

## Thermomechanical Studies of Semicrystalline Polyether-Ester Copolymers. Effect of Thermal, Mechanical, and Solvent Treatment

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### Synopsis

The thermomechanical spectra of a series of elastoplastic polyether-ester copolymers were determined at 110 Hz and between  $-120^{\circ}\text{C}$  and  $200^{\circ}\text{C}$  at five compositions. Emphasis was given to samples containing an increasing amount of poly(tetramethylene terephthalate) constituting the hard segment in these copolymers. The effects of thermal history, uniaxial drawing, and solvent absorption were examined. Specimens cut from injection-molded slabs were also included in the study. Thermal and mechanical treatment had an important effect on the dynamic mechanical properties. The relaxation spectra do not indicate distinct phase separation, but rather a structure of closely interacting hard and soft segments. The molecular origin of the various relaxations was characterized, and it is shown that as the amount of the hard component increases, features in the relaxation spectrum characteristic of poly(tetramethylene terephthalate) become prominent.

### INTRODUCTION

Current interest in the synthesis and characterization of block copolymers<sup>1-3</sup> led to the discovery of a new class of polyether-ester copolymers exhibiting elastoplastic behavior.<sup>4,5</sup> These copolymers consisting of soft segments of polyethers and hard crystalline segments of polyesters were originally classified as block copolymers,<sup>6,7</sup> the implication being that there is a phase separation into crystalline and soft domains. The hard polyester segments provide thermolabile physical crosslinks for the latter, in analogy to other classes of block copolymers, such as the polystyrene-polybutadiene and the polyurethane thermoplastic elastomers. In the former, the physical crosslinks are provided by the glassy domains separated into the rubbery matrix because of thermodynamic incompatibility.<sup>8,9</sup> In the case of the polyurethanes, it was proposed that the hard segments form a continuous crystalline superstructure reinforcing an occluded soft phase.<sup>10,11</sup>

Recently, it was pointed out<sup>12</sup> that a "block" character could not be attributed to these elastoplastics containing a medium to large percentage of soft polyether segments. The experimental results indicated a structure characteristic of semicrystalline copolymers.

The present study covers the dynamic mechanical properties of these semicrystalline copolymers with a higher content of hard segments of poly(tetramethylene terephthalate). During the course of this investigation, a dynamic mechanical study on materials similar to some of ours was published.<sup>7</sup> However,



strong blade was used. Drawing of specimens was performed by a hand-operated jig at an approximate rate of 20 cm/min.

Dynamic mechanical data, loss tangent,  $\tan \delta$ , and complex modulus  $|E^*|$  were obtained between  $-120^\circ$  and  $200^\circ\text{C}$  at 110 Hz using a direct-reading viscoelastometer (Rheovibron, Model DDV-II-C, Toyo-Baldwin, Co. Ltd., Tokyo, Japan). Some measurements were also performed at lower frequencies (3.5 and 11 Hz) to determine the apparent activation energies  $\Delta H\alpha$  for the various relaxations. A dry stream of precooled Ar prevented condensation within the chamber. Measurements were taken at approximately  $3^\circ\text{C}$  intervals except when near a peak, where a smaller temperature interval was justified. In calculating the quantity  $|E^*|$ , the small deformation of the instrument clamps was taken into account.

## RESULTS AND DISCUSSION

### Effects of Composition and Thermal Treatment

The main quantities to be discussed are the loss tangent  $\tan \delta$ , loss modulus  $E''$ , storage modulus  $E'$ , and their temperature dependence. The results are summarized in Figures 1-3 and Table II. Sample 5, having a different chemical structure, was included to examine the randomizing effect of introducing the nonsymmetrical isophthalate units along the main chain. The films were elastic

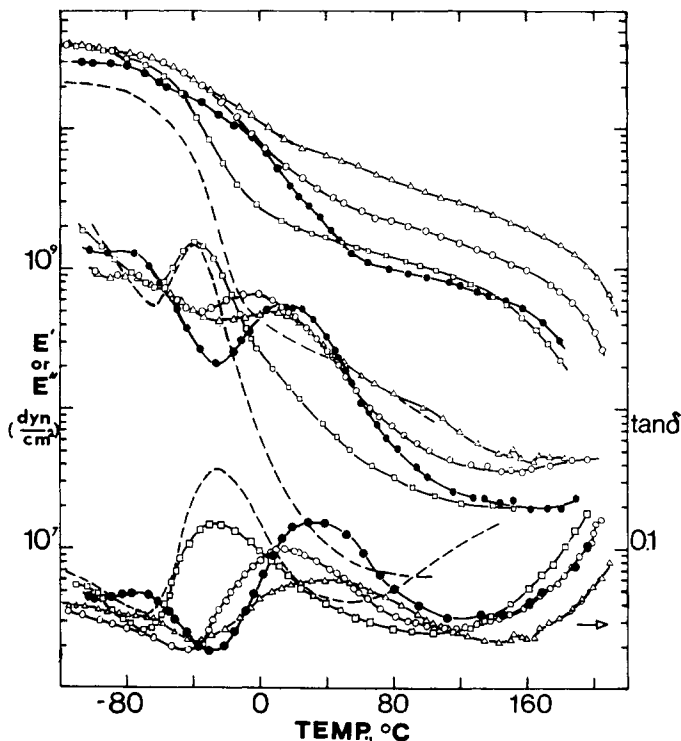


Fig. 1. Thermomechanical spectra of annealed samples at 110 Hz. Effect of composition and thermal treatment: ( $\Delta$ ) sample 1; ( $\circ$ ) sample 3; ( $\square$ ) sample 4; (—) sample 5; ( $\bullet$ ) sample 3 quenched.

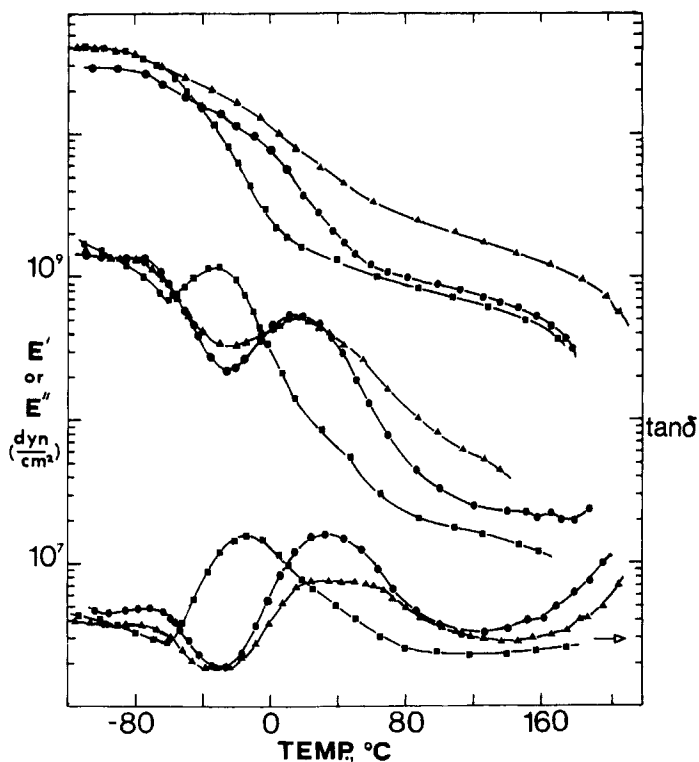


Fig. 2. Thermomechanical spectra of quenched samples at 110 Hz. Effect of composition: ( $\blacktriangle$ ) sample 1; ( $\bullet$ ) sample 3; ( $\blacksquare$ ) sample 4.

at room temperature, and the main relaxation is quite high compared to the other samples. The data on sample 2 are not included in the graphs for reasons of clarity. The results were in all cases intermediate of those of samples 1 and 3.

The mechanical spectra, especially for quenched samples, show three relaxations: the  $\beta$  peak (main relaxation); a much weaker peak in the vicinity of  $-75^{\circ}\text{C}$  ( $\gamma$ ); and, though we could not delineate it accurately, an additional peak ( $\delta$ ) near  $-120^{\circ}\text{C}$ . Quenching increases both the  $\beta$  and  $\gamma$  peaks. Annealed sample 1 shows an additional relaxation at  $152^{\circ}\text{C}$  ( $\alpha$  peak). Prolonged annealing (see below) shifts it to higher temperatures. In analogy to semicrystalline homopolymers, it may arise from reorganization processes in the hard-segment lamellae before the onset of flow.

The main relaxations of poly(tetramethylene oxide) homopolymer,  $-(\text{CH}_2)_4-\text{O}]_n$ , forming the basic constituent of the soft segment, are reported<sup>14</sup> at  $-55^{\circ}\text{C}$  and (a secondary) at  $-110^{\circ}\text{C}$ , at 100 Hz. As to their origin, the latter was attributed to the motion of consecutive  $-\text{CH}_2-$  sequences or, on the basis of dielectric studies, to the motion of the ether group.<sup>15</sup> The main peak was attributed to the segmental motion in the amorphous phase. For the poly(tetramethylene terephthalate) (P4GT), constituting the hard segments in our samples, relaxations were reported<sup>16</sup> at  $-60^{\circ}\text{C}$  (secondary) at 412 Hz and  $80^{\circ}\text{C}$  (primary) at 215 Hz. At the frequency used in this work, both peaks should appear at lower temperatures. Illers and Breuer<sup>17</sup> detected (at 1 Hz) a  $\beta$  relax-

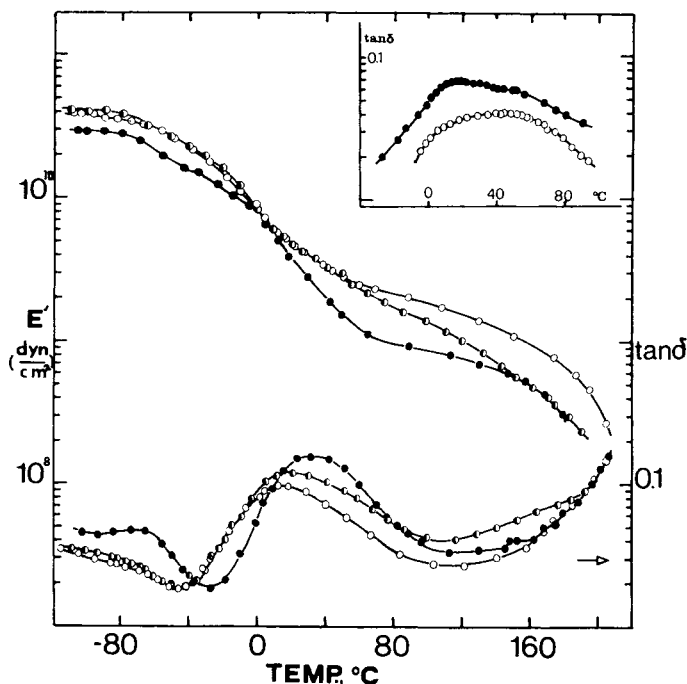


Fig. 3. Effect of thermal cycling on quenched sample 3 (●), after one run (◐), and annealed sample (○). Inset: asymmetry of main relaxation at 3.5 Hz; sample 1 annealed (○), quenched (●).

ation (primary) at 44°C and a composite  $\gamma$  peak in the range of  $-90^{\circ}$  to  $-110^{\circ}\text{C}$ . (Note: We have renamed the  $\alpha$  and  $\beta$  peaks in their publication<sup>17</sup> as  $\beta$  and  $\gamma$ , respectively, since it is more appropriate to designate the primary relaxation as  $\beta$ , especially, in semicrystalline polymers.) The  $\beta$  peak was attributed to the onset of segmental motion within the amorphous phase. For the  $\gamma$  relaxation,

a preferred interpretation would involve movement of the  $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$  groups associated with the trans (near  $-90^{\circ}\text{C}$ ) and gauche (near  $-110^{\circ}\text{C}$ ) conformation of the 1,4-butanediol unit,<sup>17,18</sup> in analogy to poly(ethylene terephthalate) (PET).

Examination of our data suggests that the  $\gamma$  peak can be attributed to the amorphous regions, and contributions are possible from the local mode motions of the 4GT component ( $\gamma$  peak). The main peak of the soft component does not show at  $-55^{\circ}\text{C}$  since it can be shifted to higher temperatures by association with the hard segments. Thus, the gradual increase of the  $\beta$ -relaxation temperature between  $-27^{\circ}\text{C}$  and  $42^{\circ}\text{C}$  (see Table II) supports the view that, in this composition range as well, these polyether-esters cannot be considered as block copolymers, but rather as semicrystalline copolymers whose  $T_g$  shifts with varying composition. As the hard-segment content (and crystallinity) increases, considerable broadening of the  $\beta$  peak is also observed. This indicates different states of order within the amorphous region. An asymmetry of the  $\beta$  peak is also observed. Measurements on quenched and annealed sample 1 at 3.5 Hz reveal that the  $\beta$  relaxation is composite (see insert of Fig. 3). It is suggested that

TABLE II  
 Temperatures of Relaxation Maxima and Their Dependence on Composition and Specimen Preparation, at 110Hz

Sample No.	$\gamma$ Relaxation (temp., °C) <sup>a</sup>			$\beta$ Relaxation (temp., °C)			$\alpha$ Relaxation (temp., °C)		
	tan $\delta$	$E''$	tan $\delta$ $E''$	tan $\delta$	$E''$	tan $\delta$ $E''$	tan $\delta$	$E''$	tan $\delta$ $E''$
	Hot Pressed								
	Annealed	Quenched		Annealed	Quenched		Annealed	Quenched	
1	w.r.	-76	w.r.	42	9	48	16	152	152
2	w.r.	w.r.		28	5	33	11	—	—
3	w.r.	-74	-91	17	3	31	18	—	—
4	w.r.	—		-27	-37	-14	-32	—	—
5	—	not studied		-24	-38	not studied		—	—
	Injection Molded								
	Unstretched	( $\lambda$ ) <sup>b</sup>	Stretched	Unstretched	Stretched	Unstretched	Stretched	Stretched (annealed)	
1	-70	w.r. (4.5)	-63	46	19	61	47	165	(165)
2	w.r.	(7.0)	-60	30	13	51	38	—	—
3	-76	w.r. (4.8)	-65	25	12	40	26	—	—
4	w.r.	(4.5)	-70	-6	-23	12	-10	—	—
5	—	(2.7)	—	-19	-35	-14	-33	—	—

<sup>a</sup>w.r. = Weak relaxation (shoulder) with no definite maximum.

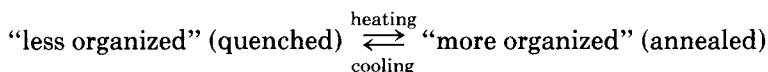
<sup>b</sup> $\lambda$  = Draw ratio of specimen at the start of the experiment.

probably the lower temperature component is given by noncrystalline segments at interlamellar regions while the higher temperature component is due to amorphous segments restricted in their motion by neighboring (or attached) crystalline segments. Asymmetry of the  $\beta$  peak dependent on the thermal history of the sample has also been reported<sup>17</sup> for PET.

Apparent activation energies  $\Delta H_\alpha$  obtained for the  $\beta$  relaxation were found to vary with composition and thermal history. This could again indicate a close interaction of soft and hard segments. For the  $\beta$  peak, sample 3, annealed,  $\Delta H_\alpha = 53 \pm 1$  kcal/mole; for sample 3, quenched,  $\Delta H_\alpha = 35 \pm 1$  kcal/mole. This would compare with the value 37.4 kcal/mole reported by Shen and co-workers.<sup>7</sup> Decreasing the amount of the 4GT component decreases  $\Delta H_\alpha$ ; for sample 4, annealed,  $\Delta H_\alpha = 46 \pm 1$  kcal/mole. For all quenched samples for the  $\gamma$  process,  $\Delta H_\alpha = 16 \pm 1$  kcal/mole. This compares favorably with the corresponding relaxation of PET given<sup>17,19</sup> as  $\Delta H_\alpha = 16$ –17 kcal/mole.

It should be pointed out that the  $\gamma$  relaxation in the vicinity of  $-75^\circ\text{C}$  was not detected in previous work<sup>7</sup> on similar materials. Those samples were prepared by film casting from 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane. It is possible that traces of the high-boiling solvent can reduce or eliminate the weak  $\gamma$  relaxation (see section on solvent effects). It was also reported<sup>7</sup> that for a sample with 54 wt % 4GT, annealing did not have any significant effect. It is suggested that at that composition, crystallinity is low so that thermal treatment had little influence. The effects of thermal history on our sample 4 were also smaller compared to those of samples 3 to 1.

It is of particular interest to note that quenching shifts the  $\beta$  peak (or the  $T_g$ ) to higher temperatures. Annealing or thermal cycling during the measurements reverses the process, see Figures 1–3 and Table II. In view of the chemical structure of these copolymers consisting of hard and soft segments, the phenomenon seems to be of the same origin as that reported by Wilkes and co-workers.<sup>20</sup> In our case the transformation,



proceeds at elevated temperatures. The modulus  $E'$  increase during annealing is due to the formation of a more crystalline and ordered structure. The increase in  $T_g$  by quenching can be attributed to the existence of strained chains and/or small crystallites within the less organized polymer, impeding segmental motion. It is pertinent to note that a time-dependent hardening at room temperature was reported<sup>5</sup> for injection-molded (-quenched) compositions with a 55 wt % 2GT hard-segment content.

The composition and thermal treatment affect the storage modulus  $E'$  as expected, see Figures 1 and 2. The  $E'$  increase is almost linearly related (above  $T_g$ ) to the wt % increase of the 4GT hard component. Annealing has also a similar effect.

In general, these copolyesters exhibit low values of damping. This would explain their excellent flex-cut growth resistance<sup>21,22</sup> (less energy is stored) and indirectly their abrasion resistance (since less energy has to be dissipated). Low-temperature relaxations of short main-chain sequences can also indicate<sup>23</sup> increased toughness, and this indeed was reported<sup>21,22</sup> to be the case for these products. Also, their excellent tear resistance<sup>21,22</sup> could be explained by the close

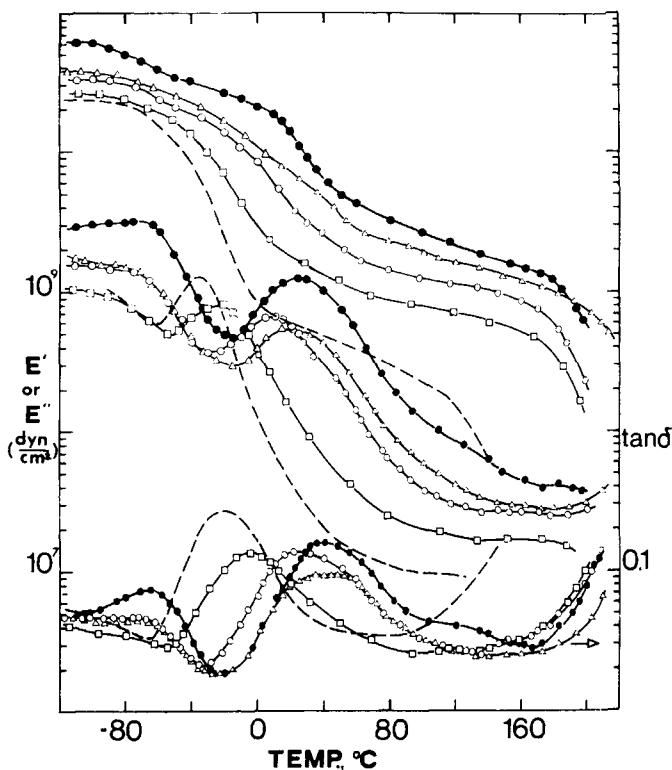


Fig. 4. Thermomechanical spectra of injection-molded specimens at 110 Hz. Effect of composition and stretching: ( $\Delta$ ) sample 1; ( $\circ$ ) sample 3; ( $\square$ ) sample 4; (---) sample 5; ( $\bullet$ ) sample 3 drawn ( $\lambda = 4.8$ ).

interacting network of hard and soft segments allowing an effective distribution of stresses.

Because of their practical importance, specimens cut from injection-molded slabs were also examined. The results are summarized in Figure 4 and Table II. The main changes, with respect to the annealed samples, are an increase of the absorption peaks  $\beta$  and  $\gamma$  (except for the low-crystallinity samples 4 and 5). There is also a shift of the main relaxations to higher temperatures, as in the case of quenched samples. The same conclusions can be drawn from a study of the  $E''$  data. The explanation is that injection molding to form a thin slab presents similarities to quenching. This is also supported by an examination of the  $E'$  modulus values at constant composition (compare Figs. 1 and 4). The composition dependence of the storage modulus reflects again the reinforcing effect of the hard segment as its amount increases (see Fig. 4).

### Mechanical Treatment

These copolymers could be drawn to high elongations ( $\lambda \cong 7$ ) at room temperature, except for the highly crystalline annealed samples 1 and 2. Drawing was much easier for injection-molded specimens. All of the samples could be easily drawn to a natural draw ratio of 4 to 5. Samples 1–3 exhibited necking and insignificant recovery, in contrast to samples 4 and 5. Stretching eliminated



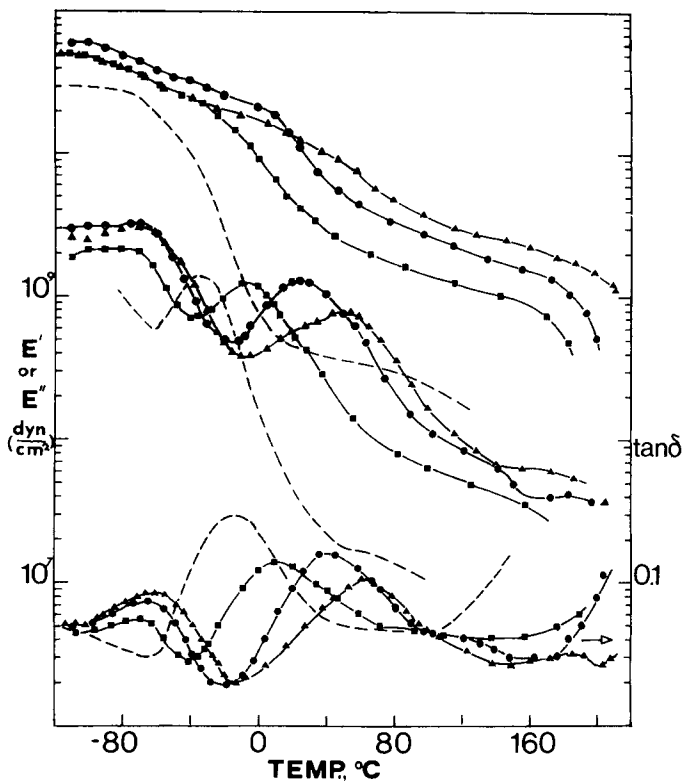


Fig. 5. Thermomechanical spectra of stretched specimens (injection molded) at 110 Hz. Effect of composition: ( $\blacktriangle$ ) sample 1 ( $\lambda = 4.5$ ); ( $\bullet$ ) sample 3 ( $\lambda = 4.8$ ); ( $\blacksquare$ ) sample 4 ( $\lambda = 4.5$ ); (---) sample 5 ( $\lambda = 2.7$ ).

opacity producing transparent specimens. Previous morphological work<sup>6</sup> on stretched sample 4 showed strong fibrillation. Observation of the surface texture of samples 1 and 2 indicated shear bands across the drawing direction.

In Figures 4 and 5, comparison of the  $\tan \delta$  and  $E''$  spectra shows a significant increase of both relaxations (samples 1–4). The effect of drawing is more pronounced as the 4GT content increases. A shift to higher temperatures takes place also (see Table II). Though we did not study the effect systematically, because of necking, the  $\gamma$  relaxation increased with the magnitude of deformation.

Comparative examination of the modulus  $E'$  shows a progressive increase in the direction quenched  $\rightarrow$  injection-molded  $\rightarrow$  annealed  $\rightarrow$  drawn for all specimens. The comparison indicates that reinforcement is the result of orientation and not of crystallization phenomena. In fact, at these elongations crystallinity is reduced.

The plastic deformation of extruded polymer solids has been examined by Peterlin.<sup>24</sup> The shift of the primary relaxation to higher times (or higher temperatures in our case) at large elongations has been studied<sup>25</sup> for the case of polypropylene. The  $\beta$  peak shifts to higher temperatures because orientation and fibrillation of the amorphous phase decreases the segmental mobility. This necessitates a higher activation energy for the segmental jumps leading to a higher relaxation temperature.

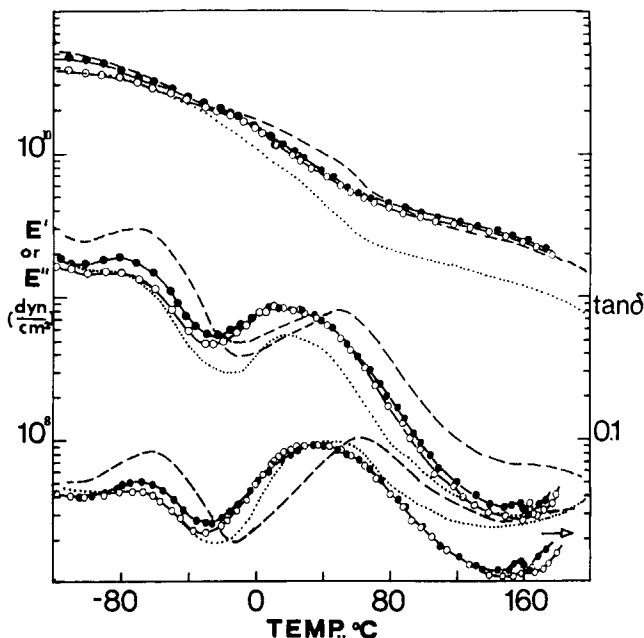


Fig. 6. Effect of thermal treatment on the thermomechanical spectrum of stretched sample 1 at 110 Hz, before annealing (—), after annealing ( $\lambda = 4.5$ ), unconstrained (O), constrained ( $\lambda = 4.7$ ) (●), unstretched (· · ·).

The increase of the  $\beta$ -peak area can be attributed to the reduction of crystallinity by cold drawing. At constant degree of deformation, the effect is higher as the amount of the 4GT component increases. The significant effect of drawing, especially at the high 4GT-content specimens, can be explained with reference to the studies<sup>19</sup> of stretched PET. The  $\gamma$ -peak increase is attributed to the reduction of crystallinity and the shift to higher temperatures to the gauche $\rightarrow$ trans transformation of the conformation of the diol unit induced by stretching. This crystallinity decrease is also supported by the work of Cella<sup>6</sup> on the morphology and stress-strain properties of these copolymers and by measurements under cyclic loading, not included in this report, carried out at this Laboratory.

The effect of annealing (three days at 100°C, *in vacuo*) was also examined for stretched specimen 1. Annealing at constant length and with one end free to relax was examined (see Fig. 6). Comparison of the relaxation spectra indicates an increase of the peak symmetry, a return of the relaxation maxima to their original values, a decrease in magnitude for both peaks, and a substantial decrease of the  $\tan \delta$  above 80°C. The weak relaxation  $\alpha$  emerges at a higher temperature (165°C) compared to samples annealed for a shorter time. This is probably the result of lamellar thickening as the annealing time is increased. Samples 3 and 4 similarly treated did not give the  $\alpha$  peak. Their damping above 80°C decreased similarly. The results indicate some recovery of crystallinity (decrease of peak height) and that the short-range order of the amorphous region has been recovered (shift of the main peaks to their original position); however, the long-range deformation persists (at least at these annealing conditions).

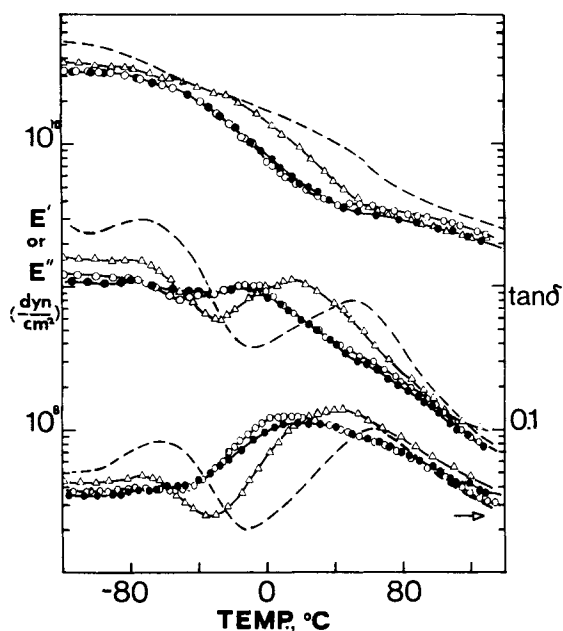


Fig. 7. Effect of solvent absorption at 110 Hz: dry, stretched ( $\lambda = 4.5$ ) sample 1 (—), with dioxane (2%) (O), with benzene (7%) (●), with 1,1,2,2-tetrachloroethane (3%) ( $\Delta$ ).

### Effect of Solvents

The effect of solvent absorption (water, dioxane, benzene, 1,1,2,2-tetrachloroethane) was examined for stretched sample 1 (see Fig. 7). Immersion in water for a period of three days at room temperature did not cause any change in the spectrum. Plasticization occurs when the other solvents are absorbed. The results are analogous to those observed for PET.<sup>17</sup> For the  $\beta$  peak, a significant asymmetry develops in the case of the benzene- and dioxane-treated samples. Its low-temperature component is plasticized more effectively shifting to lower temperature, while there is still considerable relaxation near 60°C, spreading the composite peak over a wide temperature range. Also, the  $\gamma$  relaxation is practically eliminated. Similar plasticization phenomena to a lesser extent are observed in the case of 1,1,2,2-tetrachloroethane; the  $\gamma$  peak is considerably reduced but not eliminated when the amount of solvent absorbed is sufficiently low. In view of this and of the fact that our samples thus treated cannot be validly compared with solvent-cast films, our explanation for the disappearance of the  $\gamma$  relaxation in these latter films is tentative.

Plasticization reduces the  $E'$  values, and this reduction of orientation reinforcement indicates a considerable loss of the macro order induced by stretching.

### CONCLUSIONS

1. Thermal treatment of melt-pressed and injection-molded films of these copolymers with a high content of hard segments has an important effect on their

dynamic mechanical properties. This contrasts their behavior with that of solvent-cast films.

2. The relaxation spectra correlate well with their chemical composition and are dominated by the characteristic relaxations of the 4GT homopolymer.

3. The mechanical spectra do indicate a closely interacting network of hard segments of 4GT and soft segments of PTMEG-T. This type of network can account for many of the useful properties of these elastoplastics.

4. Mechanical treatment disrupts irreversibly the crystalline superstructure orienting the hard and soft components into a fibrillar structure. Annealing removes the short-range order in the amorphous phase, but the long-range order persists. More drastic effects due to plasticization are caused by the absorption of low molecular weight liquids.

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