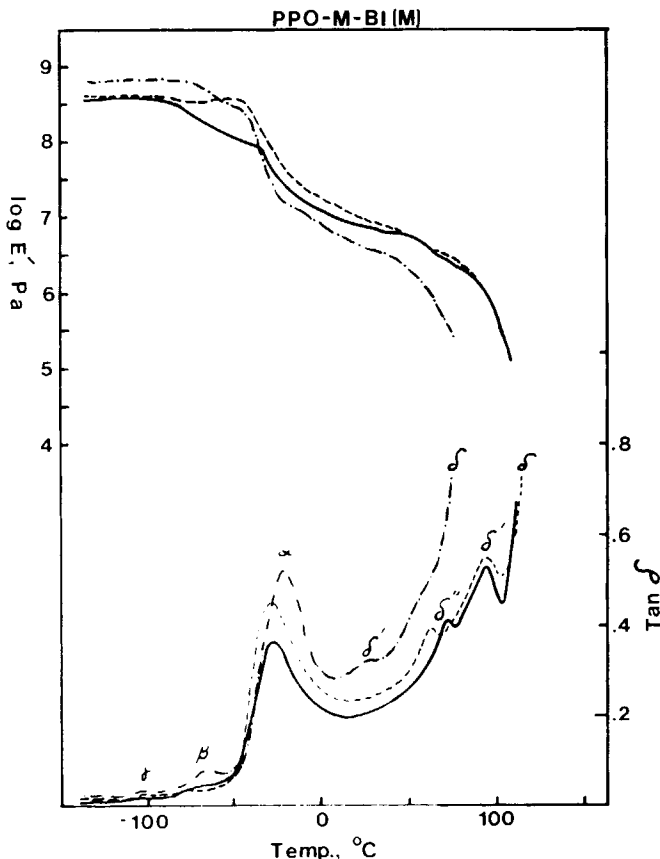


Fig. 4. Dynamic mechanical properties of PPO-M-BI(M) copolymers at 1 Hz: (---) (1-4-3) quenched sample; (—) (1-4-3) annealed sample; (-·-) (2-5-3).

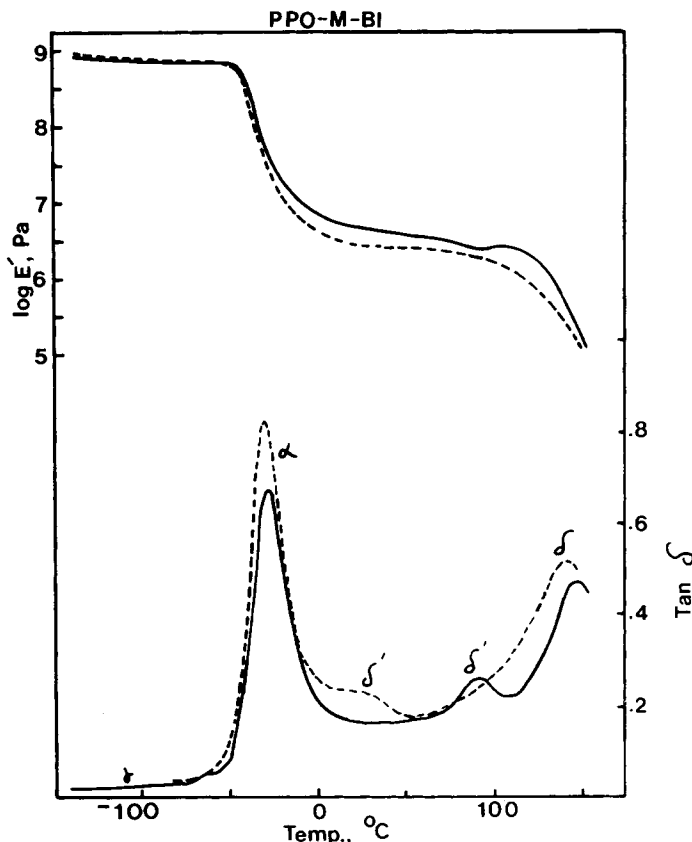


Fig. 5. Effect of thermal history on dynamic mechanical properties of PPO-M-BI (1-2-1) copolymer: (---) quenched; (—) annealed.

the ϵ -transition appears to be sensitive to both annealing/quenching and to methyl substitution on urethane. For the BI (1-2-1) copolymer the annealed sample has T_{ϵ} at 92°C but is lowered to 28°C when the sample was quenched. The latter is close to the T_{ϵ} for PBOT-PU copolymers having comparable HSC. Therefore, annealing greatly increases the temperature for the ϵ -transition. The T_{ϵ} for PPO-MOBI(M) (2-5-3) is only 25°C whereas it is about 60°C for the PBOT-PU copolymers with comparable HSC. It appears that methylation of the amide nitrogen tends to lower the T_{ϵ} . Annealed samples of PPO-M-BI(M) (1-4-3) showed two peaks for ϵ -relaxations at 70 and 92°C; quenching of the annealed film slightly lowered the former to 60°C but did not affect the latter.

Polydioxolane Polyurethane (PDO-PU)

The soft segment in PDO-PU has MW six times greater than PBOT and PPO, so that the PDO-PU copolymers have very low HSC of between 15 and 35%. This structural differences are manifest in several dynamic mechanical relaxations (Fig. 6). The α -transitions are sharp with T_{α} found between -32 and -35°C for PDO-PU of all compositions, but their intensities decrease

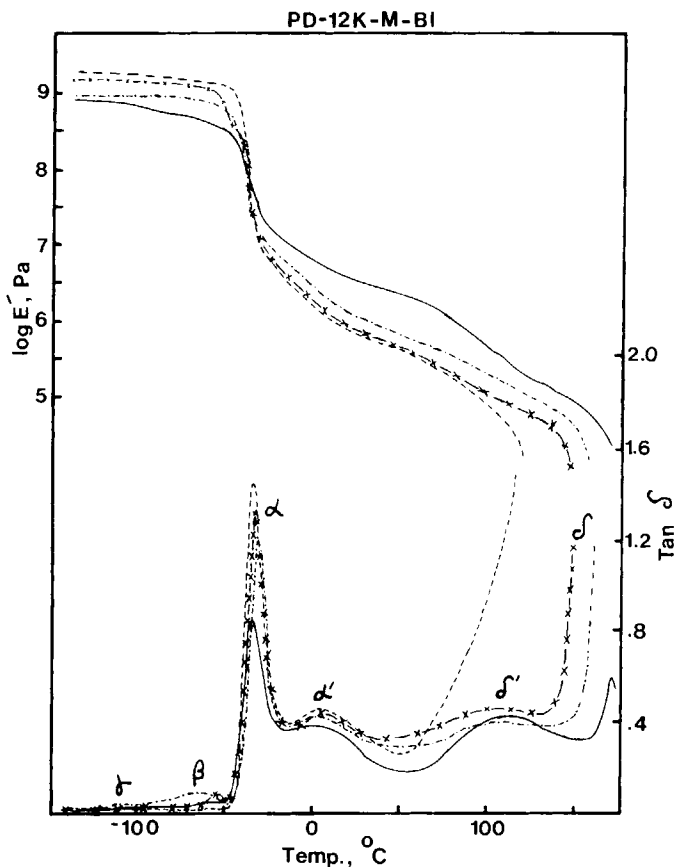


Fig. 6. Dynamic mechanical properties of PDO-M-BI (PDO MW = 12,000) copolymers at 1 Hz: (---) (1-5-4); (-x-) (1-7-6); (···) (1-9-8); (—) (1-11-10).

with the increase of HSC. The α' transition is now well resolved at temperatures between 2 and 5°C, the amplitude of which is slightly sensitive to HSC. The onset of the δ -relaxations are observed at 121, 147, 157, and 170°C for (1-5-4), (1-7-6), (1-9-8), and (1-11-10) copolymers, respectively. In the first material this process is merged with and obscures the ϵ process. Otherwise, the T_c was observed between 105 and 110°C with comparable intensities for the other copolymers. The β - and γ -transitions are quite similar to those of the other TPEs of PBOT and PPO.

Activation Energies

The dynamic mechanical properties were measured at several frequencies. A plot of frequency vs. the reciprocal of absolute temperature for the loss tangent peak gives the apparent activation energy for the particular relaxation process,

$$\Delta H^* = 2.3Rd(\log f)/d(1/T) \quad (1)$$

The values of ΔH^* thus obtained are given in Table II.

TABLE II
Apparent Activation Energies

Copolymer	Apparent activation energy (kcal mol ⁻¹)			
	γ	α	α'	ϵ
PBOT-M-BI (1-2-1)	10	60		67
PBOT-T-BT (1-3-2)	18	64		98
PPO-M-BI (1-2-1)		83		
PPO-M-BI(M) (2-5-3)	20	53		
PDO-M-BI (1-7-6)	14	76	28	

DISCUSSION OF RESULTS

The existence of a multitude of relaxation processes in block copolymers has been attributed to mixing of soft and hard segments in the domain boundaries referred to as domain-boundary mixing and mixing-in-domains of hard and soft segments.¹⁵ In fact, Kraus and Rollman¹⁶ suggested that even the styrene-diene block copolymers do not contain compositionally pure phases of polystyrene and polybutadiene or polyisoprene. Similarly, polyurethanes comprised of PTMD, TDI and butanediol are said^{4,17} not to contain pure hard and soft phases but are consisted mainly of interlayer materials. These views will be considered in the discussions of the present results.

Gamma-Relaxation

A broad γ -relaxation peak was present in all the TPEs of this work with T_γ in the region of -100 – -115°C ; their magnitude decreases with increasing HSC. The apparent activation energies lie between 10 and 20 kcal mol⁻¹; the values are greater for the TPEs with the higher HSC. This relaxation has been assigned^{5,10,18} to the local motion of the methylene sequences. The motion of pendant methyl groups should occur at much lower temperatures. Kajiyama and MacKnight⁵ were able to detect two γ -relaxation peaks; they attributed the second one to the motion of methylene group associated with the ester group. Though only one γ -relaxation was seen here, the breadth of the transition is not inconsistent with the distribution of relaxations.

Beta-Relaxations

A β -relaxation peak was found between -55 and -72°C for the present TPEs. This transition has been attributed to the motion of water hydrogen bonded to the urethane group.^{10,19-21} With the BI and BT chain extenders there are also their amide groups to contribute toward the process. This assignment is supported by the following observations. The β peak often disappears upon annealing of the TPEs; the intensity of it was increased after a copolymer film was soaked in water for a day at room temperature. A new β peak was observed at the vicinity of -75°C in the water-soaked sample of PBOT-T-BT (1-4-3) and PPO-M-BI (1-2-1). A similar treatment of PDO-M-BI (1-11-10) shifted T_β from -62 to -71°C , and the magnitude of the loss peak diminished upon annealing. A weak β -relaxation was still

present in annealed sample of PPO-M-BI(M) (1-4-3), where the amide nitrogen is methylated, suggesting that the interactions are stronger with the urethane group than with the amide group.

Alpha-Relaxations

The α -relaxation may be safely attributed to the motion of the soft segments. It is best resolved in the PDO-PU's in which case the value of $\tan \delta$ is nearly proportional to the soft segment content. Furthermore, the T_α is about the same for all the TPEs here. The apparent activation energies for the transition of 53 to 83 kcal mol⁻¹ are typical for major glass transition as are the large decrease of storage modulus associated with it.¹¹ This transition is not affected by thermal history in the present TPE's.

The T_g of PU TPEs had been previously measured by DSC. It is -48--52°C for the PPO-M-BI copolymers as compared to -30--90°C for their T_α . The T_g^1 and T_α values for PPO-T-BT are -39--43°C and -36--39°C, respectively. All the PBOT polyurethanes have DSC determined T_g values between -48 and -58°C.³ This is compared to -32--35°C found for T_α here. Therefore, if T_α is to be identified with T_g , then the T_g occurs at ca.

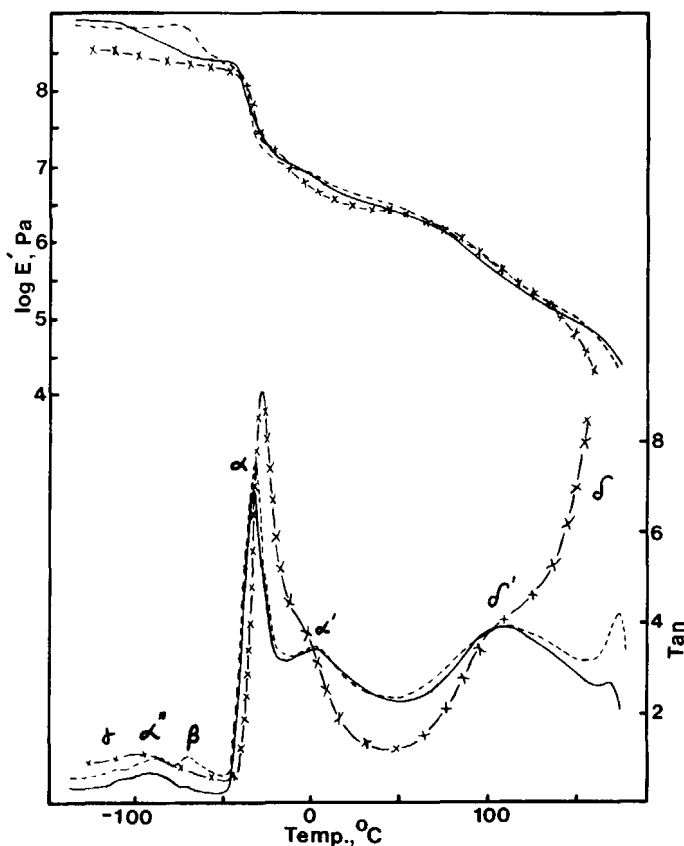


Fig. 7. Dynamic mechanical properties of PDO-M-BI copolymer at 1 Hz: (---) (1-11-10) PDO MW 12,000 quenched; (—) same polymer annealed; (-·-) (1-11-10) PDO MW 5000.

10–20°C higher in dynamic mechanical measurements than by DSC. This may be attributed to the differences in the two methods. The heating rate is 20 min⁻¹ by DSC whereas it is 1–1.5°C min⁻¹ by DMTA; the sample is under load in the latter but not in the former. Both factors should contribute toward the higher T_g by DMTA as has been amply documented.

It should be mentioned that the T_g of the soft segments in TPE is considerably higher than that of the homopolymer. For instance, PBOT has T_g of $-75.5 \pm 1.5^\circ\text{C}$, which is much lower than the T_g of -48 – 58°C for the polyurethanes made from it.

Different mechanisms have been proposed for the α' -relaxation^{4,10}: melting of small imperfect crystallites, or an interaction between the amorphous and crystalline portions of soft segment, or mixing of small amounts of hard segment in the soft domain freeing the hydrogen bonding restricted motion.

The soft segment is certainly involved in the α' -relaxation because it is most prominent in the PDO–PU copolymers which have large amounts of long soft segments. The $\tan \delta$ peaks in these substances have peak heights insensitive to HSC. The structure of the soft segment probably also influences this transition because it was not present in the PPO–PU copolymers. The effect of soft

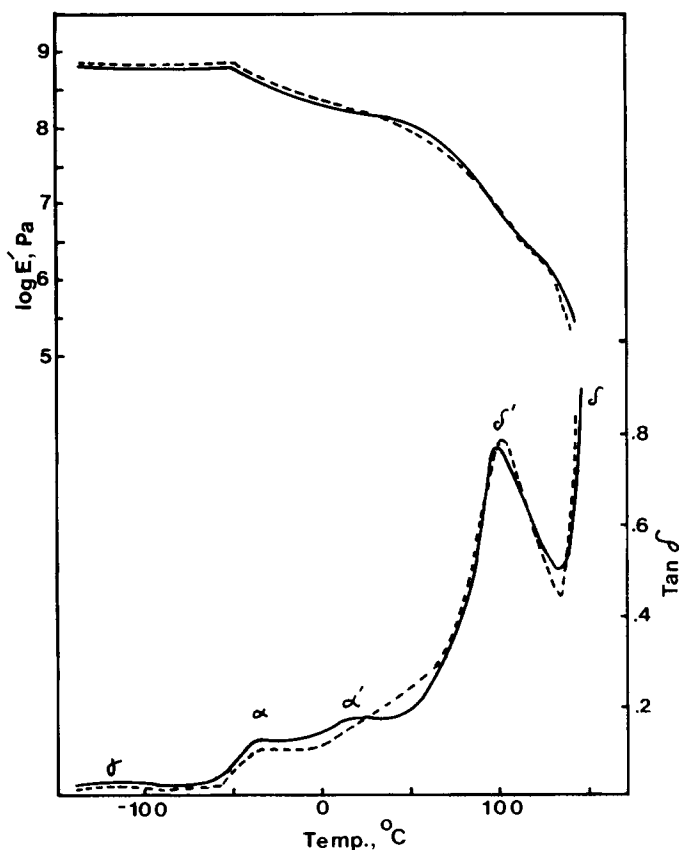


Fig. 8. Effect of thermal history on dynamic mechanical properties of PBOT–M–BI (1–4–3) at 1 Hz: (---) quenched; (—) annealed.

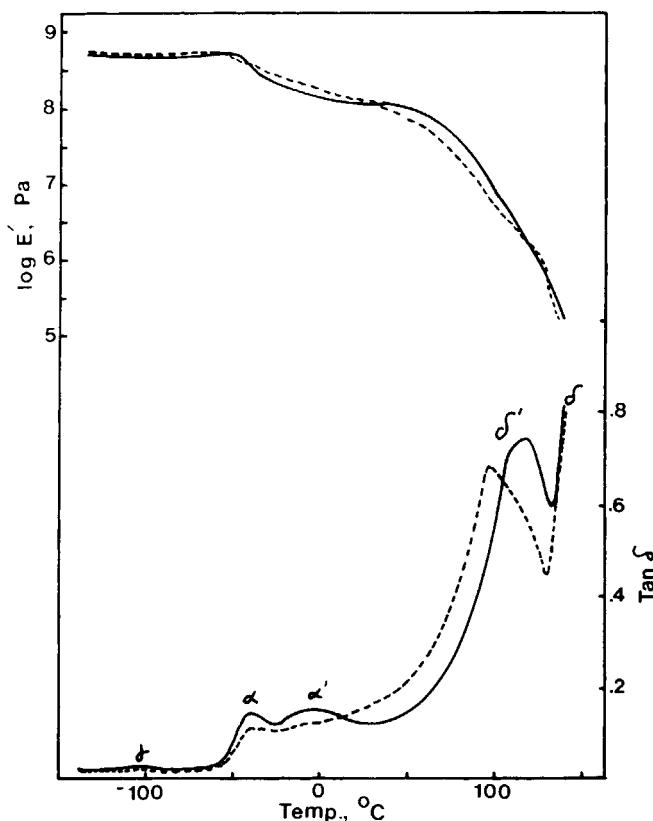


Fig. 9. Effect of thermal history on dynamic mechanical properties of PBOT-T-BI (1-4-3) at 1 Hz: (---) quenched; (—) annealed.

segment length was seen in PDO-PU material prepared with 5000 MW PDO which appears as only a shoulder on the high temperature side of its α loss peak (Fig. 7). The overall area of loss tangent in this material is much smaller than that of the corresponding copolymer containing 12,000 MW PDO.

Figures 8 and 9 showed that annealed films of PBOT-M-BI (1-4-3) and PBOT-T-BI (1-4-3) both have clearly resolved α' loss peak whereas the quenched samples do not. This observation combined with those above suggests the origin for α' -relaxation to be melting of some weakly ordered region in the soft domain such as those portions of soft segments close to the hard segment. It seems that this interpretation encompasses the three proposed mechanisms since they are all of imprecise nature. The absence of an α' -relaxation in polyurethanes chain extended with *N*-methyl derivative of BI suggests that hydrogen bonding may be involved in the weakly ordered structures.

According to the prevailing view, there is no pure soft or hard phases in polyurethanes, and α -relaxation involves disordered soft segments admixed with hard segment.⁴ Then, if there is any relaxation of predominantly soft segments, it should occur at temperatures below T_g . This may be the α'' peak at ca. -90°C seen in the quenched sample of PDO-M-BI (1-11-10) (Fig. 7)

with a corresponding noticeable loss of storage modulus. In agreement with the prevailing view, this loss is much smaller than the decrease of modulus during the α -relaxation.

Hard Segment Relaxations

The ϵ -relaxation is certainly associated with the hard segments because its transition temperature increases markedly with the increase of HSC for the PBOT and PPO systems. The T_c is quite sensitive to thermal history and is affected by methylation of the amide nitrogen as well. This suggests an influence of ordering assisted by hydrogen bonding. However, if the soft segment is excessively long as in the PDO system, neither the magnitude nor the temperature for the ϵ -relaxation is dependent on HSC. A probable origin for this transition is the melting of the weakly ordered region in the hard domain such as those portions of hard segments close to the soft segment. In other words, the ϵ and α' relaxations may be the weakly ordered counterparts of the hard and soft mixing-in-domains, respectively.

At temperatures above the ϵ -transition, the loss tangent increases rapidly accompanied by sharp decreases in storage modulus. This has been referred to as the δ -relaxation.⁴ Senich and MacKnight⁴ have shown good correlation between the T_δ and the hard segment length according to the well-known Flory equation²² relating T_m of finite chain polymer with n repeat units with that for an infinite chain polymer T_m° ,

$$1/T_m - 1/T_m^\circ = 2R/n \Delta H_n \quad (2)$$

where ΔH_n is heat of fusion per repeat unit. We also found good correlation for the present TPEs. Nevertheless, it probably is unfounded to associate T_δ with T_m for several reasons. The application of eq. (2) to relaxation temperatures for very short hard segments is without thermodynamic basis. Secondly, an actual loss peak was seldomly observed for the δ process. Finally, T_m has been measured with DSC¹ in PPO-M-BI and PPO-T-BT to lie between 155 and 168°C which are much higher than the DMTA determined T_δ except for the copolymers with very high HSC. Furthermore, DSC showed an additional T_b^1 between 128 and 134°C. This transition has been variously attributed to the dissociation of hydrogen bonds between the urethane secondary amine and the ether oxygen atoms,²³ or to an interdomain phenomenon of annealing-induced ordering.²⁴ According to DMTA the T_δ can span the range of 60–170°C depending upon the particular copolymer which covers the ranges for T_b and T_m by DSC.

It appears that the DMTA observed δ process may be either the dissociation of hydrogen bonds in the hard domain or its melting both could cause large decrease in storage modulus.

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