Glass transition temperature of copolyesters of PET, PEN and PHB as determined by dynamic mechanical analysis*

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Binary and ternary copolymers of poly(ethylene terephthalate) (PET), poly(ethylene-2,6-naphthalene dicarboxylate) (PEN) and poly(*p*-hydroxybenzoic acid) (PHB) were synthesized and dynamic mechanical measurements at temperatures ranging from −140°C up to the melting point were performed. A linear dependence of the glass transition temperature of the isotropic materials on composition was obtained. Copolymers containing more than about 30 mol% PHB are partly liquid-crystalline, and those containing more than 50 mol% PHB are completely liquid-crystalline. The PET/PEN/PHB ternary copolyester containing equal parts of each of the three components can be obtained at room temperature as a liquid-crystalline glass and as an isotropic glass, depending on thermal history. The glass transition temperature T_g of the material in the liquid-crystalline state was found to be about 30°C lower than that of samples in the isotropic state. By extrapolation to 100 mol% PHB, a glass transition temperature of about 120°C was estimated for the PHB homopolymer. Samples containing more than 70 mol% PHB show an additional peak in tan δ, which is attributed to a relaxation process in a disturbed hexagonal crystalline phase. At temperatures below T_g in all copolymers investigated several β relaxation maxima were observed. The temperature positions of these maxima do not depend on the composition.

(Keywords: liquid-crystalline copolyesters; glass transition temperature; dynamic mechanical analysis)

INTRODUCTION

Binary and ternary copolyesters of poly(ethylene terephthalate) (PET), poly(ethylene-2,6-naphthalene dicarboxylate) (PEN) and poly(*p*-hydroxybenzoic acid) (PHB) can be used to study the influence of molecular structure on molecular order and phase transitions. Many investigations have already been performed on crystallization, on transitions into liquid-crystalline states and on melting of these copolyesters.

Copolyesters of PET and PHB were first synthesized by Jackson and Kuhfuss[1] and have since been investigated by many other authors[2–8]. It has been shown that these copolyesters are liquid-crystalline if the PET content is less than 60 mol%. The PET sequences crystallize if their fraction is larger than 50 mol%. A strong tendency to deviate from a statistical distribution of the units towards block copolymers is observed[7,9]. In addition, the material seems to be quite inhomogeneous[5,7].

The crystallization and melting behaviour of PEN was investigated by Zachmann *et al.*[10], Cheng and Wunderlich[11] and Buchner *et al.*[12], and studies on copolyesters of PEN and PHB were performed by Jackson[13] and Buchner *et al.*[14]. It was shown that PEN can form two crystal modifications. The PEN/PHB copolyesters are liquid-crystalline if the PEN fraction is smaller than 70 mol% and the PEN sequences crystallize if their fraction exceeds 50 mol%.

Quite recently, copolyesters of PET and PEN and ternary copolyesters of PET, PEN and PHB were synthesized and investigated[15]. The PET/PEN copolyesters are able to crystallize if one of the components exceeds 60 mol%. It is not possible to obtain them in a liquid-crystalline state. The PET/PEN/PHB ternary copolyesters are liquid-crystalline if they contain more than 30–40 mol% PHB.

The PHB homopolymer can exist in different crystal modifications at room temperature[16–18] and, in addition, shows a crystal–crystal transition at about 320°C[16,17,19]. Although it is difficult to melt this material without degradation, a melting point of 510°C was recently reported[20].

In contrast to the extensive studies on molecular order in these copolyesters, only a few investigations on the glass transition temperature T_g are reported. The glass transition temperatures of PET and PEN as determined by d.s.c. were found to be 70°C and 120°C, respectively[11,13,21]. The liquid-crystalline PET/PHB copolyesters show a glass transition temperature of about 60°C[22] and the liquid-crystalline PEN/PHB copolyesters a T_g of about 70°C[14]. For PET/PHB copolyesters somewhat higher values of T_g were also reported[1,7]. No studies on the influence of molecular structure on T_g have been performed up to now by systematic variation of the composition of all binary and ternary copolyesters of PET, PEN and PHB. Especially the glass transition temperature of the PHB homopolymer is still ambiguous. A straightforward determination of the glass transition temperature of PHB is not possible because this material can only be obtained in the completely crystalline state.

* Dedicated to Professor Dr H. Sinn on the occasion of his 60th birthday
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By extrapolation of d.s.c. measurements on copolyesters of *p*-hydroxybenzoic acid and *m*-hydroxybenzoic acid[23] and of 2-phenylthioterephthalic acid, hydroquinone and *p*-hydroxybenzoic acid[24] to 100% PHB, a glass transition temperature of about 120°C was found. On the other hand, a glass transition temperature of about 170°C was also reported[25,26] for PHB and even larger values are assumed[27]. Another interesting problem is the comparison of the glass transition temperature of the material in the liquid-crystalline state with that found for the isotropic state.

Most of the glass transition temperature measurements cited above were performed by means of differential scanning calorimetry (d.s.c.). Dynamic mechanical analysis (d.m.a.) is another method for determination of T_g. Whereas in d.s.c. experiments the glass transition only leads to a small step in the curve, in d.m.a. measurements usually a comparatively large peak in the loss modulus and one in $\tan\delta$ are observed. Therefore the latter method has some advantage as compared to d.s.c. Of course, the d.m.a. glass transition temperatures measured at frequencies between 10 and 20 Hz are somewhat higher than the 'static' ones determined by d.s.c. This, however, is of no considerable disadvantage, especially if one studies the influence of molecular structure and composition on T_g. D.m.a. measurements on some copolyesters of PET and PHB were performed by Benson and Lewis[28]. These measurements, however, were restricted to temperatures between 0 and 200°C. Some rheological measurements of phase transitions in the temperature range of 200–350°C were performed by Sun *et al.*[29]. D.m.a. measurements were also performed by Blundell and Buckingham[30] on copolyesters containing 2,6-naphthyl groups.

In this paper we report some results obtained by d.m.a. measurements on the binary copolyesters PET/PEN, PET/PHB and PEN/PHB and on the ternary copolyester PET/PEN/PHB. The composition of the binary copolyesters was systematically varied in steps of 10 mol% so that the influence of molecular structure and composition on the glass transition temperature could be studied. The temperature of measurement ranged from −140°C up to the melting point in order also to observe peaks that occur at higher temperatures. By quenching the ternary copolyesters from different temperatures it was possible to obtain the material either in the glassy liquid-crystalline state or in the glassy isotropic amorphous state, and thus to study the influence of the liquid-crystalline structure on the glass transition temperature.

EXPERIMENTAL

PET, PEN, PHB and the copolyesters were synthesized as described earlier[12–15,31]. The intrinsic viscosities of the homopolymers and the binary copolyesters in 1,1,1,3,3,3-hexafluoro-2-propanol, as far as they were soluble, are given in *Table 1* together with the apparent molecular weights obtained from the calibration of the intrinsic viscosity based on PET. The ternary copolyester PET/PEN/PHB (35/35/30) has an intrinsic viscosity of 0.560, corresponding to an apparent molecular weight of 27 400.

Amorphous films of 150 μm thickness were obtained by melt-pressing in vacuum for 1 min at a temperature 10°C above the individual melting point of each polymer and quenching in ice–water.

The d.m.a. measurements were performed using a DMA 983 instrument from DuPont on samples cut from the quenched films with dimensions $10 \times 10 \times 0.15$ mm^3. The resonance frequency method was used, yielding frequencies between 10 and 20 Hz. The samples lay horizontally in the instrument.

The d.s.c. measurements were performed on a DuPont 910 calorimeter.

RESULTS

PET/PEN copolyesters

Figure 1a shows the d.m.a. results obtained on amorphous PEN. Three maxima in the loss modulus G'' and corresponding steps in the storage modulus G' are

Table 1 Intrinsic viscosities $[\eta]$ (dl g^{-1}) of copolyesters in 1,1,1,3,3,3-hexafluoro-2-propanol and apparent molecular weight $(M_w)_{app}$ calculated by means of the equation $[\eta] = 0.0003\,192 M_w^{0.731}$, which was found for PET

	PET/PEN		PEN/PHB		PET/PHB	
Composition	$[\eta]$	$(M_w)_{app}$	$[\eta]$	$(M_w)_{app}$	$[\eta]$	$(M_w)_{app}$
100/0	0.643	33100	0.567	27900	0.643	33100
90/10	0.777	42900	0.369	15500	0.454	20600
80/20	0.988	59600	0.321	12800	0.458	20800
76/24	*a*	*a*	0.529	25400	*a*	*a*
73/27	*a*	*a*	0.483	22400	*a*	*a*
70/30	0.515	24400	0.450	20300	0.419	18400
60/40	*a*	*a*	0.522	24900	0.481	22300
50/50	0.556	27100	0.582	28900	1.271	84100
40/60	0.583	29000	0.674	35300	0.696	36900
30/70	*a*	*a*	0.929	54800	1.470	102600
20/80	0.781	43200	*b*	*b*	*b*	*b*
10/90	*a*	*a*	*b*	*b*	*a*	*a*
0/100	0.567	27900	*b*	*b*	*b*	*b*

[a] Not synthesized
[b] Not soluble

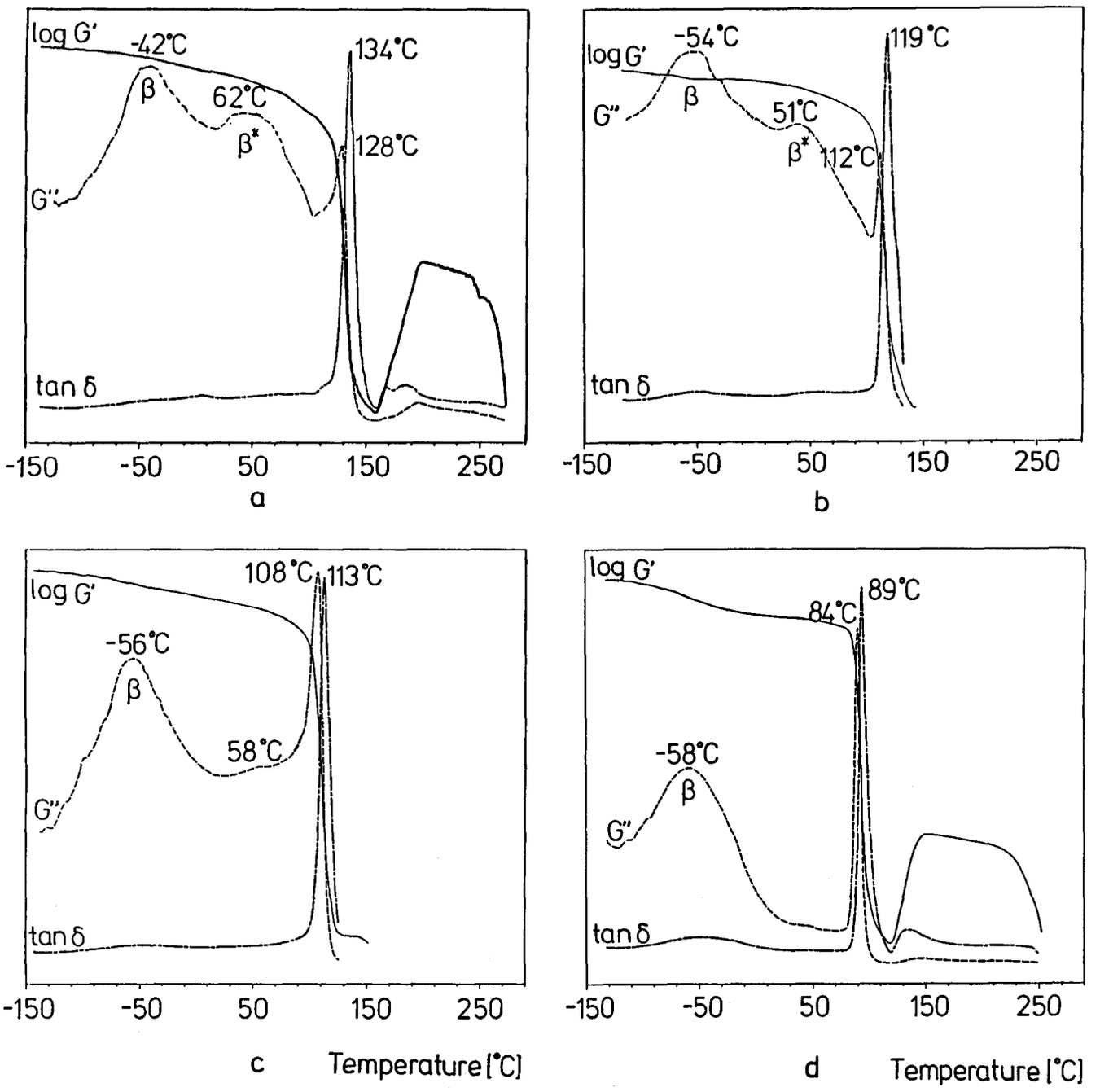

Figure 1 Shear storage modulus G', shear loss modulus G'' and loss factor $\tan\delta$ as functions of temperature during heating of amorphous (a) PEN, (b) PET/PEN (40/60), (c) PET/PEN (50/50) and (d) PET

observed, at −42°C, 62°C and 128°C, respectively. The maximum at 128°C corresponds to the glass transition, and those at lower temperatures are probably due to motion of short parts of the chains as in the case of the β relaxation maximum of PET[21]. We designate these maxima in PEN by β and β^* respectively. Whereas the glass transition also manifests itself in a strong maximum in the $\tan\delta$ curve, the low-temperature maxima are strongly suppressed in this curve. At about 176°C, with increasing temperature, a strong increase of G' is observed, which is correlated with a further small maximum in G'' and in $\tan\delta$, respectively. These effects have to be attributed to the crystallization of the samples.

Figures 1b and *1c* show the d.m.a. results for the copolyesters PET/PEN containing 40 and 50 mol% PET respectively. The glass transition maxima are found at temperatures lying almost in the middle between the T_g values of PET and PEN. The maxima corresponding to motion of shorter parts of the chains lie at about −55°C and 51°C, respectively. Similar results are obtained for copolyesters having other compositions.

The corresponding results for PET are represented in *Figure 1d*. A glass transition maximum at 84°C and a β relaxation maximum at −58°C are found.

Figure 2 shows the glass transition temperature T_g as a function of composition of the PET/PEN copolyesters. A linear dependence of T_g on molar composition is found. The two maxima at lower temperature do not change systematically with composition. The maximum at 45°C gradually disappears with decreasing amount of PEN.

PEN/PHB copolyesters

Figure 3 represents the $\tan\delta$ curves of the copolyesters PEN/PHB having different compositions. Copolyesters

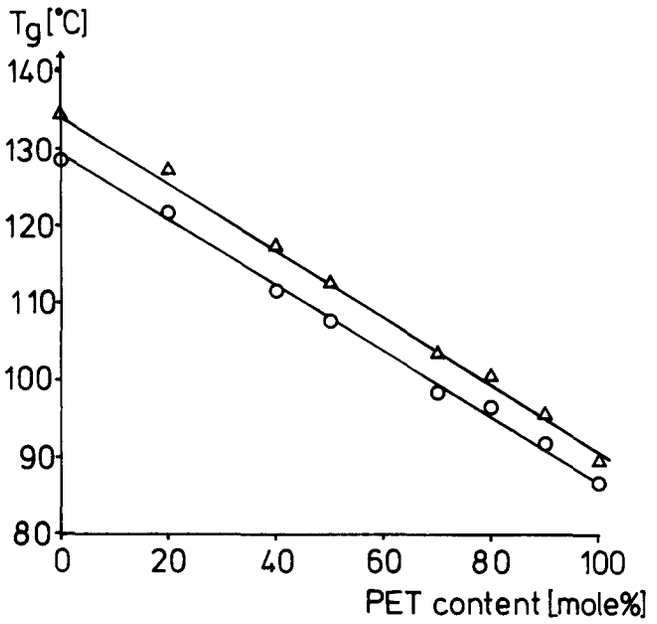

Figure 2 Glass transition temperature T_g as a function of PET content in PET/PEN copolyesters: (○) from G''; (Δ) from tan δ

containing 80 mol% and more PEN show a strong glass transition maximum at about 134°C followed by a much weaker maximum at a higher temperature, which is caused by crystallization. The latter was proved by d.s.c. measurements, which indicated the onset of crystallization at the temperature where the small maximum appears. In addition, the d.m.a. measurements have shown that the small peak is correlated with an increase of G' whereas the large peak is correlated with a decrease of G'.

When the fraction of PEN is decreased to 75 mol%, a new maximum appears at 76°C. This maximum becomes larger with decreasing amount of PEN, while the maximum at 134°C becomes smaller and disappears. As known from previous investigations[14], the PEN/PHB copolyesters are isotropic if they contain more than 75 mol% PEN. In the range of 60–76 mol% PEN, two coexistent phases are observed, a liquid-crystalline one and an isotropic one. If the copolyesters contain less than

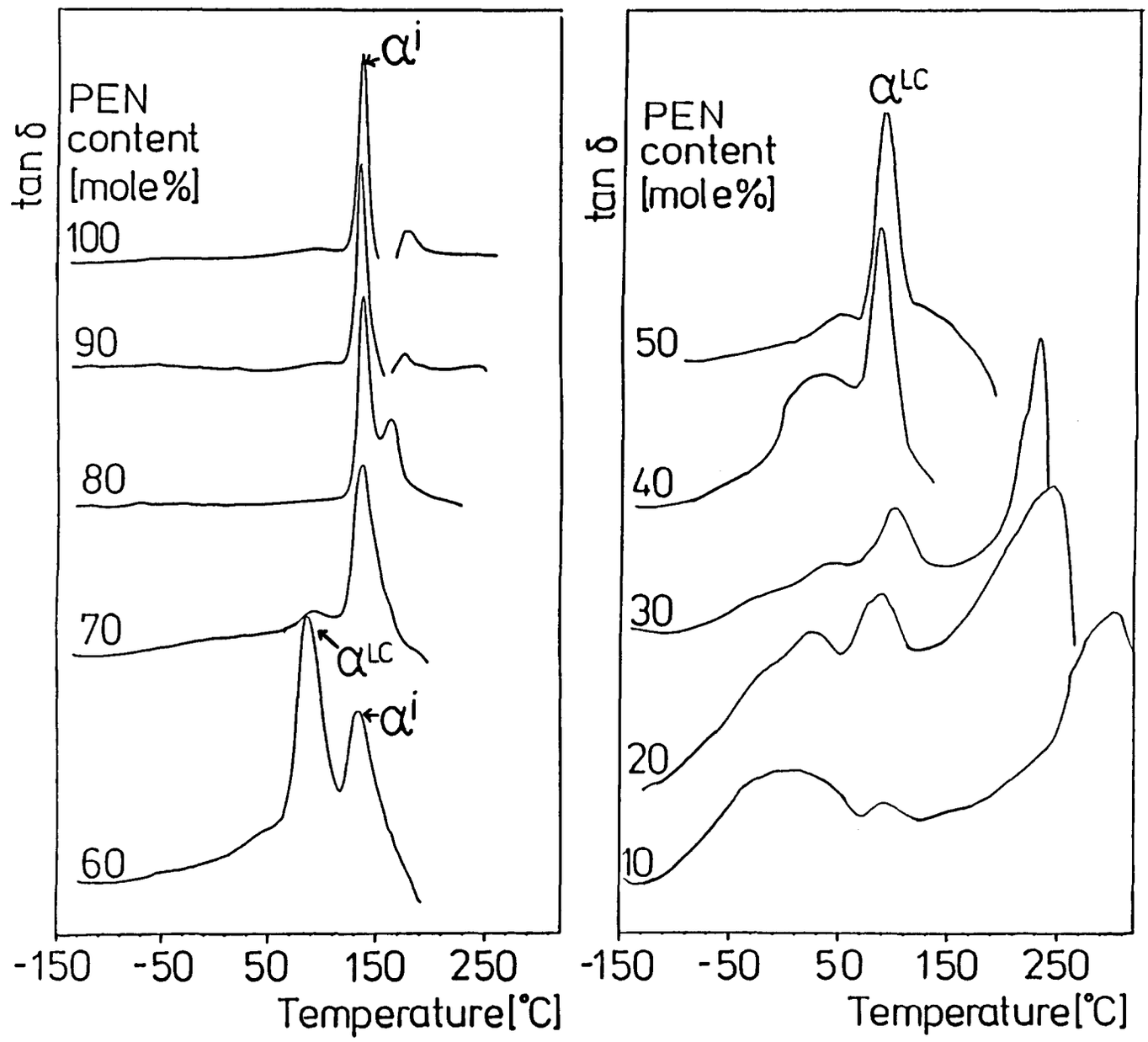

Figure 3 Shear loss factor tan δ as a function of temperature in PEN/PHB copolyesters

60 mol% PEN, they form a single liquid-crystalline phase. From this it is quite obvious that the maximum at 134°C arises from the glass transition of the isotropic phase, while that at 76°C arises from the glass transition of the liquid-crystalline phase.

The peak at higher temperature has to be attributed to crystallization. It corresponds to the small peak of the PEN homopolymer at 180°C, which, in the copolyesters, shifts to smaller temperatures with increasing PHB content. The conclusion that the second peak is caused by crystallization is also supported by investigations of the influence of melting temperature on this peak. With increasing melting temperature, the peak attributed to crystallization disappears, probably because, after melting at higher temperature, crystallization becomes more difficult.

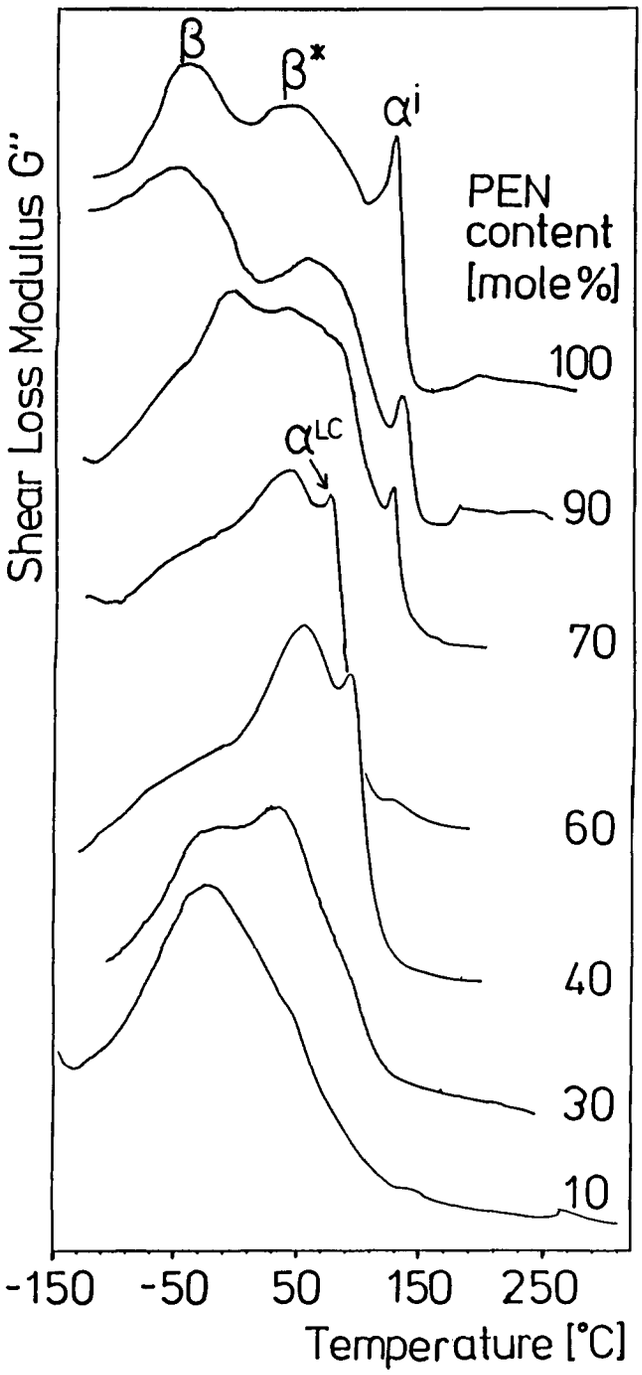

Figure 4 Shear loss modulus G'' as a function of temperature in PEN/PHB copolyesters

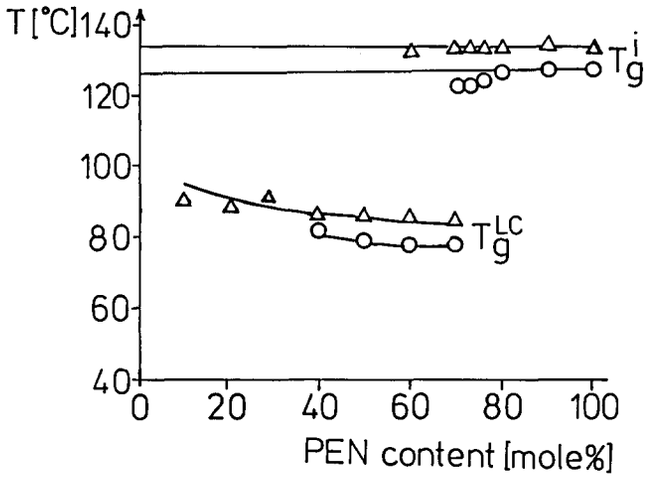

Figure 5 T_g as measured by d.m.a. as a function of PEN content in PEN/PHB copolyesters: (○) from G''; (Δ) from tan δ

In the copolyesters containing 30, 20 and 10 mol% PEN, two other maxima appear, one below 40°C and the other one above 230°C. The maximum above 230°C is very strong compared to the glass transition temperature maximum at 135°C. In wide-angle X-ray scattering diagrams, a broad crystal reflection of the high-temperature crystal modification of PHB is observed[14] (modification III) in samples containing less than 30 mol% PEN, whereas samples containing more than 30 mol% PEN do not show any PHB crystal reflections. Therefore, we conclude that the maximum in tan δ at high temperature arises from the chains in the crystalline PHB phase.

The maximum below 40°C seems to correspond to the β^* relaxation maximum in PEN. This can be seen more clearly if the curves representing the temperature dependence of G'' are considered (*Figure 4*). With decreasing PEN content, the temperature of the β maximum first increases and then decreases. The β maximum almost disappears at a PEN content between 40 and 60 mol%. In the copolyester containing 70 mol% PEN, the glass transition maximum of the liquid-crystalline state appears as a comparatively sharp peak on the right side of the much broader β maximum. It is interesting to note that, in the material containing less than 40 mol% PEN, the glass transition maximum of the isotropic phase and the high-temperature maximum appearing above 230°C in the G'' curves are much smaller than in the tan δ curves.

Figure 5 represents the temperature position of the glass transition maximum of G'' and of tan δ as a function of composition. For the sake of simplicity, we denote this temperature as the glass transition temperature T_g, well knowing that the measured glass transition temperature depends on the timescale at which the measurement is performed and, for example when measured by d.s.c. is a few degrees lower. At all compositions, the temperature of the maximum of the tan δ curve is slightly larger than that of the G'' curve. The temperature of the maximum corresponding to the glass transition of the isotropic phase (T_g^i) is the same for all compositions that show this maximum. The peak corresponding to the glass transition of the liquid-crystalline phase (T_g^{LC}) is found at a considerably lower temperature and also shows almost no dependence on composition.

PET/PEN/PHB copolyesters

In addition to the binary copolyesters discussed above, a function of temperature for PET/PHB copolyesters

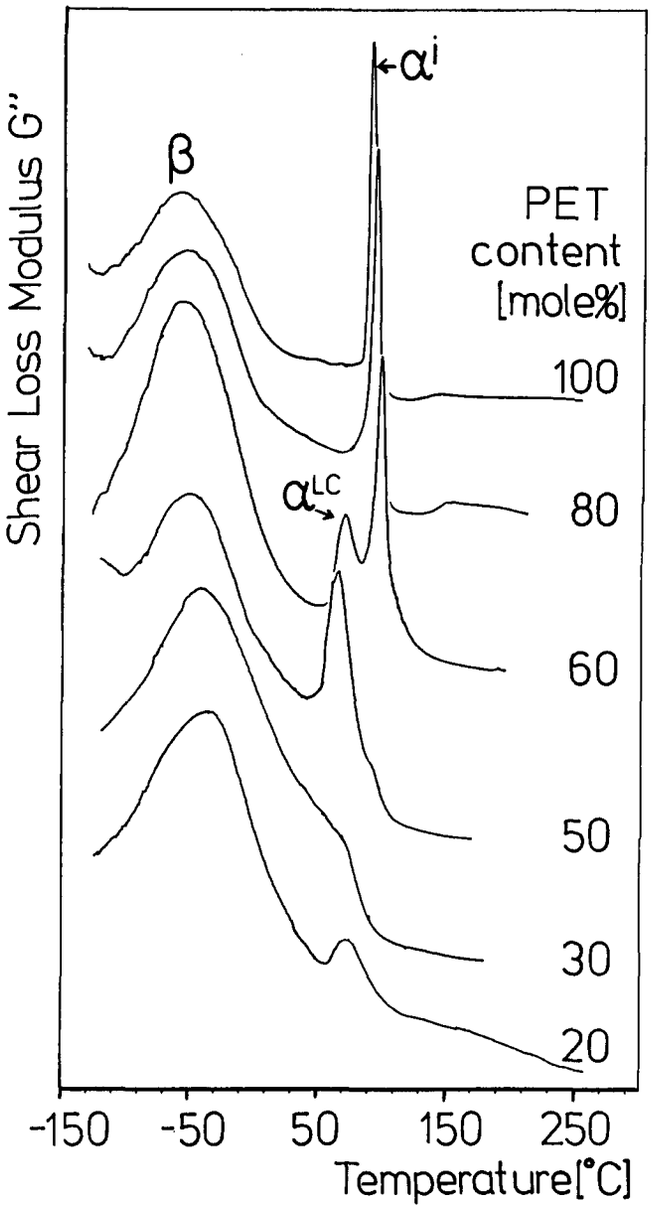

Figure 6 Shear loss modulus G'' as a function of temperature in PET/PHB copolyesters

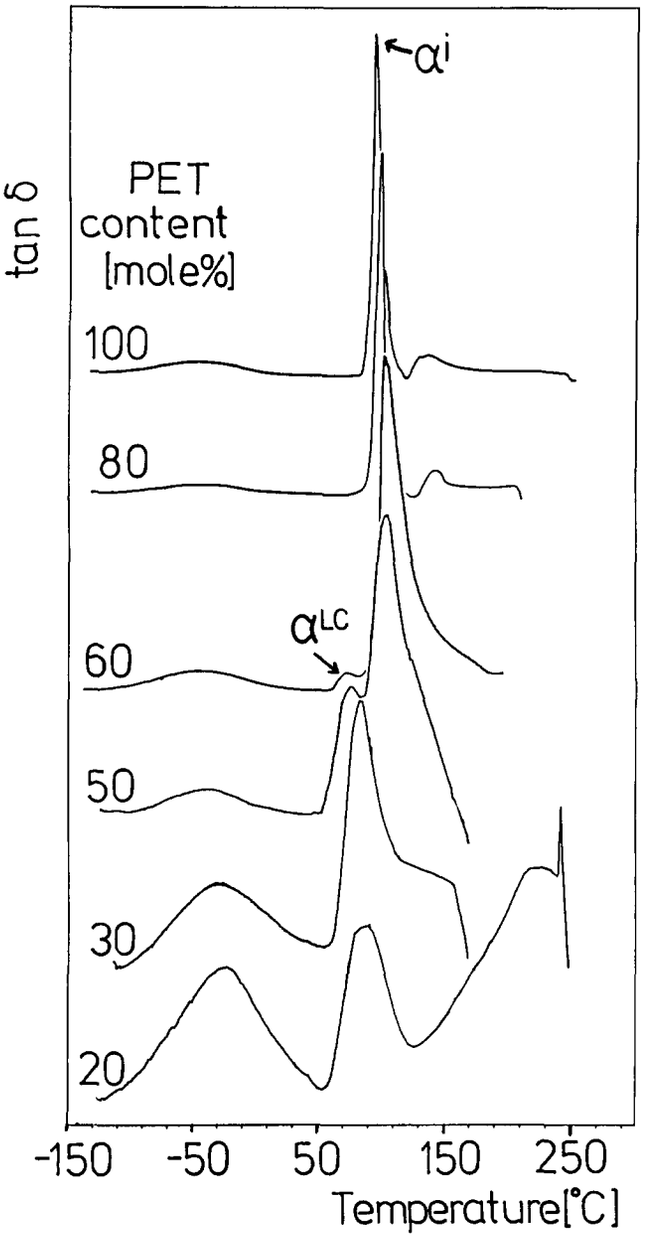

Figure 7 Shear loss factor tan δ as a function of temperature in PET/PHB copolyesters

containing different amounts of PET. These copolyesters become liquid-crystalline if the PET content is less than 60 mol%. In the range of 40–60 mol% PET a liquid-crystalline phase is coexisting with an isotropic one. The temperature of the glass transition maximum of the PET homopolymer (about 80°C) increases when the amount of PET in the copolyester decreases to 80 and 60 mol%. As in the case of PEN/PHB, the appearance of a liquid-crystalline phase at 60 mol% PET is associated with the appearance of a new maximum in tan δ at lower temperatures. Therefore, as in the case of PEN/PHB, we attribute the maximum at higher temperature to the glass transition of the isotropic state and the one at lower temperature to the glass transition of the liquid-crystalline state.

The copolyester having a PET content of 20 mol% shows an additional maximum at 230°C. We believe that the maximum at high temperature results from the motion of PHB segments in the crystalline PHB phase, as in the case of the PEN/PHB copolyesters.

Figure 8 represents the glass transition temperature as a function of composition. In contrast to the results on

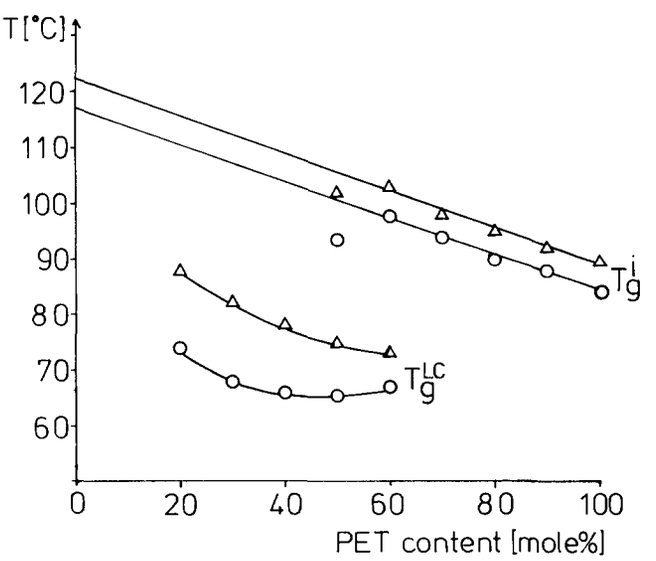

Figure 8 T_g as measured by d.m.a. as a function of PET content in PET/PHB copolyesters: (○) from G''; (△) from tan δ

the PEN/PHB copolyesters, the glass transition temperature of the isotropic phase (T_g^i) increases considerably with decreasing PET content, and that of the liquid-crystalline phase (T_g^{LC}) also depends on composition. By extrapolation of the T_g^i values obtained from the G'' curve to zero PET content, one obtains the temperature of 120°C, which, within the error of the experiment, is the same as that extrapolated from the PEN/PHB copolyesters.

PET/PEN/PHB copolyesters

In addition to the binary copolyesters discussed above, we have also investigated the ternary copolyester PET/PEN/PHB having the composition 35/35/30 (mol%). This copolyester is not able to crystallize. Above 260°C, it forms an isotropic melt. A very interesting behaviour is observed if the sample is quenched from different temperatures down to 0°C.

A sample that has been quenched from 110°C to 0°C is turbid, which is obviously due to the fact that it is in the state of a liquid-crystalline glass. The d.s.c. curve obtained during heating of this sample is shown in *Figure 9a*. A glass transition is observed at 60°C, where the sample is transformed from the state of a liquid-crystalline glass into an equilibrium liquid-crystalline state. Between 130 and 260°C, a broad endothermic peak appears. At 260°C the sample becomes transparent. Therefore, this peak indicates the transition to the isotropic melt.

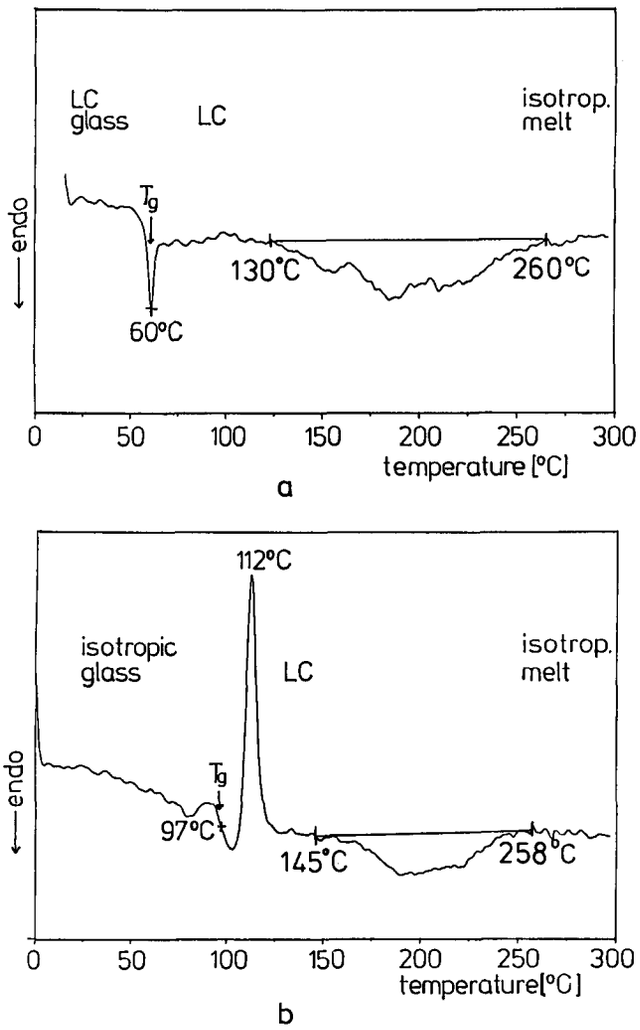

Figure 9 D.s.c. plot obtained during heating of PET/PEN/PHB (35/35/30) after quenching from (a) 110°C and (b) 290°C

In contrast, if the sample is quenched from 290°C in ice–water, it remains transparent; the state of the isotropic melt has been frozen in. The d.s.c. curve obtained during heating of this sample is represented in *Figure 9b*. A glass transition is observed at 97°C followed by an exothermic peak at 112°C, which indicates the transition from the isotropic into the liquid-crystalline state. When heated up further, again the transition into the isotropic melt is observed, which, however, starts at a somewhat higher temperature than in *Figure 9a*.

Figure 10 represents the results obtained by d.m.a. Before the measurements, the samples were annealed for 60 s at 110, 170, 210 and 290°C, respectively, and quenched in ice–water. One recognizes that the sample quenched from 110°C (*Figure 10a*) shows a strong maximum in tan δ at 73°C. If the sample is quenched from 170°C (*Figure 10b*) the maximum at 73°C has moved to 78°C and has decreased in intensity while a new maximum appears at 113°C. A further decrease of the first maximum and a further increase of the second one is observed if the annealing temperature is raised to 210°C and 290°C (*Figures 10c* and *10d*, respectively). Corresponding peaks are also observed in the G'' curves.

A comparison with the d.s.c. results (*Figure 9*) shows that the maximum in tan δ occurring between 73 and 78°C arises from the liquid-crystalline glass whereas those observed between 107 and 113°C come from the isotropic glass. The gradual changes in the intensities of these peaks with increasing quenching temperature prove that in the temperature region from 130°C to 250°C, with increasing temperature, the fraction of the material in the liquid-crystalline state decreases while that in the isotropic state increases. This is in agreement with the broad melting peak in *Figures 9a* and *9b*. This melting is also detected by a small peak in the tan δ curve at about 150°C.

The gradual decrease of the liquid-crystalline fraction with increasing temperature is correlated with a change in the densities of the samples measured at 23°C after quenching them from different temperatures in ice–water (*Figure 11*).

DISCUSSION

The glass transition of the copolyesters in the liquid-crystalline state

All liquid-crystalline copolyesters investigated in the present work show glass transition temperatures that are lower than those of the copolyesters in the isotropic state. In the case of the ternary copolyester PET/PEN/PHB (35/35/30), it is possible to show this directly because this copolyester, depending on thermal history, can be obtained in either a glassy liquid-crystalline state or a glassy amorphous state. This is so because, during cooling, the transition from the isotropic state to the liquid-crystalline state occurs so slowly that it can be prevented if cooling occurs sufficiently rapidly; as a consequence, the state of the isotropic melt can be frozen in if the melt is quenched in ice–water.

In the case of the copolyesters PEN/PHB and PET/PHB containing less than 30% PEN and 40% PET, respectively, it is not possible to freeze in the state of the isotropic melt. Here, the glass transition temperatures of

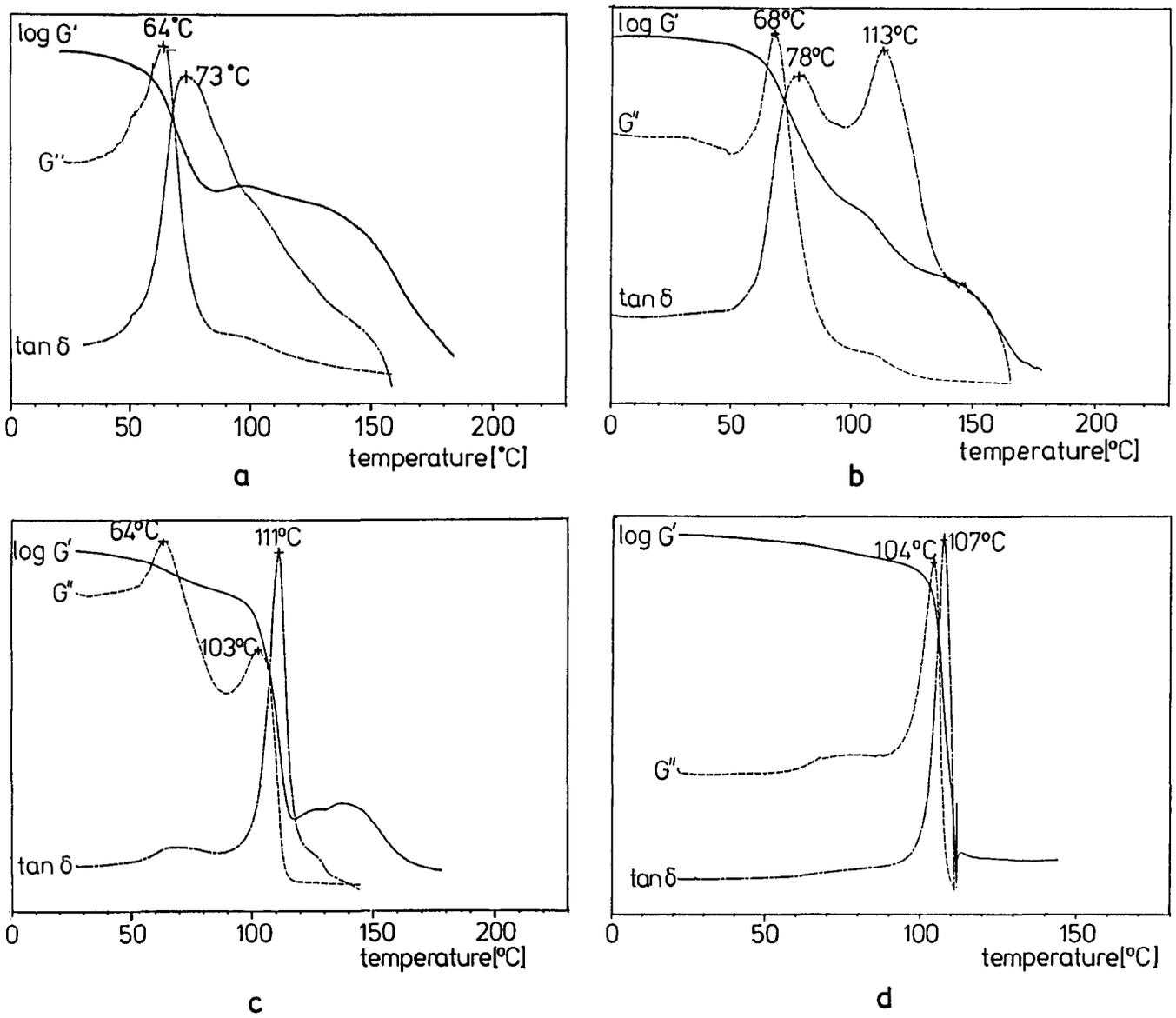

Figure 10 Shear storage modulus G', shear loss modulus G'' and loss factor tan δ as functions of temperature during heating of PET/PEN/PHB (35/35/30) after quenching from (a) 110°C, (b) 170°C, (c) 210°C and (d) 290°C

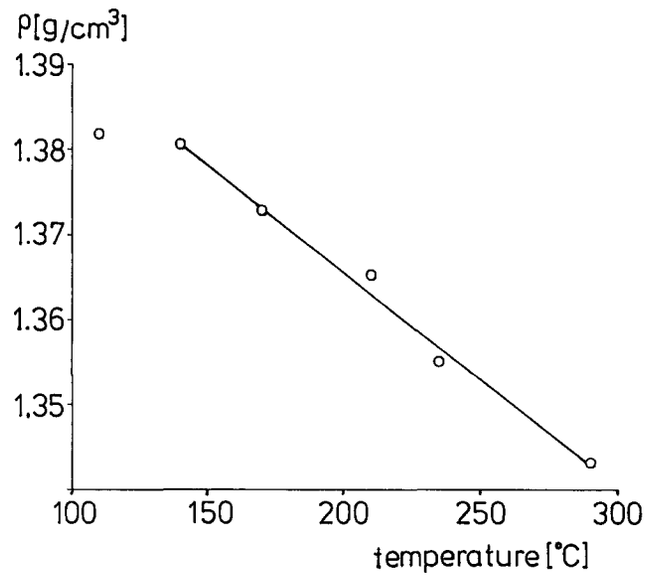

Figure 11 Density at 25°C of PET/PEN/PHB (35/35/30) samples quenched from different annealing temperatures T as a function of the annealing temperature T

the isotropic and liquid-crystalline states can be measured on the same materials because these materials, even in equilibrium, are only partly liquid-crystalline. In these materials, too, the T_g values of the isotropic fraction were found to be larger than the T_g values of the liquid-crystalline fraction. One may argue that, according to Nicely[5], in these copolyesters the molecules in the isotropic state have a smaller content of PHB units than those in the liquid-crystalline state and that, therefore, a comparison of the two glass transition temperatures is not justified. It is probably correct that the content of PHB units is not the same in the different regions. However, this does not affect the conclusion that the liquid-crystalline state has a smaller T_g value than the isotropic state, for the following reasons. In the case of PEN/PHB, T_g does not depend on composition and therefore the exact fraction of PHB units is not relevant. In the case of PET/PHB, a smaller fraction of PHB units in the isotropic phase would result in an apparent T_g value that is lower than the one expected under the assumption of a uniform distribution, and therefore cannot be responsible for a T_g value that is too large.

How can we explain that T_g is lower in the liquid-crystalline state than in the isotropic state? According to general understanding, at the glass transition temperature the free volume of the polymer assumes the smallest value necessary to allow the molecules to perform the motion that makes the sample fluid. In the isotropic state, segmental motion leading to changes in the conformations of the chains makes the sample fluid. In the liquid-crystalline state, only rotation of the elongated chains around their axes, translational motions of the chains and some motion of small atomic groups occur. The free volume necessary to perform these latter kinds of motion is considerably smaller than the one that allows segmental motion. In certain circumstances this smaller free volume in the liquid-crystalline state is reached at lower temperatures than the large free volume in the isotropic state necessary for segmental motion. However, this is not always the case, as shown in the following.

In *Figure 12*, the full line represents the volume as a function of temperature in the case that the material is transformed into the liquid-crystalline state during cooling. The broken line shows the volume change if, during cooling, a transformation to the liquid-crystalline state is avoided. In *Figure 12a* the situation is illustrated in which the glass transition of the isotropic state (T_g^i) is larger than that of the liquid-crystalline state (T_g^{LC}). In contrast, *Figure 12b* illustrates the case $T_g^i < T_g^{LC}$. The critical volume at the glass transition of the isotropic state (V_c^i) and that at the glass transition of the liquid-crystalline state (V_c^{LC}) can be easily calculated. Using the symbols introduced in the figure and denoting the thermal expansion coefficient of the isotropic state by α^i and the one of the liquid crystalline state by α^{LC} one can write:

$$V_c^i = V_t^i - \alpha^i(T_i - T_g^i)$$

and

$$V_c^{LC} = V_t^{LC} - \alpha^{LC}(T_i - T_g^{LC})$$

From these two equations one obtains:

$$T_g^{LC} - T_g^i = (1/\alpha^{LC})[\Delta V_t - \Delta V_c - (T_i - T_g^i)(\alpha^i - \alpha^{LC})]$$

with

$$\Delta V_t = V_t^i - V_t^{LC}$$

and

$$\Delta V_c = V_c^i - V_c^{LC}$$

Let us assume that, to a first approximation, $\alpha^i = \alpha^{LC}$. In this case

$$T_g^{LC} > T_g^i \qquad \text{if } \Delta V_t > \Delta V_c$$

and

$$T_g^{LC} < T_g^i \qquad \text{if } \Delta V_t < \Delta V_c$$

and one can conclude the following: the glass transition temperature of the liquid-crystalline phase is smaller than that of the isotropic phase if the difference of the volumes at the clearing point T_i is smaller than the volume difference at the glass transition temperature.

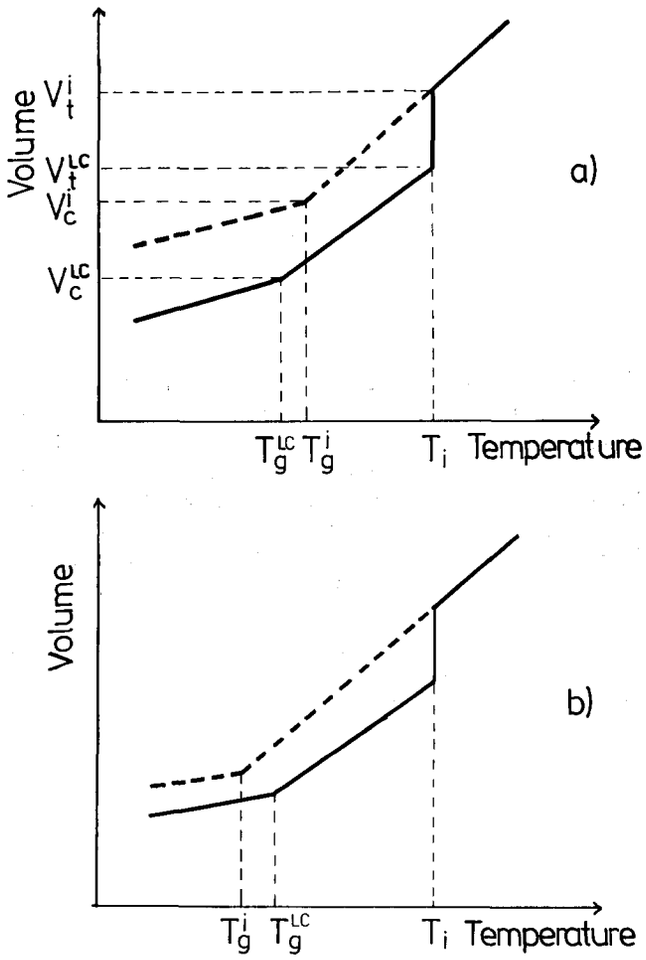

Figure 12 Schematic representation of volume as a function of temperature in the case of (a) $T_g^{LC} < T_g^i$ and (b) $T_g^{LC} > T_g^i$

Dependence of the glass transition temperature on the composition: glass transition of PHB

In all materials investigated in this work, the glass transition temperature of the isotropic phase changes linearly with the composition according to the equation of Gordon and Taylor. The value at 50 mol% PET in *Figure 8* is the only exception to this linear relationship; it is smaller than expected. This effect can be explained if one considers that, in these samples, the composition of the molecules is not uniform. Two phases are coexisting, an isotropic one and a liquid-crystalline one. The isotropic phase is supposed to have a smaller content of PHB units than the liquid-crystalline phase[5]. From this it follows that the T_g values of the isotropic phase are smaller than expected because the actual content of PHB is smaller than the average content.

By extrapolations of the T_g values obtained from the G'' maxima of the isotropic phase of the PEN/PHB and PET/PHB copolyesters to 0 mol% PEN and PET, respectively, a value of about 120°C is obtained for the glass transition temperature of isotropic PHB. Though the range of extrapolation is quite large, the agreement of the extrapolated values of the two different types of copolyesters supports the assumption of a T_g value of about 120°C. This value is also supported by extrapolations of T_g values of other copolyesters[23,24]. If the T_g values of the liquid-crystalline phase are extrapolated to 0 mol% PEN and PET content, respectively, a temperature of about 90°C is obtained, which might be considered to be the glass transition temperature of PHB in the liquid-crystalline state.

In our investigation we did not find any indication that the glass transition temperature of PHB lies at 170°C or at higher temperatures, as suggested by some

authors[25–27]. In the copolyesters containing more than 70 mol% PHB we have found a tan δ peak between 220 and 270°C. We believe that this maximum is caused by the onset of melting of small PHB crystals. Evidence of such a melting process was obtained by means of previous X-ray investigations[14].

The G″ peaks below T_g

Below T_g, the loss modulus G'' of PET shows an additional peak at −58°C, the β peak, and G'' of PEN shows two additional peaks at −42°C and 62°C, which we designate by β and β^*, respectively.

The PET peak at −58°C has been investigated by different authors[21,32]. It was suggested that it consists of two superimposed peaks, one at lower temperature arising from the onset of hindered rotation of the CH_2 groups and one at higher temperature arising from the motion of COO groups together with the phenyl rings[21]. Measurements of the second moment of the proton n.m.r. line support the assumption that CH_2 rotation starts at very low temperatures[33]. The appearance of a maximum in dielectric measurements proves that COO groups contribute to this maximum, too.

It is interesting to note that PEN shows a maximum at −42°C and an additional one at 62°C. The maximum at −42°C can be attributed to local motions of the CH_2 groups. The COO groups connected to the naphthalene rings do not contribute to this peak. This is concluded from the result that measurements in phenyl/naphthyl liquid-crystalline polymers not containing CH_2 groups indicate that this maximum tends to disappear, if the phenyl content approaches zero[30,34]. What is the origin of the maximum at 62°C? This peak is associated with an increase in heat capacity[11] and also appears in copolyesters containing no CH_2 groups[30,34]. Therefore, this peak must arise from the naphthalene rings and the COO groups. By studying different kinds of copolyesters, Blundell and Buckingham[30] have concluded that the peak arises from the naphthalene ring rather than from the COO groups, because a corresponding peak in the dielectric loss factor is found in all copolyesters in which the motion of the naphthalene ring is connected with the motion of either a COO group or an ether oxygen atom.

In the PET/PEN copolyesters both maxima discussed above appear at temperatures that do not depend on the composition (*Figure 1*). The intensity of the maximum at −58°C is also not affected by the composition, while the intensity of the peak at 50°C increases in proportion to the PEN content. This also indicates that the latter maximum is connected with the naphthalene rings, while the first one arises from the phenyl rings present in both chemical components of the copolyesters.

In the PEN/PHB copolyesters (see *Figure 4*), with increasing content of PEN the β^* maximum at 62°C and the α maximum disappear while the β maximum at −42°C stays constant. A similar effect is observed in the PET/PHB copolyesters (see *Figure 6*). The constant intensity of the β maximum is probably due to the presence of the phenyl rings and the COO groups of the PHB units, which also contribute to this maximum and replace the benzene rings and COO groups of PET and the CH_2 groups of PEN, respectively.

The decrease of the α maximum with increasing PHB content is due to the fact that the fraction of the mobile liquid-crystalline phase becomes smaller and smaller. This phase is replaced by the hexagonal PHB phase, which gives rise to the peak in tan δ lying above 200°C.

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