

Transitions and Relaxations of Linear Polyesters Related to Poly(ethylene Terephthalate). II. Glassy and Gamma

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Synopsis

The β -relaxation at T_g of the terephthalate and isophthalate series is due to molecular motions of the backbone chains in the amorphous region, but differs for the isophthalate series in that the *p*-phenylene group does not exhibit the free rotation possible for the *m*-phenylene group. Consequently, the relaxation times of the terephthalate series are longer than for the isophthalate series. The γ -relaxation (T_γ) for the higher homologues of the terephthalate series cannot be explained in terms of the poly(ethylene terephthalate) analogy. For poly(ethylene terephthalate) and poly(tetramethylene terephthalate), an induced cooperative type of motion of all the moieties is possible, whereby overlapping processes caused by "rocking vibrations" are observed as one γ -peak. The resolution of the γ -loss peaks for the above-mentioned polyesters into components is not possible at the experimental frequency of 110 Hz. For poly(hexamethylene terephthalate) and poly(decamethylene terephthalate), the "rocking vibrations" between the moieties of the skeletal chain are reduced so that even at a test frequency of 110 Hz, the γ -loss peaks could be resolved into two or three components. In the case of poly(decamethylene terephthalate), three components are resolved; the lowest temperature peak γ_1 is attributed to hindered motions of the methylene portions, the γ_2 peak is attributed to motions of the carbonyl group in the gauche conformation, and the γ_3 peak is attributed to the carbonyl group in the trans conformation of the skeletal chain in the amorphous region. The general observations obtained by other techniques were confirmed by the forced vibration analyses. As the length of the methylene chain increased, T_g decreased. As crystallinity increased, the β -relaxation moved to higher temperatures and the damping peak was smaller and broader. The damping peak moved to lower temperatures and increased in size as the length of the methylene chain increased. The damping peak was larger for the isophthalate homologue than for the corresponding terephthalate polyester.

INTRODUCTION

A study of molecular motions in polymers as a function of temperature is desirable as an aid to an understanding of mechanical properties. An approach is to find transition temperatures such as the glass transition (T_g) and lower-temperature (T_γ) transitions or γ -relaxations. These are then interpreted in terms of motions of the backbone chains or moieties of the molecules and cooperative motions of the amorphous and/or crystalline regions.¹

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The purpose of this paper is to record relationships between chemical structure and transition or relaxation temperatures for homologous series of poly(methylene terephthalates), poly(methylene isophthalates), and equimolar random copolyesters of the two acids. The three series, except for $-(\text{CH}_2)_5-$, were limited to even numbers of methylene groups in the glycol portion of the polyesters. Relaxations occurring below T_g are included in addition to those at T_g . The experimental methods involved measurements of specific heats using a dynamic calorimeter and of the storage modulus, loss modulus, and loss factor ($\tan \delta$) using a dynamic mechanical viscoelastometer. By far the most data are available for poly(ethylene terephthalate).² This includes heat capacities³ and some measurements using the differential scanning calorimeter. Heat capacity studies have been used to measure and explain transitions and relaxations of polymers.⁴

Dynamic mechanical properties have been studied because of their importance. Such tests are suitable for studying relaxations at temperatures below and at T_g but not at T_m . Between T_g and T_m , measurements are good for highly oriented and semicrystalline polymers such as poly(ethylene terephthalate). For thermoplastic polymer in the amorphous state or having small degrees of crystallinity, the modulus between T_m and T_g is too low and the viscous component too high to permit accurate testing, since finite deformations cause creep. This can be avoided by crosslinking or curing, as is done for elastomers. However, once finite deformations are observed for the thermoplastic samples, the theories of viscoelasticity do not apply.

Although the relaxation behavior of the polyesters has been studied for glycols from C_2 to C_{10} ⁵ most research has been on poly(ethylene terephthalate).^{5,6,7} A comparison of the dynamic mechanical properties of poly(ethylene terephthalate) and poly(ethylene isophthalate) has been reported.⁸ Likewise, data on the damping modulus⁹ for some of the polymers indicated changes of the temperature for maximal damping with frequency as well as with composition. For the purpose of this discussion, the transition responsible for damping will be termed the β -relaxation, and it lies near T_g for semicrystalline polymers. T_β depends on crystallinity and orientation, and the peak moves to higher temperatures and decreases in size but broadens with increased crystallinity.¹⁰ This is true also for the isophthalate series which has peaks at lower T_β values and less crystallinity than the corresponding terephthalate polyesters. T_β is suggested⁵ to be related to motions of the $-\text{O}-(\text{CH}_2)_n-$ and phenylene portions of the molecular chain.

Transitions or relaxations below T_g are related to some specific mode of molecular motion. Ward et al.^{6,11,12} found that the γ -peak of poly(decamethylene terephthalate) agreed closely with that of polyethylene (-120°C) and inferred that the γ -loss peak was due to hindered rotation of the methylene groups in the amorphous regions of the polymer. The peak was a broad, overlapping type not affected by crystallinity.¹⁰ It was noted also that the γ -peak was asymmetric, being steeper on the low-temperature side for the higher homologues. On increasing the number of methylene groups, the asymmetry reversed. It was concluded that the trans content in the amorphous phase should decrease as the number of methylene groups increased. This is reflected as a reversal of asymmetry.⁶

Illers and Breuer¹³ discussed the γ -loss peak in connection with Schmidt

and Gay's¹⁴ infrared data and suggested that the γ -loss peak in poly(ethylene terephthalate) arises from three processes or unresolved peaks. They attributed the -165°C peak to hindered rotation of methylene groups, the -105°C peak to motions of the carbonyl groups associated with the gauche configuration of the polymer chain, and the peak at -70°C to motions of carbonyl groups associated with the trans configuration of the polymer chain. Takayanagi¹⁵ and Illers and Breuer¹³ found that the magnitude of the mechanical γ -peak arises both from the noncrystalline and crystalline regions of the polymers.

Armeniades and Baer¹⁶ came to the same conclusion. They suggested that the role of the carbonyl motions is augmented by the internal friction of aromatic terephthalates and polycarbonates which have similar γ -loss peaks despite the absence of aliphatic chain segments. They show that the methylene motions γ_1 are the weakest component of the γ -relaxation in poly(ethylene terephthalate), the major components of the loss peak arising from the γ_2 and γ_3 components attributed to carbonyl motions. Moreover, Armeniades and Baer showed that the Illers and Breuer explanation of the effect of crystallinity on the γ -peak was not consistent with morphologic and spectroscopic evidence which shows that cold crystallization of poly(ethylene terephthalate) proceeds initially by perfection of existing order within small domains with a minimum of gross morphological reorganization. Substantial growth of large spherulitic structures, causing considerable reduction in gauche as well as trans amorphous content, occurs at higher annealing temperatures. They concluded that the decrease in γ -loss with crystallinity was quite pronounced in specimens annealed at high temperatures to high crystallinity in contrast to Illers and Breuer. Takayanagi et al.¹⁵ produced similar results to those of Armeniades and Baer although they did not elaborate on the point. Armeniades and Baer assigned the predominant γ -loss components to carbonyl motions, because this cannot occur in crystalline structures with coplanar phenyl groups. At low crystallization temperatures, the polymer contains numerous small, relatively imperfect crystallites, while a large fraction of the chain segments may still retain sufficient mobility to allow the loss motions. These are progressively suppressed by the growth of large, well-developed crystallites at higher annealing temperatures.

Sacher¹⁷ proposed that the dielectric β -loss peak was due to the cooperative movements of a few repeating units instead of the normal local mode which is viewed as independent motions of groups of atoms within a repeating unit. He suggested that the local mode process was more closely approximated by field induced wagging and rocking "vibrations" than by restricted or hindered rotations, especially since the latter implies a dynamic mobility between trans and gauche isomers. The wagging dipoles following the alternating electric field and were accommodated by the rocking of the phenylene group around its twofold axis of symmetry. This would necessarily involve the cooperative motion of adjacent segments. He concluded from dielectric and mechanical measurements that the γ -loss in poly(ethylene terephthalate) arose from the overlapping distributions of "normal modes" of field-induced cooperative motions, extending over several repeat units and involving the trans and gauche isomers of the methylene sequences. These motions resemble wagging and rocking vibrations and occur in both crystalline and amor-

phous phases. He suggested that the model may also be applicable to other poly(methylene terephthalates).

Nemoz et al.¹⁸ studied the dynamic loss of poly(hexamethylene terephthalate) and disagree with the other workers.^{13,16,17} They suggested that the γ -loss consists of two processes, γ_1 and γ_2 , and these are due to motions of methylene linkages in the gauche and trans configurations, respectively, in the amorphous regions, γ being the lower temperature peak. Their hypothesis is due to the observation that γ_1 decreases rapidly with increased crystallinity in poly(hexamethylene terephthalate) and therefore suggests that the gauche content diminishes at high crystallinity. Only trans isomers can be found in the crystalline regions.⁶ They concluded that the γ_1 peak must be due to the gauche methylene motion in the amorphous phase.

EXPERIMENTAL

Chemicals, polymerization technique, preparation of test films, characterization and coding of polymers, and the differential scanning calorimetric technique were described in part I.¹⁹

Dynamic mechanical testing was accomplished using a Rheovibron. Samples were cut from the films with a razor blade. The width was measured with a traveling microscope and the thickness, by a Starrett micrometer. The thickness over a sample varied not more than $\pm 5\%$. The length of the sample was cut perpendicular to the radius of the circular, pressed film. Temperature coefficient experiments using the Rheovibron were performed using the same specimen for four frequency readings. This was done to minimize any effect of physical dimensions on $\tan \delta$. Samples were inserted, cooled to -160°C by liquid nitrogen, and allowed to heat at a rate of $1^\circ\text{C}/\text{min}$, and readings were taken usually every 5°C . Error constants were found to be similar for all the polyesters at low temperatures, $T < T_g$. The magnitude depended on the frequency used. It was sufficient to obtain them for one member of the respective series, 10GTCoI, 6GI, and 4GT, for example.

RESULTS AND DISCUSSION

Studies at T_β , the Glass Transition Temperature— β -Relaxation

The thermograms obtained using the DSC were repeated until consistent results were obtained. The heat capacity values were then analyzed. According to Wunderlich,²⁰ heat capacities of linear polymers can be estimated by an empirical scheme from 60°K to 240°K . The effects of crystallinity, conformation, and intermolecular forces are of little importance above 60°K . These factors become important at and above the glass transition temperature because of different motion in amorphous and semicrystalline polymers.²¹ Using Wunderlich's scheme of additivity of heat capacities of different polymer segments over a repeating unit, the theoretical heat capacities of 4GT, 6GT, and 10GT were calculated at -30°C to be 58, 67, and 84 cal/mole- $^\circ\text{C}$, respectively, compared with the observed values of 57, 66 and 83 cal/mole- $^\circ\text{C}$, which is considered good agreement. The heat capacities of the copolymers and of the isophthalate series were not calculated because the heat

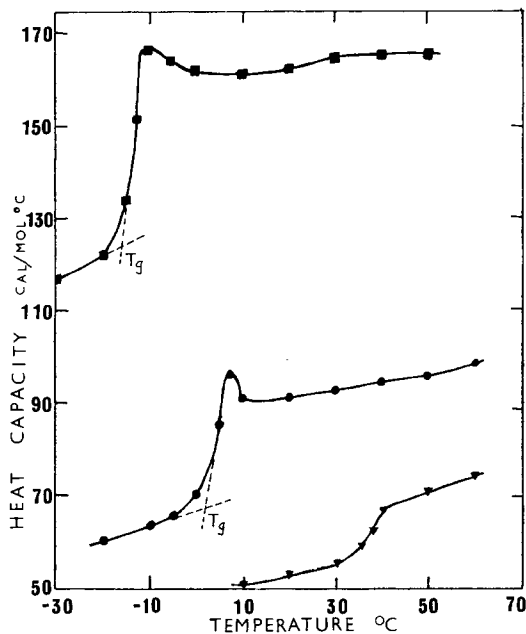


Fig. 1. Heat capacities of isophthalate series of polyesters: (▼) 4GI; (●) 6GI; (■) 10GI.

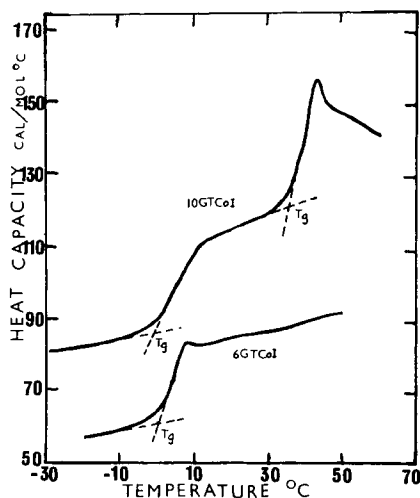


Fig. 2. Heat capacities of copolymer polyesters: lower, 6GTCoI; upper, 10GTCoI.

capacity contributed by the *m*-phenylene group was not available. The experimental data are in Figures 1 and 2.

Fortune and Maleon²² have reported that the increase in heat capacity of many substances at the glass transition temperatures can be rationalized by dividing the molecules into "beads" which are the smallest sections of the solid that can move as a unit by internal rotation in the liquid phase. The heat capacity increase calculated per mole of "bead" through the glass transition is 2.7 ± 0.5 cal/mole-°C. This is the rule of constant ΔC_p and may be true only for amorphous materials. The values in Table I were calculated.

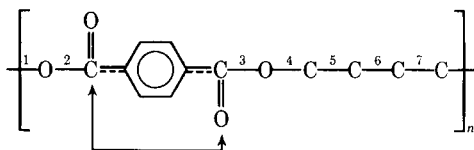
TABLE I
Number of Beads for Various Polymers

Sample	ΔC_p , cal/mole-°C	No. of "beads"
4GT	1.4	7
6GT	1.9	9
10GT	2.1	13
4GI	1.3	9
6GI	2.7	11
10GI	2.7	15

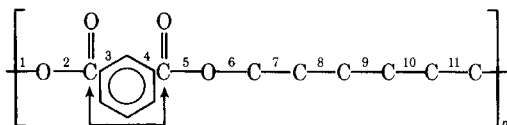
TABLE II
Heat Capacities at T_g

Sample	C_p , cal/mole-°C	T_g from DSC, °C
4GT	72.5	45
6GT	77	8
10GT	86	-9
4GI	56	34
6GI	66	-1.5
10GI	125	-15

The assigning of the number of beads for the terephthalate series is as follows:



There are seven "beads" in 4GT. The group indicated constitutes one gigantic bead, implying that the carbonyl group does not rotate at the glass transition temperature. The dotted lines indicate resonance between two carbon atoms, and the indicated unit resonates as a whole, oscillating about the backbone C—O bonds. It has been found that the energy for rotation about this bond is smaller than for a C—C bond.²³ The assigning of the number of beads for the isophthalate series is different.



There are 11 "beads" in 6GI. The indicated unit does not oscillate as a whole as in the case of the terephthalate series. The oscillation of the *m*-phenylene ring contributes a large moment of inertia. This case seems to be similar to that of polystyrene for which the C_p is much greater than could be accounted for by independent backbone motion plus phenyl oscillation.⁴ Table II lists the C_p values at the glass transition temperatures. Two observations were made, an increase in C_p for the higher homologues in both series and lower C_p values for the isophthalate series than for the terephthalate series except for 10GT and 10GI.

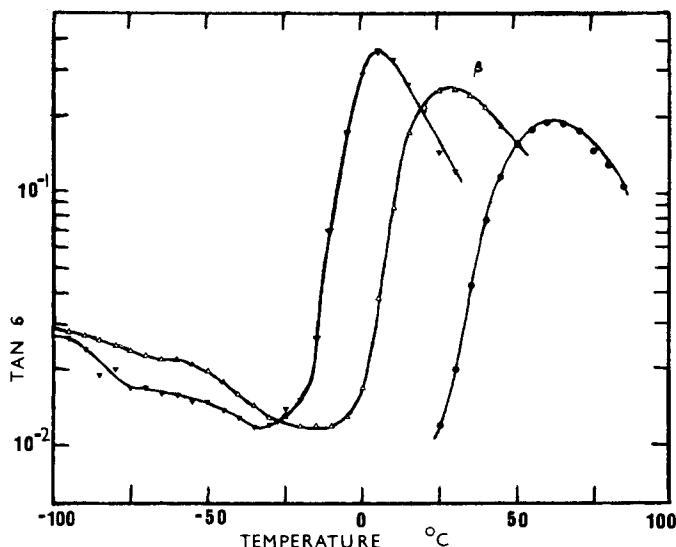


Fig. 3. $\text{Tan } \delta$ vs. temperature for isophthalate series of polyesters: (●) 4GI; (Δ) 6GI; (▼) 10GI.

Morphology is an important factor in determining C_p at T_g . There is more free volume frozen into the solid state due to the asymmetrical repeating unit in the isophthalate series which results in increased mobility of chain segments. The intermolecular forces of the isophthalate series "melt out" at T_g . Stiffness of the backbone chain is an important factor due to the high potential barriers which prevent rotation about σ -bonds.

The flexibility of the isophthalate series was discussed before in relation to the "bead" concept. The resonance of the *p*-phenylene group with the adjoining carbonyl group increases the potential barrier to rotation, thereby increasing the stiffness. Moreover, the moment of inertia is small due to its center of symmetry being in the center of the ring. If the heat capacity data of 10GT and 10GI at temperatures below T_g are extrapolated, the heat capacity curves would appear to intersect. Below this intercept, the C_p of the terephthalate series would be higher than for the isophthalate series. This is only speculation at this time, since experiments were not done at such low temperatures.

The isophthalate series shows lower intermolecular attraction. The isophthalate polyesters dissolve in methylene chloride, whereas the terephthalate polyesters swell except for 6GT, which dissolves.

The transition temperature T_β was measured from dynamic mechanical data. The loss peak at T_β is called the primary dispersion because it is the most conspicuous of all the loss peaks. Various authors^{6,11,13,18,24} have studied the mechanical relaxation of 2GT and its higher homologues. The terms relaxation and transition are frequently used interchangeably. The data for the three series were similar. Those for the isophthalate series are shown in Figure 3.

The β -relaxation of 2GT in respect to magnitude, location, and breadth is a function of the degree of crystallinity and also the manner in which a particular degree of crystallinity is attained. These aspects have been thoroughly

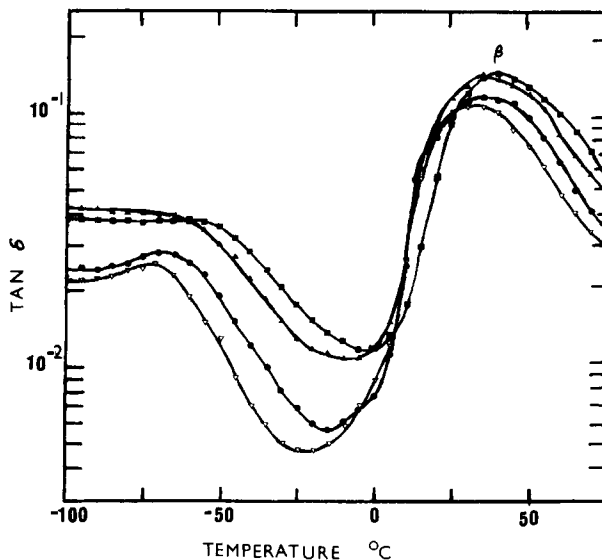


Fig. 4. $\text{Tan } \delta$ vs. temperature as a function of frequency for the terephthalate series of polyesters: (∇) 3.5 Hz; (\bullet) 11 Hz; (\blacktriangle) 35 Hz; (\blacksquare) 110 Hz.

studied for 2GT, but the experimental data for the higher poly(methylene terephthalates) are far less extensive. The mechanical β -process is due to the micro-Brownian motions in the amorphous phase of the polymer, is related to T_g , and correlates in location with the dielectric β -process. Ward⁶ suggested that the β -transition in 2GT could be treated as a composite process at a molecular level, first involving rotations of the methylene groups and then, as the temperature is raised, rotations of the phenylene and carbonyl unit, eventually including most of the molecules in the noncrystalline regions. As the methylene sequence length increases, there is a sharper rise in ΔC_p at the glass transition.

Possible explanations could be more free volume, lower intermolecular forces at T_g , or faster relaxation time of the higher homologues. All three are expected, since the longer the sequence length, the greater the free volume is expected to be. The longer the sequence length, the harder it is for the polyester to attain the trans configuration needed for crystallization or close packing. 2GT has small polar intermolecular forces;²³ so, as the glycol length increases, it naturally approaches that of polyethylene. As for the shorter relaxation time, this could be due to the decreased steric strain in the glycol moiety, which can change conformation either to the gauche or trans configurations to relax the strain.

As the number of methylene groups increases, the temperature $T_{\beta_{\max}}$ decreases from 75°C for 4GT to 43°C for 6GT and 20°C for 10GT. The same is true for the isophthalate series: 60°C for 4GI, 30°C for 6GI, and 5°C for 10GI. The decrease in $T_{\beta_{\max}}$ is asymptotic, presumably to the value of polyethylene. The substitution of a *m*-phenylene for a *p*-phenylene linkage moves the β -relaxation to a lower temperature regardless of the length of the methylene group. The decrease in $T_{\beta_{\max}}$ is about 13° to 15°C. $T_{\beta_{\max}}$ by dynamic mechanical measurements is 10° to 35°C higher than $T_{g_{\text{DSC}}}$. This is

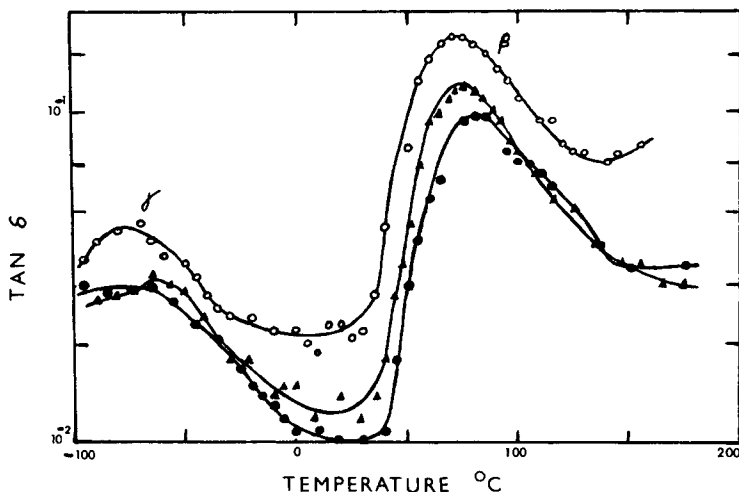


Fig. 5. Effect of thermal history on $\tan \delta$ for poly(tetramethylene terephthalate): (O) amorphous (quenched); (▲) annealed at 170°C; (●) annealed at 85°C.

due to the different methods of measurement and the frequency of the test method. The data are summarized and compared in Table III. The difference is greatest for the terephthalates and least for the copolyesters.

The terephthalate series has wide β -loss peaks which are almost identical in height. When the loss peaks were compared with the heat capacity data, it was noted that there is no abrupt change in the heat capacity (ΔC_p) over a narrow temperature range as in the isophthalate series. It would seem that for 10GT, the width of the β -peak is narrower than for the lower homologues. The heat capacity data reveal more of the transition behavior in this case as discussed above.

The β -loss peaks for the isophthalate and copolymer series are steeper on the lower-temperature side and are generally narrower in width than for the terephthalate series. A comparison with the heat capacity data confirms the abrupt change in heat capacity over a narrow temperature range at T_g . The relaxation spectrum detected by mechanical measurements appears in the calorimetric measurements. The dynamic mechanical measurements of the β -loss peaks reveal very little about the molecular motions in this region. It is useful in measuring localized motions, as will be discussed later.

The apparent activation energy (ΔH_A) of the β -loss can be calculated and the values for 4GT, 6GT, and 10GT are about 80 kcal/mole of repeating unit. The value for semicrystalline 2GT²⁵ is also 80 kcal/mole. The value for amorphous 2GT is 160 kcal/mole. The activation energies for selected polymers are in Table III.

The isophthalate series has lower activation energies than the terephthalate series, and the copolyesters are intermediate between the two. Since the activation energy is very sensitive to crystallinity, and the samples are not of the same crystallinity, it is very difficult to discuss the subject in terms of the property-chemical relationships or modes of molecular motions at T_g . For a high-modulus, semicrystalline polymer (at room temperature), the measurement of the apparent energy of activation is not a good means of studying re-

TABLE III
 Relaxation and Transition Temperatures

Sample	$T_{\beta_{\max}}$, °C	$T_{\gamma_{\max}}$, °C	$T_{E'_{\max}}$, °C	$T_{\beta_{\max}}$ — $T_{\gamma_{\max}}$, °C	$T_{\#DSC}$, °C	T_m , °C	$T_{E''_{\max}}$, °C	ΔH_A , kcal/ mole
4GT	75	-60	65	135	45	213	160	70
6GT	43	-95	25	138	8	147	-117.5	88
10GT	20	-97	10	117	-9	110	-120	88.5
4GI	60	—	—	—	34	135	—	—
6GI	30	-100	17.5	130	-1.5	90	-105	40.6
10GI	5	-105	-2.5	110	-15.0	40	-120	—
4GTCoI	57.5	-75	32.5	132.5	35	75	-82.5	60.8
6GTCoI	22.5	-100	15	122.5	1	73	-105	70
10GTCoI	10	-100	-10	110	0.37	72	-110	—

^a Compare with Table I for DSC data.

laxation mechanisms. The frequency of the instrument varies from 3.5 to 110 Hz, and consequently the temperature range over which the maxima occur is small, leading to unreliable results. Data obtained as a function of frequency are shown in Figure 4. Similar data were obtained for the isophthalate series. The differences due to frequency are small, but there is a tendency for $\tan \delta$ to be higher for higher frequencies and for the peaks to shift toward higher temperatures.

A brief study was made of the effects of thermal history. Previous samples were considered to be as uniformly prepared and annealed as possible. The magnitude of variations using the dynamic mechanical method when samples were subjected to changes in preparatory procedures was of interest. From Figure 5 for 4GT crystallized at 170°C, the $T_{\beta_{\max}}$ was less than for the sample crystallized at 85°C, presumably due to larger spherulites being formed at 170°C than at 85°C. Sample 5GT was amorphous but crystallized rapidly, yielding a large, broad T_{β} peak as expected.²⁶ Comparison of 6GT and 6GI showed a $T_{\beta_{\max}}$ of 45°C for the former and of 25°C for the latter, both for amorphous quenched samples. The annealed, crystalline samples yielded values some 10° higher. The stretched, oriented sample showed higher crystallinity and less damping. The explanation generally for the above appears to be that the entropy change for the isophthalate esters was greater,²⁷ resulting in a lower melting point,²⁸ again a case of the effect of positional isomerism.²⁹ The terephthalate was stiffer than the isophthalate polyesters, had a lower rate of crystallization, was less crystalline, but was easily drawn or annealed to increase the crystallinity.³⁰ It has been observed that T_{β} increases with crystallinity if 2GT is crystallized below 150° but decreases if it is crystallized above 150°. This is due to the formation below 150°C of many small spherulites which restrict amorphous phase motions,³¹ whereas above 150°C fewer larger spherulites are formed and the amorphous phase is not so restricted.¹³ It has also been reported that T_{β} was not affected by crystallinity. The sample showed larger lamellae with few spiral growths when crystallized at 75–80°C.³² The present samples were annealed one day at 75° so that large spherulites should be expected. In general,^{7,13} as crystallinity increases, the $T_{\beta_{\max}}$ moves to higher temperatures and decreases in magnitude.

Both T_m and T_β decrease with increasing length of the methylene chain in agreement with data obtained from mechanical properties⁵ and NMR.⁶ The new data were obtained using forced vibrations at fixed frequencies and under slight strain. The T_m was unchanged but $T_{\beta_{\max}}$ was slightly higher for the semicrystalline polymers. For quenched samples the T_β was at lower temperatures, about 0–7° for the even-numbered methylene chains and 20° for the single odd-numbered methylene chain.

The $\tan \delta$ increased with the number of methylene units and was higher for the isophthalate ester than for the terephthalate esters. The loss modulus peak was 5–10° below the $\tan \delta$ peak and nearer T_g . The value for 4GT was greater than for 5GT (which may have crystallized during the test), and that for the 6GT was less than for 6GI. The dynamic modulus was higher for the terephthalate type, that for 4GT being greater than for 6GT and both being greater than for 5GT.

In general, there appears to be no cause to expect that thermal history has changed the comparative results but will have affected the detailed numerical data somewhat. It was on this basis that the data of this study were interpreted, in terms of trends rather than fundamental data.

Measurements at $T < T_\beta - T_\gamma$ Relaxation

With so many possible γ -loss peaks, the subject is complicated and the conclusions uncertain. Usually, it is assumed that if certain motions occurred in 2GT, then it is possible that the higher homologue of the terephthalate series have similar motions. Figure 6 shows the data for the terephthalate series. Results for the isophthalate series were similar.

The γ -loss peaks for the six and ten methylene homologues are seen as two distinct overlapping processes. It could be due to the motions of CH_2 groups in the gauche and trans isomers of the amorphous region, similar to the postulation by Nemoz et al.¹⁸ The γ_2 -peak is less pronounced in 6GI. Since 6GT and 6GI differ only in the phenylene linkage, the reduced γ_2 -loss must be attributed to motions of the carbonyl group rather than hindered motions of the methyl group, CH_2 , as postulated by Nemoz et al.¹⁸ 6GTCoI shows a more pronounced γ_2 -loss peak than 6GI. This is in agreement since the γ_2 -loss is intermediate between the two homopolymers from which it was derived. The γ_1 -peak is approximately the same for the three different polymers. This is due to hindered motions of the CH_2 groups since all the polymers have six CH_2 groups in the repeat unit. Whether the γ_2 -loss peaks are due to the motions of the carbonyl group in the gauche or trans conformations is uncertain because the frequency of the experiment at 110 Hz was not sensitive enough to resolve overlapping peaks.

In Figure 7, the resolving power is better since E'' is used as a parameter. Three γ -loss peaks are observed for 10GT: the γ_1 -peak at the lowest temperature is due to hindered methylene motions, γ_2 is due to motions of the carbonyl group in the gauche configuration, and γ_3 is due to motions of the carbonyl in the trans configuration.

It is interesting to note that the γ -loss peak widens as the number of methylene group increases for the terephthalate series (Fig. 6). The explanation is that for 2GT to 4GT, the short methylene sequences are sterically strained by motions caused by any moieties in the repeating unit. Hence the γ -loss

peaks do not resolve into two or three processes in an experiment at 110 Hz. This steric strain results in induced cooperative movements of the carbonyl group and the glycol residue. The phenylene ring itself is too bulky to move in a mechanical experiment. This argument follows that of Sacher¹⁷ who ex-

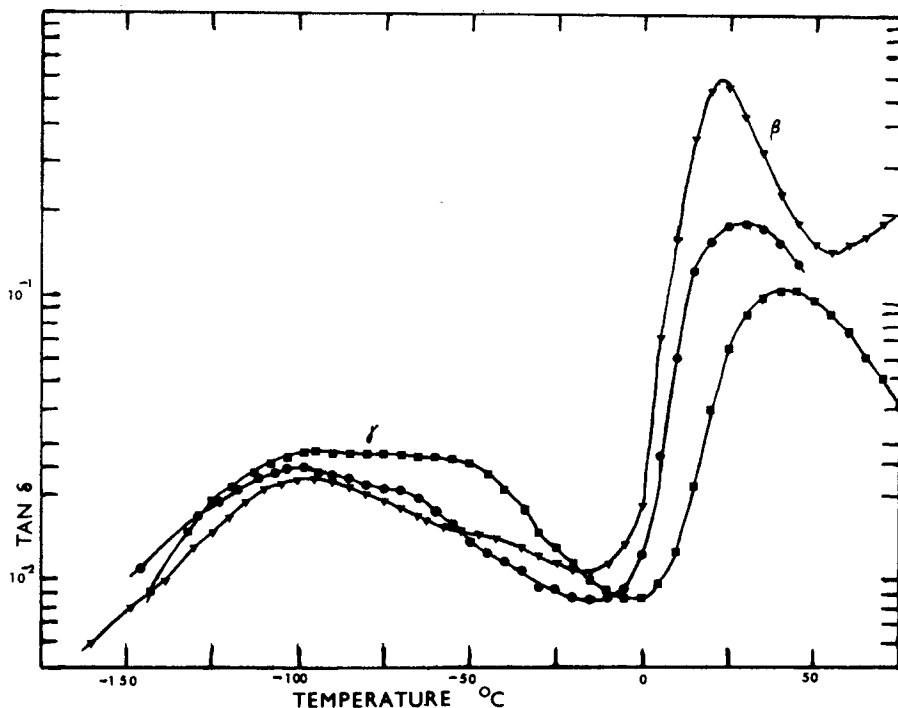


Fig. 6. $\tan \delta$ vs. temperature for polyhexamethylene polyesters: (■) 6GT; (●) 6GI; (▼) 6GTCoI.

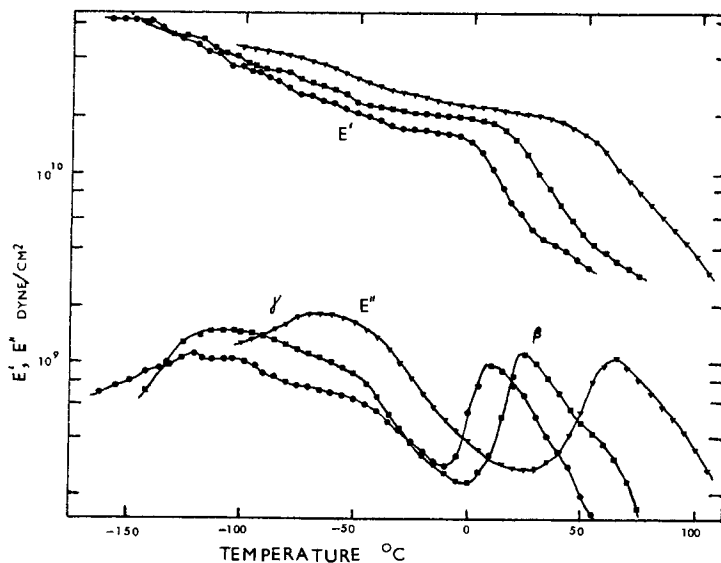


Fig. 7. Dynamic and loss moduli vs. temperature for terephthalate series of polyesters: (▼) 4GT; (■) 6GT; (●) 10GT.

plained that the γ -loss peak is a cooperative process involving all the moieties over several repeat units and that there is a "rocking vibrations" of all the atoms involved. This makes it difficult to resolve the peak into components at 110 Hz.

For 6GT to 10GT, the "rocking vibrations" seem to diminish. This means that the γ -loss peaks could be separated into components, each component being associated with a particular type of motion. In the case of 10GT, the resolution is very good. This could mean that the longer methylene sequence acts as a "buffer" to induced cooperative movements of the glycol residue by a relaxation process. It is not believed that a Schatzki crankshaft type mechanism takes place in the glycol residue although there are up to ten carbon atoms. While energetically possible, statistically it is not probable taking into account that an equilibrium amount of trans and gauche isomers are present in the amorphous regions.¹⁴

The terephthalate series have "extended" γ -peaks over a wide temperature range of about 100°C. The isophthalate series have much smaller γ -peak widths over the same temperature range. As the number of CH₂ groups in the terephthalate series increases, a more gradual slope of the γ -peak on the higher temperature side is noted. In the case of 10GT, three distinct peaks are observed. The same observation is observed for the isophthalate series. The γ -peak of the copolymers lies between the γ -loss peaks of the homopolymers. The motions of the carbonyl group with regard to the γ -loss peaks were discussed above. However, the carbonyl group motion is probably hindered rotation of the C=O group rather than of the whole group. The rotation about the C—O bond is more difficult due to resonance as in the case of the terephthalate series. A distinction could be made between motions of the carbonyl groups and methylene groups by classifying the latter as methylenedioxy groups O—(CH₂)_x—O since this group implies a "cooperative motion."

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