Influence of Liquid Crystalline Order on the Dielectric Relaxation of Random Copolyesters of PET, PEN, and PHB

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ABSTRACT: The dielectric constant and dielectric loss values for random copolyesters of poly(ethylene terephthalate) (PET), poly(ethylene 2,6-naphthalenedicarboxylate) (PEN), and poly(*p*-hydroxybenzoic acid) (PHB) have been determined in the 10^3-10^6 Hz frequency range. The variation of the dielectric properties with temperature has been related mainly to two processes: (1) The α relaxation, which is associated to the glass transition and which has been shown to be dependent on the molecular order of the systems. Copolymers with liquid crystalline order exhibit an α relaxation process occurring at lower temperatures than the amorphous ones. (2) The β process which has been assigned to a local motion of the ester groups attached to both sides of the aromatic rings. The β process also depends on the molecular order. The existence of a liquid crystalline state increases the dipolar correlation of both the β and the α relaxation processes.

1. Introduction

Much research activity continues to be directed to the understanding of the structure and chain dynamics in copolymers formed by poly(ethylene terephthalate) (PET), poly(ethylene 2,6-naphthalenedicarboxylate) (PEN), and poly(*p*-hydroxybenzoic acid) (PHB).[1−6] X-ray diffraction and neutron scattering studies have analyzed the crystallization behavior and the transitions into the liquid crystalline states and on the melting of these copolyesters.[4,7−10] These investigations reveal the following: (1) the copolyesters form liquid crystalline states only if the content of PHB is larger than 30−40%; (2) the copolyesters crystallize, on cooling from the mesophase, when the PEN or PET content exceeds 50%; (3) for PET-*co*-PEN copolymers no liquid crystalline states are formed; and (4) a simultaneous crystallization of both components never occurs.[2] The mechanical properties of these materials have been investigated using the microhardness technique, and a relationship between this property and changes in the microstructure has been observed.[2,3]

By using dynamic mechanical analysis (DMA) several maxima in mechanical losses as a function of increasing temperature have been found.[4] All copolymer compositions present a β relaxation, attributed to the motion of the ester groups, and a α relaxation, associated to segmental motions appearing at temperatures higher than the glass transition temperature. Between the α and β relaxation PEN rich copolymers exhibit an additional maximum, β^*, associated to the motion of the naphthalene rings.[4,11] Of particular interest is the observation in the liquid crystalline phase of the PEN-*co*-PHB and PET-*co*-PHB copolyesters of two well differentiated maxima which correspond to the glass transition temperatures of the liquid crystalline and amorphous phase, respectively. Furthermore, it was found that the α relaxation of the liquid crystalline material was lying about 30 °C lower than that of the amorphous material. From this it was concluded that the glass transition of the liquid crystalline phase takes place at correspondingly lower temperatures. However, no evidence was given till now that T_α, in the liquid crystalline state is really a glass transition. The examination of the frequency dependence of the process could provide additional information concerning this question.

Dielectric spectroscopy is also a technique which has been shown to provide powerful information about the molecular dynamics of polymers and liquid crystals.[12−14] In particular, dielectric measurements complement dynamic mechanical analysis (DMA), for example, by determining the frequency dependence of the various processes over a wider range of frequencies. Dielectric measurements in PEN-*co*-PET copolyesters have been already used to elucidate the nature of the observed transitions.[11]

The aim of the present paper is to supplement previous investigations by DMA and NMR measurements and to report new results on the dielectric relaxation of the copolymers PEN-*co*-PHB and PET-*co*-PHB and of the terpolymer PET-*co*-PEN-*co*-PHB. As mentioned above, these systems may exhibit a liquid crystalline phase depending upon PHB concentration. In particular, we will discuss the influence of liquid crystalline order on the relaxation processes of these copolymers over a broad range of frequencies and temperatures using a wide range of compositions.

2. Experimental Part

A series of PEN-*co*-PHB and PET-*co*-PHB copolyesters having PEN:PHB molar ratios of 30:70, 40:60, 60:40, and 76:24 and PET:PHB ratios of 30:70, 60:40, 70:30, and 80:20 were investigated.

The copolymers were synthesized as described previously.[4] Amorphous films were obtained by melt pressing in vacuo for 1 min at a temperature 10 °C above the individual melting point of each polymer and subsequent quenching in ice water. The films had a thickness of approximately 100 μm. Circular gold electrodes, having several diameters between 1 and 3 cm, were brought onto the film surfaces by sputtering. The same films measured with electrodes of different diameters show

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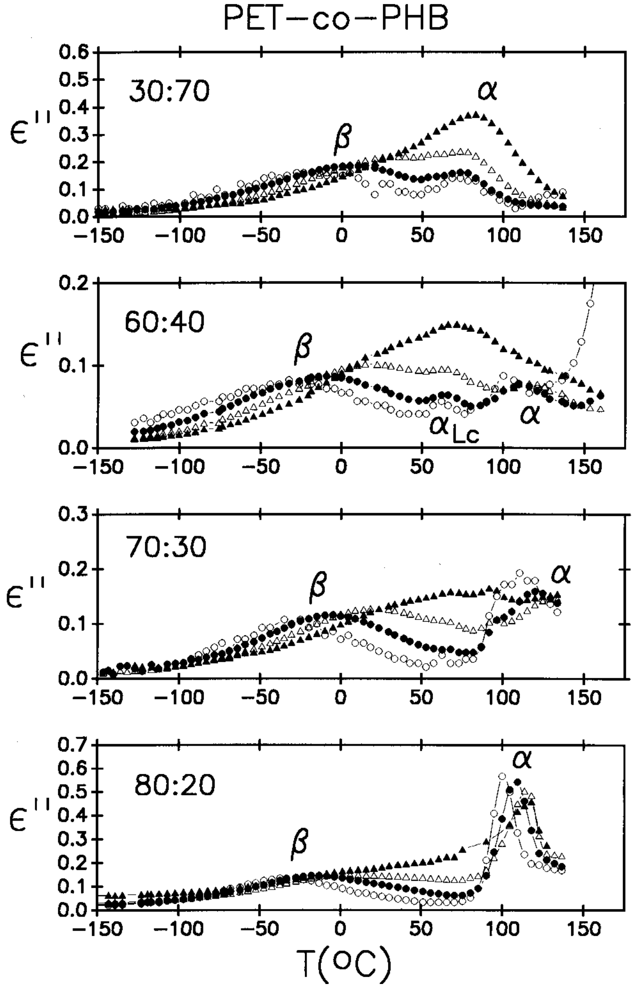

Figure 1. Isochronal dielectric loss ϵ'' as a function of temperature for PET-*co*-PHB copolymers with different molar ratios at 10^3 (○), 10^4 (●), 10^5 (△), and 10^6 (▲) Hz.

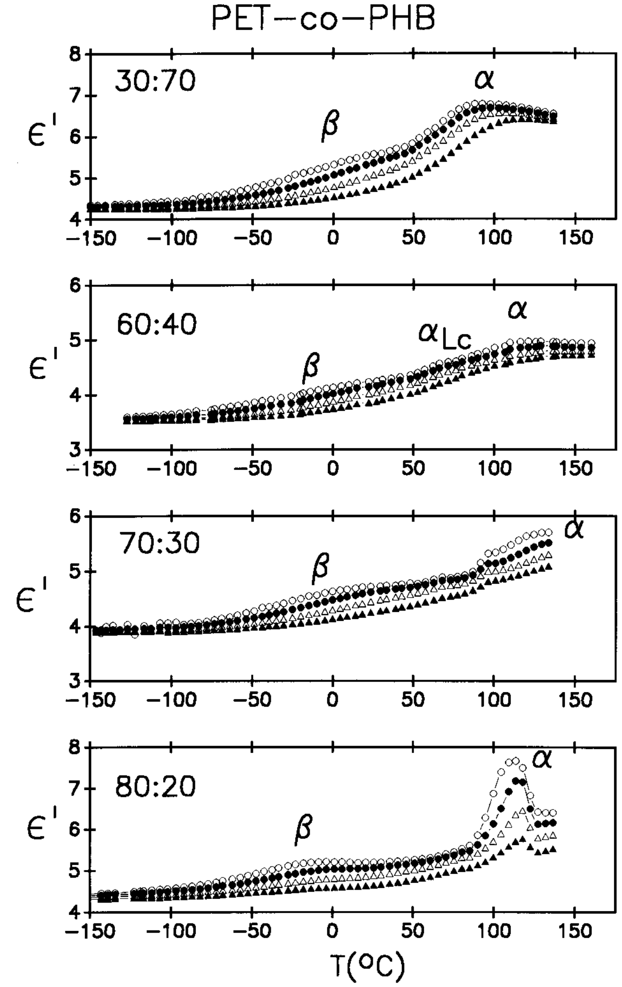

Figure 2. Isochronal dielectric permittivity ϵ' as a function of temperature for PET-*co*-PHB copolymers with different molar ratios. Same symbols as in Figure 1.

no qualitative differences. Each film was placed between two gold-plated stainless steel electrodes. The dielectric cell was introduced in a homemade furnace operating at a temperature controlled nitrogen atmosphere. Measurements of the complex dielectric permittivity ($\epsilon^* = \epsilon' - i\epsilon''$) were performed in the frequency range of 10^3–10^6 Hz by using a Hewlett-Packard impedance analyzer HP 4192A. The dielectric measurements were made at constant temperature from −150 to 150 °C at 5 °C steps. The error during the measuring time was estimated as ±0.1 °C. The thickness inhomogeneity of the films controls the error of the ϵ' and ϵ'' values which can be estimated to be below 15%.

3. Results

3.1. PET-*co*-PHB Copolyesters. Figures 1 and 2 show plots of the dielectric loss ϵ'', and the dielectric constant, ϵ', as a function of the temperature at different frequencies for the various PET:PHB compositions investigated. Two main relaxation processes, α and β, in order of decreasing temperature, are detected in the investigated temperature range. Both processes appear as a maximum in ϵ'', and a concurrent step in ϵ'. The decrease of ϵ' observed for 80:20 at $T > 120$ °C is due to the onset of crystallization. Both the α and β maxima move toward higher temperatures when the frequency is increased. Of particular interest is the behavior of the 60:40 PET-*co*-PHB system which exhibits three dielectric relaxations in the investigated temperature range as shown in Figures 1 and 2. In this case the observed relaxations have been labeled as α, α_{LC}, and β in order of decreasing temperature. The 70:30 PET-*co*-PHB copolyester exhibits a reproducible step and sharp maximum in both ϵ' and ϵ'' around 100 °C.

The temperature of maximum loss of the α and β processes at 10^3 Hz (T_α and T_β) for the PET:PHB systems is represented as a function of PHB content in Figure 3. As one can see, T_β remains almost constant around −25 °C up to a PHB concentration of 40%. For higher PHB concentrations, T_β rises gradually toward higher values. On the other hand, T_α exhibits two well separated regions showing a stepwise decrease at a PHB concentration of 40%. For PHB concentrations lower than 40%, T_α shows values which are close to 100 °C. However, at 40% PHB, in addition to the T_α value observed at 100 °C, a second value at 65 °C appears. For PHB concentrations higher than 40%, the low value of $T_\alpha \approx 65$ °C is the only one observed. This result is in full agreement with previous DMA measurements.[4]

It is of special interest to investigate the frequency dependence of the relaxation maximum which could not been performed by DMA. Figure 4 shows the variation of the logarithm of the maximum frequency as a function of the reciprocal temperature. The maxima of α relaxation in the liquid crystalline material give rise to a slope of the plot which is slightly higher than for the amorphous material and which is considerably different from that of the β maximum.

The dielectric strength of a given relaxation is defined as $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$, where ϵ_0 and ϵ_∞ are the relaxed and

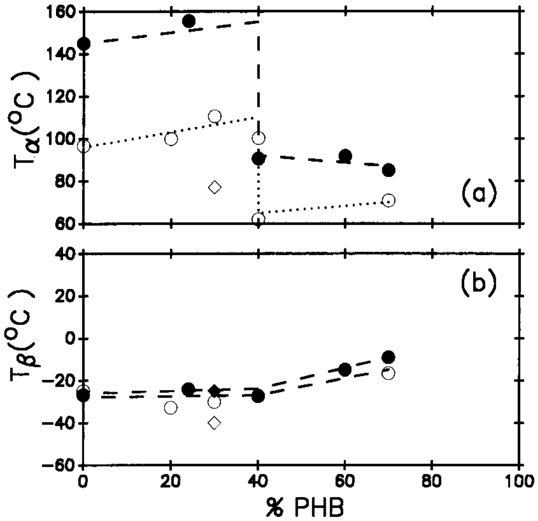

Figure 3. T_α (a) and T_β (b) at 10^3 Hz as a function of the PHB molar fraction for PET-*co*-PHB (○) and PEN-*co*-PHB (●). Data for PET-*co*-PEN-*co*-PHB (35:35:30), both liquid crystalline (◇) and isotropic (◆), are also included.

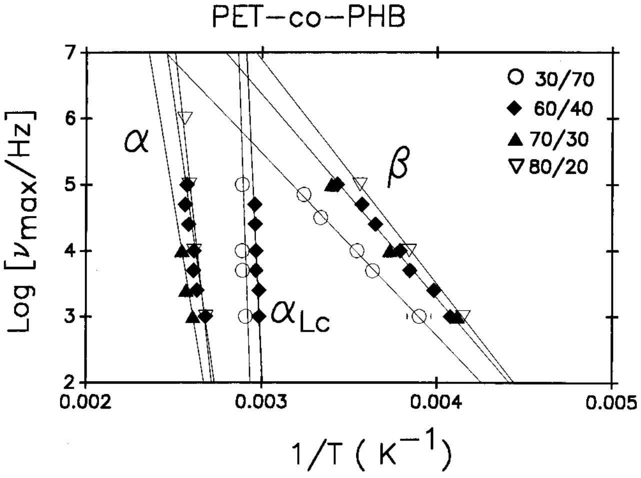

Figure 4. Log [ν_{max}] as a function of the reciprocal temperature for PET-*co*-PHB copolymers with different PET:PHB molar ratios: 80:20 (▽), 70:30 (▲), 60:40 (◆) and 30:70 (○). Lines for the α and α_{LC} processes are a guide for the eye.

unrelaxed dielectric permittivity values. In ideal cases, the value of $\Delta\epsilon$ can be obtained from Cole−Cole plots.[15] However, when dealing with weak and broad relaxations, as in some of the copolyesters investigated here, the experimental frequency window does not cover the whole relaxation spectrum and the procedure is not feasible. An estimation of the dielectric strength of the relaxations can be made by following graphical procedures involving the isochronal (ϵ'' vs T) plots.[16,17] For the β process the measured ϵ' value, at 10^3 Hz, for the lowest measured temperature is taken, as an approximation, for ϵ_∞. On the other hand, the ϵ' value at the temperature for which ϵ'' reaches a minimum, between the β and the α maxima, is taken as ϵ_0. This value is used as the ϵ_∞ value of the α process. Finally, the ϵ' value measured at its maximum can be used as ϵ_0 for the α process. This procedure has been illustrated graphically in Figure 5.

Figure 6(b) shows the plot of $\Delta\epsilon_\beta$, calculated as described above, versus the PHB concentration. The $\Delta\epsilon_\beta$ value shows first a slight increase with PHB concentration up to 40% PHB; then for the highest PHB concentration, a larger $\Delta\epsilon_\beta$ value is observed. The dielectric strength values for the α relaxation process ($\Delta\epsilon_\alpha$), which have been calculated by similar graphic procedure, are shown in Figure 6(a). Here, $\Delta\epsilon_\alpha$ first decreases, showing a minimum value around 40% PHB content, and then slightly increases for higher PHB concentrations.

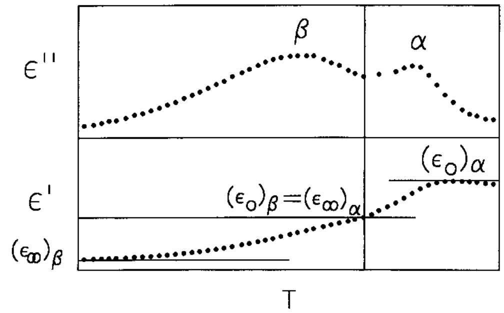

Figure 5. Schematic view of the graphical procedure used to estimate $\Delta\epsilon$ values.

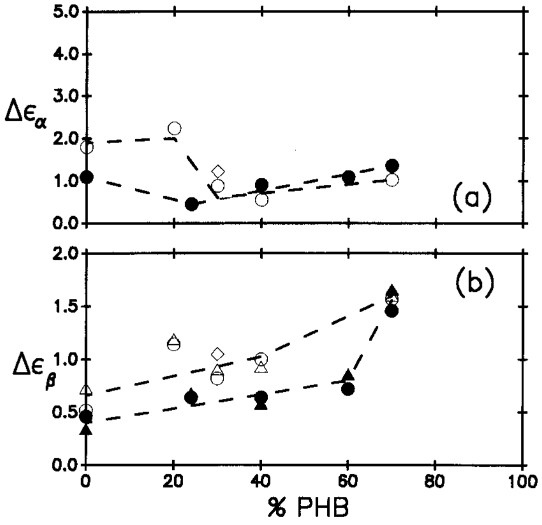

Figure 6. $\Delta\epsilon_\alpha$ (a) and $\Delta\epsilon_\beta$ (b) as a function of the PHB molar fraction for PET-*co*-PHB (○), PEN-*co*-PHB (●), and PET-*co*-PEN-*co*-PHB (35:35:30) (Lc) (◇). $\Delta\epsilon_\beta$ values derived from the fitting according to the HN relaxation function are also included: PET-*co*-PHB (△) and PEN-*co*-PHB (▲).

3.2. PEN-*co*-PHB Copolymers. Figures 7 and 8 illustrate the isochronal plot of ϵ'' and ϵ' as a function of the temperature measured at different frequencies, for the PEN-*co*-PHB copolymer series. As in the PET-*co*-PHB case, two main relaxation processes, α and β, are observed for all compositions. In the 30:70 copolymer, the α relaxation for ϵ'' is accompanied by a lower temperature shoulder. For the 60:40 PEN-*co*-PHB sample, a weak relaxation process is observed around 150 °C and 10^3 Hz, accordance with previous DMA measurements.[4] The 76:24 sample exhibits reproducible peaks in ϵ'' around 130 °C prior to the α relaxation process.

The maximum loss temperatures for the α and β process at 10^3 Hz (T_α and T_β) of the PEN-*co*-PHB systems are represented as a function of PHB content in Figure 3(a) and 3(b), respectively. The T_α dependence on PHB content follows a similar tendency as that observed for the PET-*co*-PHB copolymers. As already found by DMA measurements, a sudden decrease in T_α is observed when the PHB content reaches the value of 40%, which is explained by the change from an amorphous to a liquid crystalline state. The variations of $\Delta\epsilon$ for the α and β relaxations versus the PHB concentration calculated using the graphical procedure described in the previous paragraph are shown in Figures

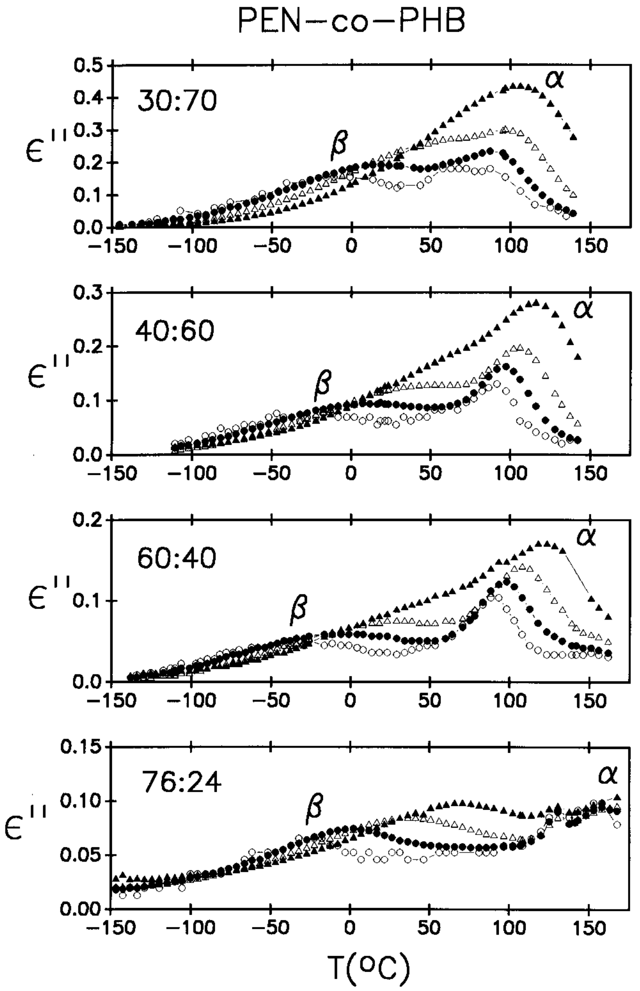

Figure 7. Isochronal dielectric loss ϵ'' as a function of temperature for PEN-*co*-PHB copolymers with different molar ratios at 10^3 (○), 10^4 (●), 10^5 (△) and 10^6 (▲) Hz.

6(a) and 6(b), respectively. Qualitatively, PEN-*co*-PHB systems present similar behavior features as that observed for PET-*co*-PHB showing a minimum at about 40% PHB concentration. Figure 9 shows the plot of the logarithm of the experimental $\nu_{\max}$ values for both the α and β relaxation processes as a function of the reciprocal temperature.

3.3. PET-*co*-PEN-*co*-PHB Ternary Copolyester. The ternary copolyester PET-*co*-PEN-*co*-PHB (35:35:30) is a material in which both the liquid crystalline and the amorphous states can be frozen-in by appropriated thermal treatments.[5,6] At thermal equilibrium, the terpolymer is liquid crystalline up to $T > 160$ °C. A progressive isotropization of the system is observed at higher temperatures, which is completed to 290 °C. Upon quenching from this temperature, the isotropic state can be frozen-in. A recovery of the liquid crystalline order is achieved once again, provided the sample is heated above 100 °C. The glass transition temperature of the amorphous state, $(T_g)_I = 95$ °C, is higher than the corresponding one of the liquid crystalline state, $(T_g)_{LC} = 60$ °C.[5,6]

Figures 10(a) and 11(a) show the variation of ϵ'' and ϵ' as a function of temperature at given frequencies for the quenched amorphous terpolymer. Similarly, as in the case of the binary copolymers, a β relaxation process is observed at lower temperatures. Also, in the case of the terpolymers the β maximum moves toward higher temperatures when the frequency is increased. At higher temperatures, in the temperature region for which the amorphous to liquid crystal transition has been observed, a sharp and strongly asymmetric maximum in ϵ'' is detected.

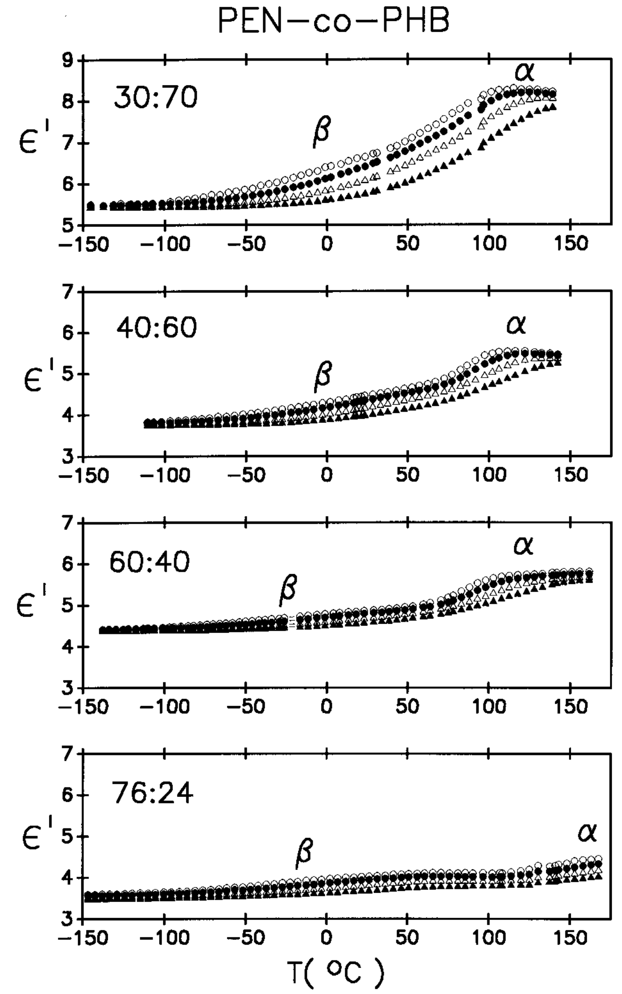

Figure 8. Isochronal dielectric permittivity ϵ'' as a function of temperature for PEN-*co*-PHB copolymers with different molar ratios. Same symbols as in Figure 7.

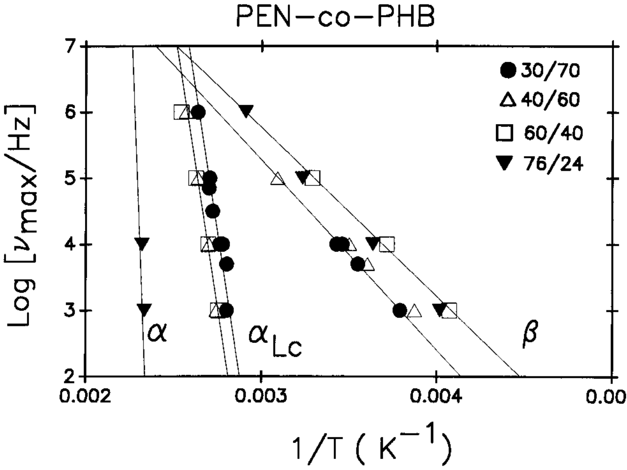

Figure 9. Log[$\nu_{\max}$] as a function of the reciprocal temperature for PEN-*co*-PHB copolymers with different PEN:PHB molar ratios. 76:24 (▼), 60:40 (□), 40:60 (△) and 30:70 (●). Lines for the α and α_{LC} processes are a guide for the eye.

Due to the fact that the sample is heated "in situ" above 100 °C, after the first run, the sample is expected to be, essentially, in the liquid crystalline state. Figures 10(b) and 11(b) show the change of ϵ'' and ϵ' as a

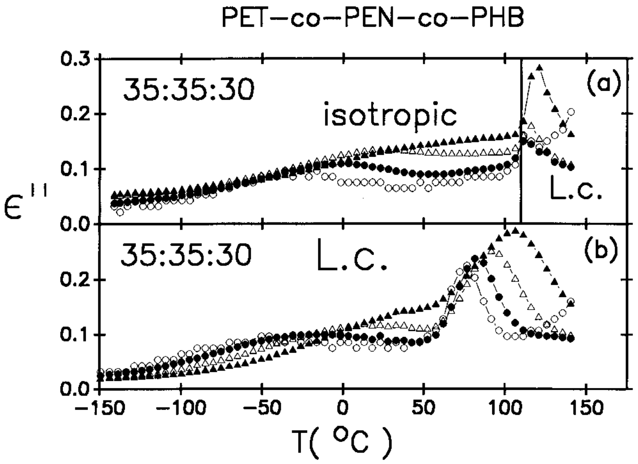

Figure 10. ϵ'' values as a function of temperature for PET-*co*-PEN-*co*-PHB (35:35:30) terpolymers in the isotropic (a) and liquid crystalline state (b): 10^3 (○), 10^4 (●), 10^5 (△) and 10^6 (▲) Hz.

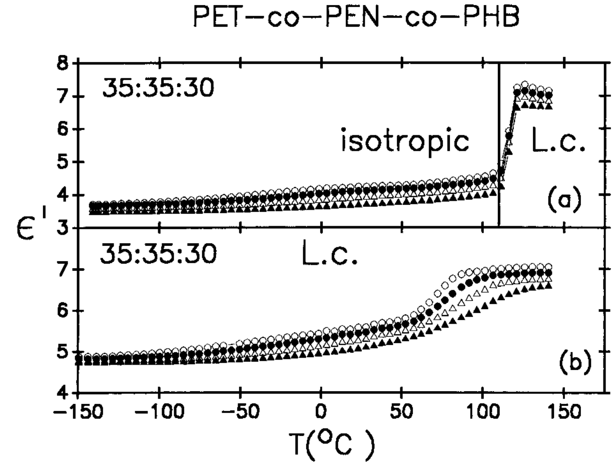

Figure 11. ϵ' values as a function of temperature for PET-*co*-PEN-*co*-PHB (35:35:30) terpolymers in the isotropic (a) and in the liquid crystalline state (b). Same symbols as in Figure 10.

function of the temperature at different frequencies for the terpolymer during a second heating run. Here, similarly as in the case of the binary copolymers, two main relaxation processes, α and *β*, are observed.

4. Discussion

4.1. Interpretation of the *β* Relaxation.

4.1.1. Relaxation Time and Dielectric Strength. As in most copolyesters, the *β* process observed in all PET-*co*-PHB and PEN-*co*-PHB copolymers investigated can be associated to the local motion of the ester groups attached to the polymeric chain.[11,16,18−20] The maximum loss frequency allows one to define an average relaxation time $\langle\tau\rangle = (2\pi\nu_{\max})^{-1}$,[13] which, for a subglass relaxation processes, usually follows a temperature dependence as:

$$\langle\tau\rangle = [h/(kT)]\exp(-\Delta S/K)\exp(\Delta H/kT) \qquad (1)$$

where ΔS and ΔH are the molar entropy and enthalpy of activation, respectively, and h and k are the Planck and Boltzmann constants, respectively.[21] The temperature dependence of the relaxation time is led by the exponential factor. By neglecting the influence of the entropy prefactor eq 1 gives rise to the well-known Arrhenius law by identifying ΔH with the activation energy of the process. By fitting straight lines in Figures 4 and 9 to the experimental data corresponding to the *β* process, activation energies E_A of about 53 kJ/mol are obtained. This value is in agreement with the expectations for the local movement of the ester groups of the polymeric main chain.[11,20,22]

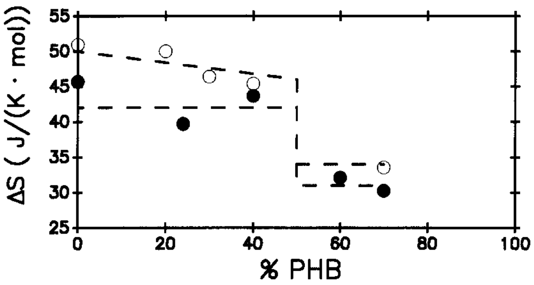

Figure 12. ΔS values for the *β* relaxation process estimated from eq 1 for PET-*co*-PHB (○) and PEN-*co*-PHB (●).

As shown in Figure 3(b), the transition temperature of the *β* relaxation measured at 10^3 Hz increases for PHB concentrations higher than 40%. This result leads in Figure 9 to a separation of the 30:70 and 40:60 curves from the 60:40 and 76:24 ones. It is to be noted that, around a 40% PHB concentration, both PET-*co*-PHB and PEN-*co*-PHB copolymers show up a liquid crystalline phase.[4] According to eq 1, the entropic exponential factor may shift the relaxation straight lines parallel to the reciprocal temperature axis (Figures 4 and 9) depending on the value of ΔS. Thus, our measurements can be explained by assuming that the entropy of activation for the *β* relaxation process ($[\Delta S]_{\mathrm{LC}}$) in the liquid crystalline samples is smaller than that for the amorphous samples ($[\Delta S]_{\mathrm{a}}$). This is a reasonable result considering that liquid crystalline polymers are characterized by the existence of some order which is absent in isotropic amorphous phases.

We have estimated the ΔS values by introducing the calculated value of ΔH in eq 1. The data shown in Figure 12 exhibit a stepwise decrease in ΔS for a PHB content lower than 40%. This observation indicates that, in spite of the local character of the motion associated to the *β* process, the state of molecular order in these copolyesters may substantially affect the dynamics of the process.

The relaxation strength, $\Delta\epsilon$, of a polymeric chain with dipolar units can be expressed by the Kirkwood–Fröhlich equation:[22]

$$\Delta\epsilon \propto \frac{N}{T}\, g(T)\, \mu^2(T) \qquad (2)$$

where N is the number of dipoles, μ is the effective dipole moment, and g is the correlation factor which contains contributions of both inter- and intrachain dipolar correlation. Experiments performed in poly(ethylene terephthalate) have shown that $\Delta\epsilon_\beta$ decreases with increasing degree of crystallinity.[20] The freezing of the dipoles in the crystals stops the motion which is restricted to occur in the remaining amorphous phase. In our case we observed that $\Delta\epsilon_\beta$ progressively increases as liquid crystalline order appears (Figure 6(b)). By considering that PEN and PET monomeric units have two ester dipoles and PHB units only have a single one, we would expect a reduction of the overall amount of dipoles, N, per monomeric unit as the molar fraction of PHB increases. Therefore, the observed increase of $\Delta\epsilon_\beta$ has to be attributed to an increase of the correlation factor g. This effect can be understood as resulting from

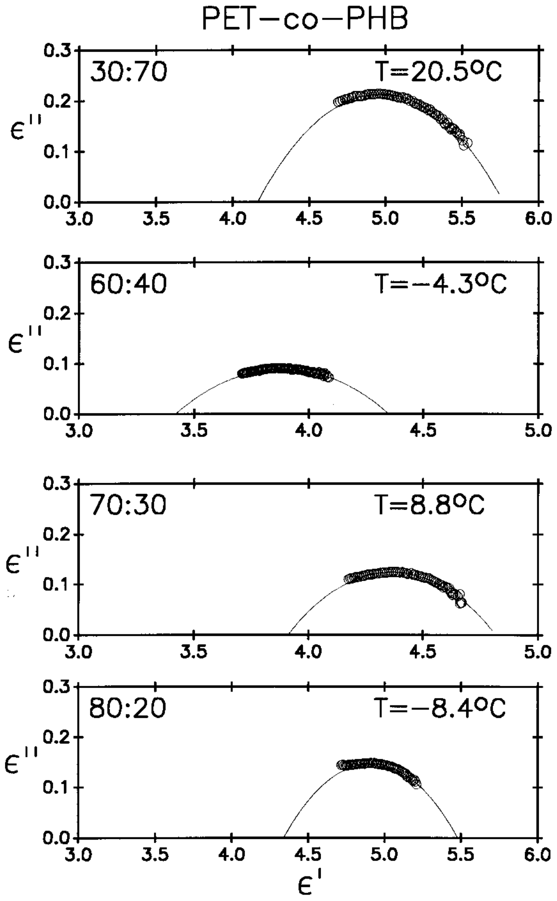

Figure 13. Cole−Cole plots in the temperature region of the β relaxation process for the PET-*co*-PHB copolymers.

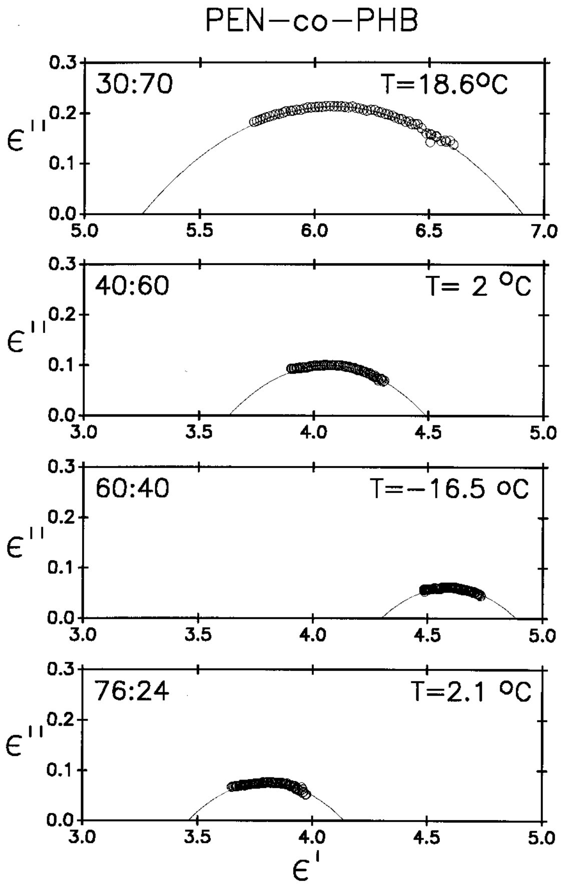

Figure 14. Cole−Cole plots in the temperature region of the β relaxation process for the PEN-*co*-PHB copolymers.

an enhancement of the order induced in the liquid crystalline state.

4.1.2. Phenomenological Analysis of the β Relaxation. From the Cole−Cole plots, in the temperature region of the β relaxation process (see Figures 13 and 14) for PET-*co*-PHB and PEN-*co*-PHB, respectively, a fitting of the experimental results can be attempted by using the Havriliak−Negami (HN) equation:

$$\epsilon^* = \Delta\epsilon^* + \epsilon_\infty \qquad (3)$$

with:

$$\Delta\epsilon^* = \frac{\epsilon_0 - \epsilon_\infty}{[1 + (i\omega\tau_0)^b]^c} \qquad (4)$$

where ϵ_0 and ϵ_∞ are the relaxed and unrelaxed dielectric constant values, τ_0 is the central relaxation time, and b and c are parameters which describe the shape of the relaxation time distribution function.[15] For symmetric curves ($c = 1$), the HN equation renders the Cole−Cole equation. In our case the best fitting of experimental results to eqs 3 and 4 can be obtained by symmetric curves ($c = 1$) as shown by the continuous lines in Figure 13 (PET-*co*-PHB) and Figure 14 (PEN-*co*-PHB) which represent best fits of the experimental results to eqs 3 and 4. The fitting parameters corresponding to Figures 13 and 14 are presented in Tables 1 and 2. The $\Delta\epsilon_\beta$ values derived from the fittings are in agreement with those derived from the graphical procedure shown in Figure 6. This fact further supports the interpretation of the $\Delta\epsilon_\beta$ variation with the PHB molar concentration proposed in the previous section. It is worth mentioning that the $\Delta\epsilon_\beta$ values derived for the PET-*co*-PHB 70:30 copolyester are higher than the reported ones by Gedde et al. for PET-*co*-PHB 20:80 ($\Delta\epsilon_\beta \approx 0.8$).[1] It is noted that in PET-*co*-PHB copolymers a high degree crystallinity can develop, provided the molar fraction of PHB is higher than 80%.[5] On the other hand, it has been shown that $\Delta\epsilon_\beta$ decreases as crystallinity increases, owing to the immobilization of the dipoles within the crystalline phase.[20] We can assume that the low $\Delta\epsilon_\beta$ vaue reported for the 80:20 copolymer may be due to a higher degree of crystallinity in this sample.

Table 1. b_β, $\Delta\epsilon_\beta$, and $\tau_{0\beta}$ Obtained from the Fitting of Equation 3 in the Case of the β Relaxation Process for PET-*co*-PHB Copolyesters

PET:PHB	T (°C)	$\Delta\epsilon_\beta$	b_β	$\tau_{0\beta}$
30:70	20.5	1.6	0.33	1.2×10^{-6}
60:40	−4.3	0.93	0.24	3.9×10^{-6}
70:30	8.8	0.9	0.34	1.8×10^{-6}
80:20	−8.4	1.14	0.32	5.5×10^{-6}

Table 2. b_β, $\Delta\epsilon_\beta$, and $\tau_{0\beta}$ Obtained from the Fitting of Equation 3 in the Case of the β Relaxation Process for PEN-*co*-PHB Copolyesters

PEN:PHB	T (°C)	$\Delta\epsilon_\beta$	b_β	$\tau_{0\beta}$
30:70	18.6	1.6	0.32	2.2×10^{-6}
40:60	2	0.86	0.29	2.3×10^{-6}
60:40	−16.5	0.58	0.26	3.8×10^{-6}
76:24	2.1	0.68	0.28	3.7×10^{-6}

4.2. Interpretation of the α Relaxation. In preceding investigations by means of DMA, the α relaxation has been attributed to the glass transition. While this was generally accepted in the case of isotropic copolyesters, the assignment to a glass transition in the case of the liquid crystalline copolyesters remained somewhat questionable, in particular, because the T_g values found were lower than those for the amorphous state. As the frequency dependence of the glass transition is assumed to follow a Vogel–Fülcher type relation while other transitions can be described by the Arrhenius equation, frequency dependent measurements can result in important new information concerning this question.

Our results in Figures 4 and 9 clearly demonstrate that the frequency dependence of the maxima in the liquid crystalline state is similar to that of the α maximum in the isotropic amorphous state. Though not sufficient points are available to determine the paramters of the Vogel–Fülcher equation, there exist sufficient data to recognize that the activation energy is much larger than that of the β process. Furthermore, it has been demonstrated in a previous publication[23] that, in the case of the ternary copolyester, crystallization already occurs just above the glass transition of the liquid crystalline phase which is well below that of the amorphous phase. Thus, the interpretation of T_α as the glass transition temperature of the liquid crystalline state is now well founded.

As PHB segments are introduced in the copolymer chains, an initial linear increase of T_α resembling a Gordon Taylor behavior is observed. For a PHB molar fraction of 40%, T_α starts to deviate from the linear behavior. Previous DMA experiments have shown that in the 60:40 PET-*co*-PHB system there is a coexistence of an amorphous and a liquid crystalline phase with well differentiated glass transition temperatures.[4]

One may ask at this stage why the glass transition of the liquid crystalline state is lower than that of the isotropic amorphous state. One explanation for this effect can be given if one considers the nature of the molecular motions above T_g occurring in the liquid crystalline and amorphous states. It is accepted that at the glass transition temperature the free volume of the polymer assumes the smallest value which is necessary to allow the molecules to perform the motions which make the sample fluid. In the isotropic state, segmental motions involving several backbone units lead to conformational changes of the chains and provoke a decrease of the viscosity of the system. The motions occurring close to T_g in the liquid crystalline state can be of rotations of the elongated chains around their axes, translational motions of the chains, and some motions of small atomic groups. The free volume necessary to perform these latter kinds of motions is considerably smaller than the one which allows segmental motion in the amorphous isotropic case and therefore can be achieved at lower temperatures.

The copolyester PET-*co*-PHB (60:40) shows two a maxima. In accordance with previous DMA investigations,[4] we can associate the first of the relaxations observed (Figure 1) to the α process occurring in the isotropic amorphous phase, while the second one, in order of decreasing temperature, will be attributed to the corresponding α process of the liquid crystalline phase (α_{LC}). This behavior is quite different from the β process in which T_β is higher for the liquid crystal than for the isotropic state.

The relaxation strength $\Delta\epsilon_\alpha$, as derived by a graphical method, exhibits a minimum around 40% PHB (Figure 6). For molar concentrations smaller than 40% there is a decrease of $\Delta\epsilon_\alpha$ as the samples approach this value. As pointed out before, the inclusion of PHB segments in the polymeric chain provokes a reduction of the overall number of dipoles per monomeric unit. The segmental motions above T_g extending over several backbone units are more affected by the reduction of the number of dipoles than by the local motions involved in the β relaxation. For PHB molar fractions higher than 40% the copolyesters exhibit a liquid crystalline structure. Thus, as pointed out for the β relaxation, an enhancement of the dipolar correlation leading to the observed increase of $\Delta\epsilon_\alpha$ is expected. As observed for the β relaxation process, the $\Delta\epsilon_\alpha$ estimated for PET-*co*-PHB (70:30) is higher than that reported for PET-*co*-PHB (80:20) ($\Delta\epsilon_\alpha \approx 0.38$).[20] According to the interpretations of this finding, for the β relaxation process we can attempt to attribute this effect to the onset of PHB crystallinity for PHB molar content >80%.

4.3. Amorphous to Liquid Crystalline Transition in the Ternary Copolyester. The sharpness and asymmetry exhibited by the high temperature relaxation process observed in the terpolymer in the amorphous state (Figure 10(a)) suggest that these effects are due to the occurrence of the amorphous to liquid crystalline transition observed in this temperature range by other methods.[5,6] In DMA and calorimetric measurements the glass transition has been observed at temperatures slightly below this transition into the liquid crystalline state. In the present dielectric measurements, due to the higher frequency, the α relaxation is shifted to high temperatures and is, thus, masked by the transition into the liquid crystalline state. The observed maximum in ϵ'' can be attributed to the tail of the α relaxation characteristic of the liquid crystalline state which, for $T > 100$ °C, exhibits a $\nu_{max} > 10^5$ Hz. This result is supported by the second run experiment (Figure 10(b)) which shows that the α relaxation of the liquid crystalline sample occurs at lower temperature than in the amorphous case. Moreover, the small peaks in the first runs (quenched amorphous samples) of 70:30 PET-*co*-PHB and 76:24 PEN-*co*-PHB can be attributed, according to the results of Figure 10(a), to transitions probably occurring in regions in which the PET:PHB or PEN:PHB ratio deviates from the average.

The $\Delta\epsilon$ values for the β and α relaxation for the terpolymer fit within the general trend for the copolyesters represented in Figure 6 if one considers the amount of PHB present in the former (30%). Similarly, it occurs with the characteristic temperatures of the α and β processes at 1 kHz (Figure 3). As is shown in this figure, the T_α for the liquid crystalline terpolymer is located at the level of the liquid crystalline plateau lying between the measured values of the liquid crystalline PET-*co*-PHB and PEN-*co*-PHB copolymers. This finding suggests that, locally, the distribution and mixing of PET-PHB and PEN-PHB segments is rather homogeneous with almost an absence of phase segregation.

5. Conclusions

The dielectric relaxation of binary and ternary random copolymers of PET, PEN, and PHB exhibits mainly two processes (α and β) in the investigated temperature range:

The α relaxation is attributed to the glass transition of the copolyesters, which depends on the state of molecular ordering of the copolymers. Lower T_α (1 kHz) values are observed for the amorphous samples. The frequency dependence of T_α in the liquid crystalline state is very small, and similar to that in the amorphous state. This result can be considered as additional evidence for the interpretation of T_α as a glass transition. This lower glass transition in the liquid crystalline state is explained by considering that, in the liquid crystalline state, the motions occurring close to T_g are expected to be of a more localized nature as those characteristic of the isotropic amorphous state. The free volume necessary to perform motions more localized in the liquid crystalline state can be reached at lower temperature than the larger free volume necessary for more extended segmental motions occurring in the isotropic state.

The β process is assigned to a local motion of the ester groups attached to the aromatic rings, which also depends on molecular order. Higher T_β (1 kHz) values are observed as liquid crystalline order appears (PHB > 40%). Such an effect can be explained by assuming that the entropy of activation of the β process for the liquid crystalline samples is smaller than the corresponding one for the isotropic amorphous samples due to the existence of nematic order in the liquid crystalline state.

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