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Dielectric relaxation of poly(ester-ether-carbonate) multiblock terpolymers

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Abstract The dielectric properties of a series of poly(ester-ether-carbonate) multiblock terpolymers have been investigated as a function of ether and carbonate composition in the frequency range of 10^3 – 10^6 Hz. The degree of polymerization of the samples was determined by viscosimetry measurements. The weight fraction, degree of crystallinity, and melting temperatures were characterized by means of x-ray diffraction and DSC methods. Dielectric behavior has been discussed in terms of Havriliak–Negami formulation. The

variation of the dielectric properties with temperature has been associated with two relaxation processes: a) the γ -relaxation process observed at low temperature, which is associated to local motion of polar groups attached to both the soft and the hard segments, and b) the β process assigned to long-range molecular motions above the glass transition temperature.

Key words Dielectric relaxation – block copolymers – thermoplastic elastomers

Introduction

It is known that two dissimilar polymers are thermodynamically incompatible with each other when the specific interaction between them does not lead to a negative heat of mixing [1]. Addition of incompatible species in a block copolymer has profound effects on the phase behavior and on the morphology of the resulting separated microphases. Microphase separated block copolymers exhibit thermal and mechanical properties unlike those exhibited by the single homopolymers. For this reason, it is important to well understand the relationship between physical properties, chemical composition, and microstructure [2–7]. Several papers have been recently devoted to the segmental dynamics of these block copolymers [8–9].

Microphase separation in block copolymers may lead to multimicrophase systems. For example, a block copolymer consisting of poly(tetramethylene oxide) (PTMO) and polyamide 12 (PA12) segments may form a four-phase system [11]. Similar effects have been described in a poly(ester-ether-siloxane) block terpolymer [12].

Such a multi-microphase structure is characteristic of thermoplastic elastomer polymeric materials exhibiting combined properties of vulcanized rubbers and plastics. Thermoplastic elastomers are composed of amorphous “soft” segments characterized by a low glass transition temperature and “hard” segments having high strength and high melting temperatures [2]. Recently, aliphatic poly(carbonate) (PC) has been used as a soft segment to obtain polyurethane or polyester based block copolymers [13–15].

In the present paper, we report results relating to the molecular dynamics of new poly(ester-ether-carbonate) multiblock terpolymers with varying amount of ether and carbonate soft segment content, as revealed by dielectric spectroscopy.

Experimental

Synthesis of the terpolymers

Figure 1 shows the general formula representing the poly(ester-ether-carbonate) terpolymers (PEEC). For the synthesis of the terpolymers a three-stage poly-condensation method, similar to that used in the preparation of poly(ester-carbonate) copolymers [12], was used:

- Dimethylterephthalate and 1,4-butanediol were first heated in the temperature range of 150–200 °C, in the presence of tetrabutoxy-titanate as first catalyst, until more than 90% of the stoichiometric amount of methanol was evaporated.
- The temperature was then increased up to 200 °C under reduced pressure. Under these conditions oligomers of butylene terephthalate (PBT) were obtained.
- Different amounts of α,ω -dihydroxypoly(oxytertramethylene) (PO4, Terathane 1000 from Dupont (USA), $\overline{Mn} = 1000$, $\rho = 0.974$ g/cm³) and/or α,ω -dihydroxypoly(alkylenecarbonate) (PC, Duracarb 124 from PPG Inc. (USA), $\overline{Mn} = 1500$, $\rho = 1.076$ g/cm³) were finally added. At this point, magnesium hydrohexabutoxytitanate was employed as a second catalyst and a phenol derivative (Irganox 1010, Ciba Geigy) as antioxidant agent. The reaction was carried out at 260 °C and 0.5–0.7 hPa of reduced pressure until the product of highest melt viscosity, under these conditions, was obtained.

Characterization of Duracarb 124 by elementary analysis, infrared spectroscopy and NMR reveals that this compound is a poly(alkylene-ether-carbonate) with an

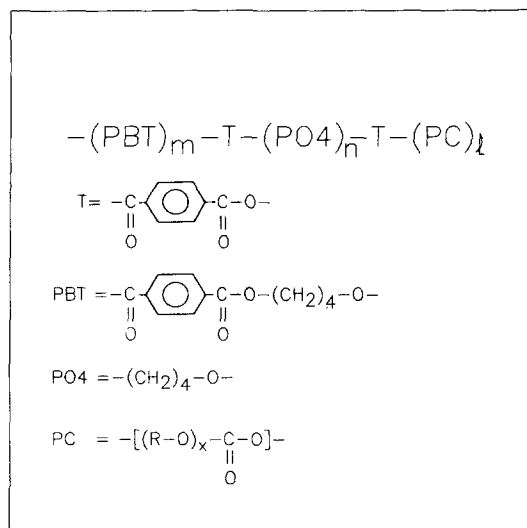


Fig. 1 Scheme of the investigated terpolymers. $n \approx 14$, m values given in Table 1, $l \approx 10$ and $x \approx 1.12$, $\text{R} = \text{C}_6\text{H}_{12}$ isomers. The given data are average values derived from stoichiometric ratio and NMR analysis

ether content of $\approx 8\%$, R being essentially C_6H_{12} isomers (see Fig. 1). Terpolymers with a varying content of PO4 and PC segment between 0 to 40% in weight and a constant PBT segment content of 60% were prepared. The degree of polymerization and the limiting viscosity number $[\eta]$ as determined at 30° from solution in phenol-trichloroethylene (1:1 vol) of the synthesized terpolymers are given in Table 1.

Sample preparation and techniques

The obtained polymers were extruded from the reactor and granulated. The granulated polymers were dried for 8 h at 70 °C under reduced pressure (≈ 7 hPa) and finally injection molded at ≈ 50 MPa. Films for dielectric measurements were prepared by compression molding between thin Teflon films at a temperature 20 °C higher than the corresponding melting point of each terpolymer. The films, with a thickness of approximately 300 μm , were

Table 1 Characteristics of poly(ester-ether-carbonate) block terpolymers

Sample	Segment content, wt%			m^+ polycon. degree	T_g^* °C	$[\eta]$ dL/g	T_m °C	X_c %
	PBT	PO4	PC					
60/40/0	60	40	0	7.7	-56	1.16	201	18.3
60/32/8	60	32	8	8.4	-45	1.19	179	20.6
60/20/20	60	20	20	9.4	-32	1.16	151	14.8
60/12/28	60	12	28	10.1	-10	1.04	131	13.7
60/0/40	60	0	40	11.1	1	1.02	102	7.8

subsequently quenched at room temperature. Calorimetric measurements were carried out using a Perkin-Elmer DSC-4 scanning calorimeter. Calibration was made by using indium standards. Wide-angle x-ray diffraction (WAXD) experiments were performed using a Rigaku goniometer at room temperature and Ni filtered $\text{CuK}\alpha$ radiation from a Rigaku rotating anode generator.

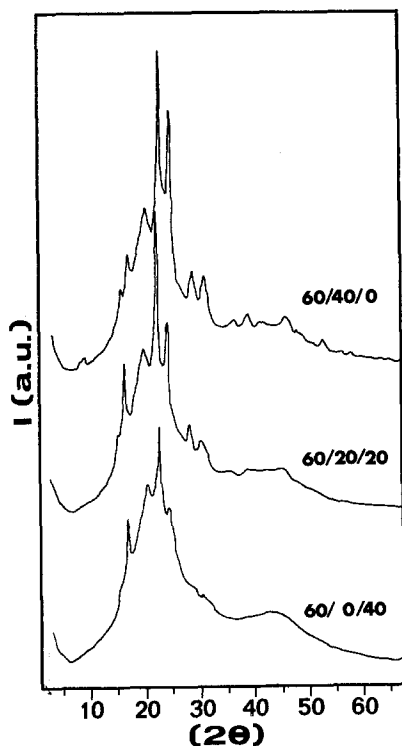
Dielectric permittivity ($\epsilon^* = \epsilon' - i\epsilon''$) measurements were performed in the frequency range of 10^3 to 10^6 Hz by using a Hewlett-Packard impedance analyzer HP 4192A. Films were provided with circular gold electrodes 3–4 cm in diameter by sputtering. The films were placed between two gold-plated stainless steel electrodes. The dielectric cell was introduced in a home-made cryostat operating in a temperature-controlled nitrogen atmosphere. The temperature error during the measuring time was estimated to be ± 0.1 °C.

Results

Wide-angle x-ray diffraction

X-ray scattering patterns of the investigated terpolymers show (Fig. 2) the existence of well defined Bragg maxima superimposed over two amorphous halos centered at about 22 and 42 ($2\theta^\circ$). The position of the Bragg maxima

Fig. 2 WAXD diffractograms of (a) 60/40/0, (b) 60/20/20, (c) 60/0/40



correspond to the α crystal phase of the PBT homopolymer [2]. With increasing PC content, at the expense of the PO4 component, a relative decrease in the scattering intensity of the Bragg peaks and the disappearance of the higher scattering reflections is observed.

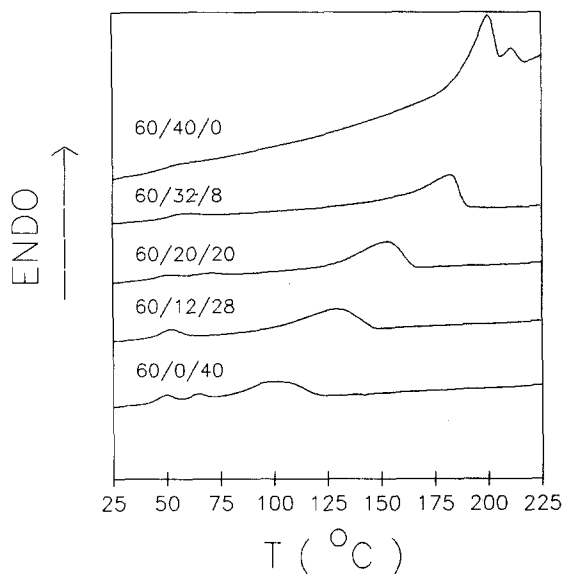
Calorimetry

Thermograms of the PEEC terpolymers investigated are shown in Fig. 3. It is seen that the melting temperatures decrease as the PC soft-segment content increases. The 60/40/0 system exhibits a multiple endothermic melting behavior. All systems show the presence of a small endothermic transition about 50 °C which for the 60/0/40 terpolymer appears in the form of two endothermic peaks. The lowest transition temperature (not shown in Fig. 3) corresponding to the glass transition increases with the PC segment content (see Table 1). In an attempt to characterize the degree of crystallinity of the systems, the area under the melting endotherms has been measured and normalized by the sample mass. By using 34.63 cal/g [17] as the value for the 100% crystalline PBT estimates of crystallinity can be obtained. The values are presented in Table 1.

Dielectric relaxation measurements

The dielectric loss, ϵ'' , and dielectric constant, ϵ' , values for the two PEEC extreme terpolymers (60/40/0 and 60/0/40)

Fig. 3 DSC traces for PEEC terpolymers. PBT/PO4/PC at different ratios. Heating rate: 20 °C/min



are shown in Figs. 4 and 5 respectively. The dielectric loss values for 60/40/0 (Fig. 4a) reveal the existence of a broad relaxation appearing at $\approx 0^\circ\text{C}$ for 10 kHz. We will refer to this relaxation as β , similarly as in the case of PBT-PO4 copolymers [19, 20]. The β process is accompanied by a lower temperature relaxation, γ , which appears as a shoulder at $\approx -90^\circ\text{C}$ and 1 kHz. As frequency is increased the maximum loss peak for both relaxations shifts towards higher temperatures. The large increase of ϵ'' at higher temperatures ($\approx 100\text{--}110^\circ$) for two frequencies is characteristic of semicrystalline polymers and is due to Maxwell-Wagner-Sillars polarization which appears due to the existence of interfaces between crystalline and amorphous domains [21].

For the 60/0/40 system (Fig. 5) also two relaxation process, β and γ (in order of decreasing temperatures) are detected. Both, the β and the γ relaxation appear at higher temperatures than those for the 60/40/0 copolymer. Here, both relaxation maxima are clearly separated from each other even at lower frequencies (1, 10, and 100 kHz).

Both relaxation processes appear as maxima in the dielectric loss measurements (Figs. 4a and 5a) and as con-

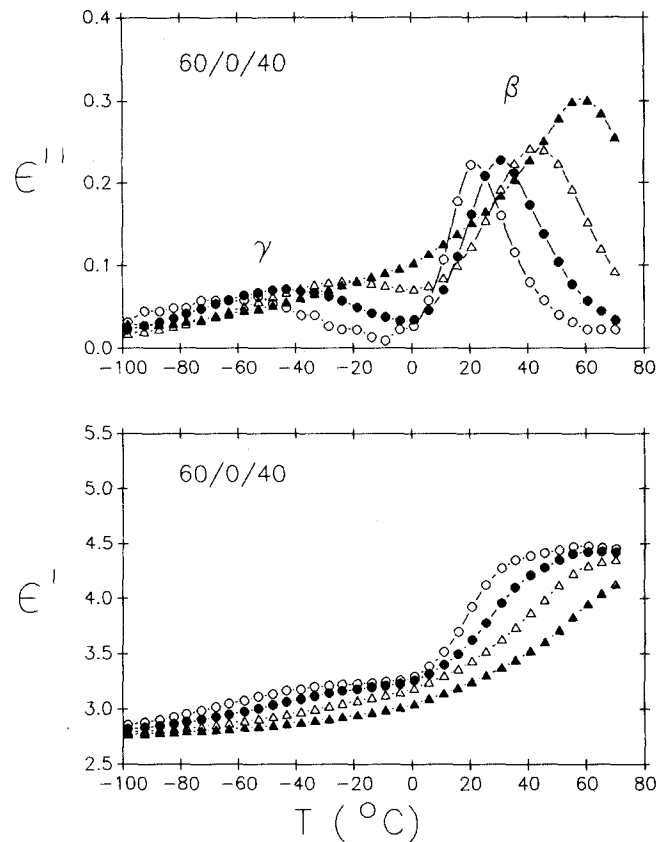


Fig. 5 ϵ'' (a) and ϵ' (b) for the 60/0/40 terpolymer as a function of the temperature. (○) 1 kHz, (●) 10 kHz, (△) 100 kHz and (▲) 1000 kHz

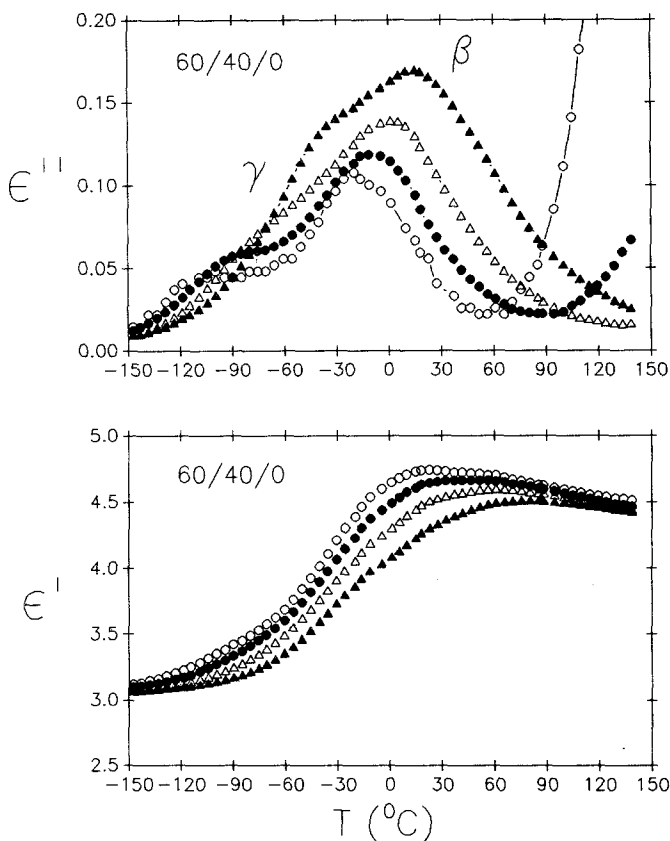


Fig. 4 ϵ'' (a) and ϵ' (b) for the 60/40/0 terpolymer as a function of the temperature. (○) 1 kHz, (●) 10 kHz, (△) 100 kHz and (▲) 1000 kHz

current steps in the dielectric constant measurements (Figs. 4b and 5b).

The effect of varying the amount of PC and PO4 segment content in the dielectric relaxation of the terpolymers is illustrated in Figs. 6 and 7. The maxima in ϵ'' corresponding to both the β and γ processes shift towards higher temperatures as the amount of PC segments increases and PO4 segments decrease.

The frequency of the maximum loss, ν_{\max} , for the β and γ processes are represented in Fig. 8 as a function of the reciprocal temperature for different samples. The present values have been derived from the isochronal plots of ϵ'' vs. temperature of Figs. 4–7 with the exception of the 60/40/0 and 60/32/8 systems. In these latter cases the weakness and broadening of the γ process prevents from accurate measuring of ν_{\max} from the isochronal plots. For this reason the corresponding values were measured from the isothermal ϵ'' vs frequency and Cole–Cole plots (Fig. 9). In the case of the 60/20/20 terpolymer the high mixing of the γ and β processes do not allow to obtain the ν_{\max} values with accuracy.

The β process exhibits a temperature dependence as observed for the relaxation associated to the motions

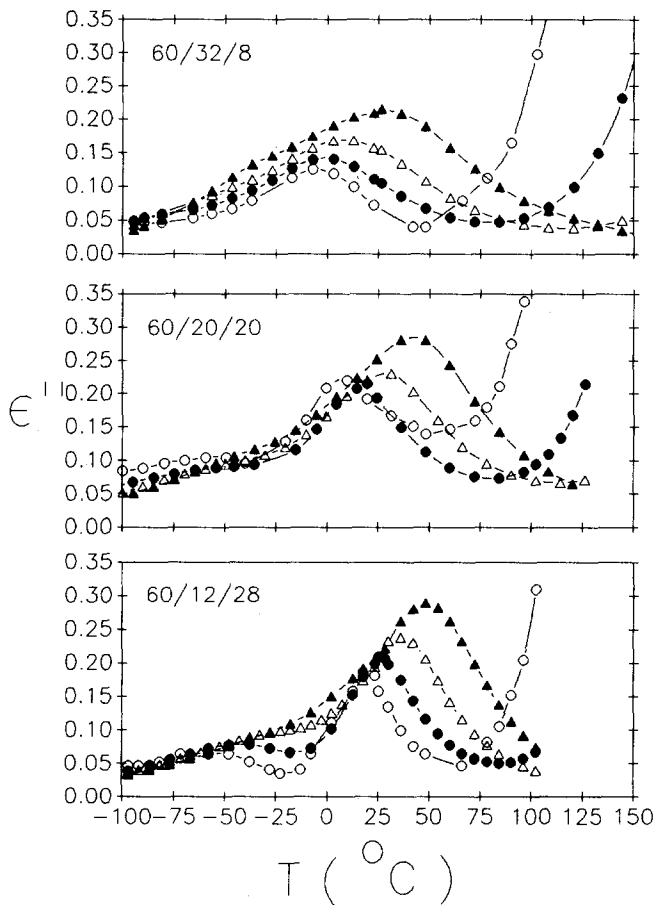


Fig. 6 ϵ'' data for different terpolymers as a function of the temperature. (○) 1 kHz, (●) 10 kHz, (△) 100 kHz and (▲) 1000 kHz

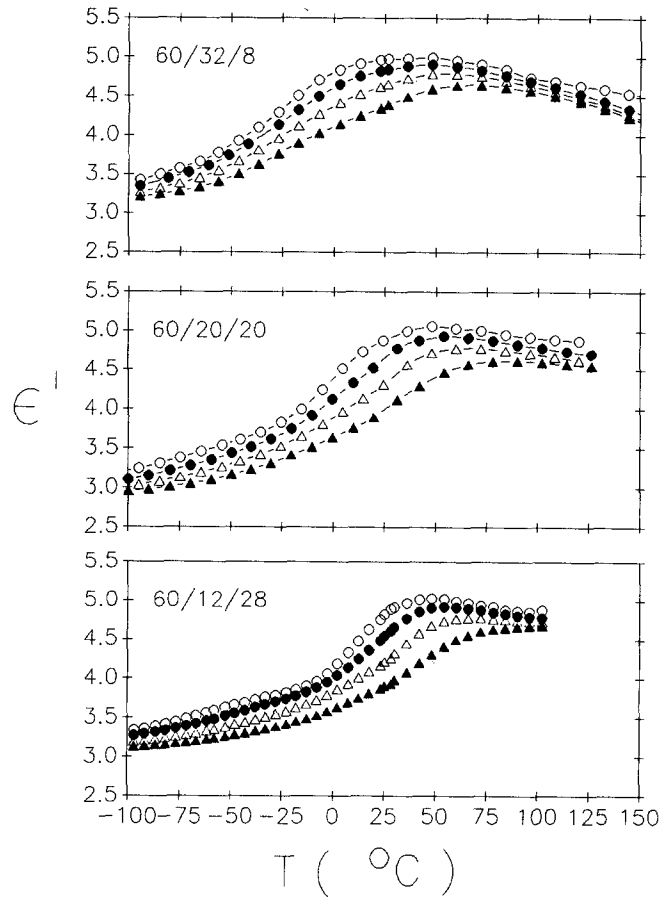


Fig. 7 ϵ' data for different terpolymers as a function of the temperature. (○) 1 kHz, (●) 10 kHz, (△) 100 kHz and (▲) 1000 kHz

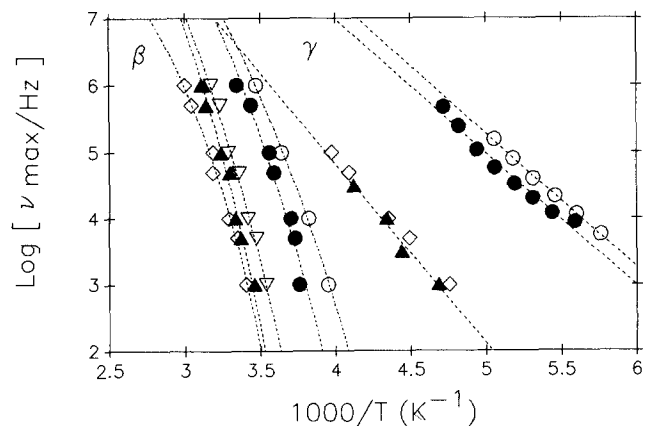
appearing above the glass transition temperature [22]. The dotted line shown in Fig. 8 for the β process has been obtained by fitting the experimental results to the Vogel-Fulcher equation:

$$\text{Log} \langle \nu_{\text{max}} \rangle = B + \frac{A}{T - T_0}, \quad (1)$$

where A, B, and T_0 are constants characteristic for the system. The fitting parameters obtained are shown in Table 2.

The γ process exhibits an Arrhenius-type dependence as observed for relaxations corresponding to small scale local motions [22]. A strong dependence with the PC segment content for the γ process is also observed by comparing the obtained data in Fig. 8 at a given frequency. Thus, there is an increase of the γ process temperature as the PC segment content increases. The activation energies for the γ process for the different systems, calculated from the data of Fig. 8 are shown in Table 2.

Fig. 8 Frequency of maximum loss as a function of the inverse temperature for: (○) 60/40/0, (●) 60/32/8, (▽) 60/20/20, (▲) 60/12/28 and (◇) 60/0/40



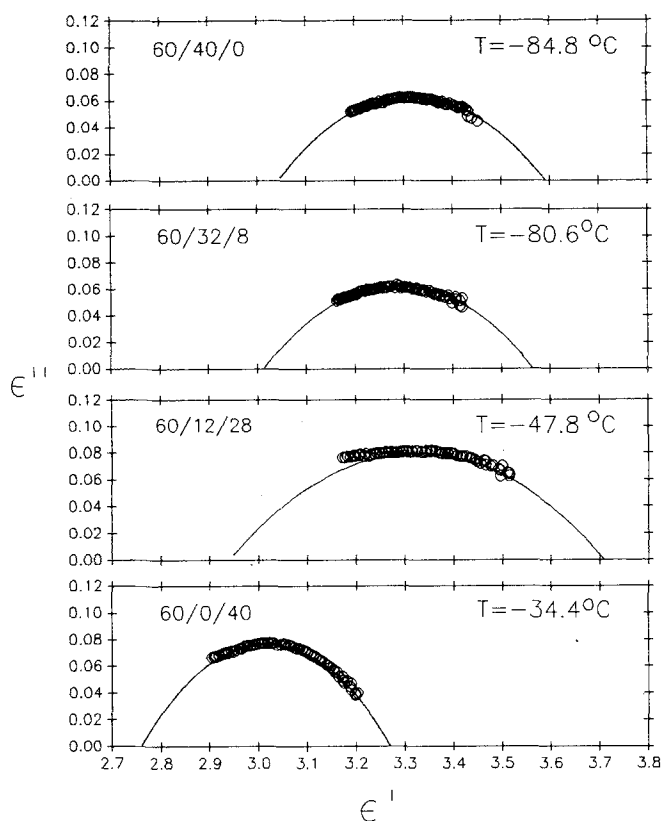


Fig. 9 Cole-Cole plots in the temperature region of the γ relaxation process for the labeled terpolymers

Table 2 A, B, T_0 parameters from the fitting of Eq. (1) in the case of the β relaxation process and E_A for the γ relaxation

SAMPLE	- A	B	$T_0(K)$	$E_A(Kcal/mol)$
60/40/0	1045	14	157.9	8.1 ± 1
60/32/8	1123.4	14.7	167.99	10 ± 0.7
60/20/20	1230.2	15.2	182	—
60/12/28	999	14.5	204	12 ± 0.5
60/0/40	562.9	11.1	223.7	12.2 ± 0.5

Discussion

Structural and thermal behavior

Similarly to the case of other hard-soft systems the WAXD patterns (Fig. 2) of the PEEC terpolymers show the presence of a crystalline phase essentially formed by PBT segments which are the crystallizable units.

The melting of the crystalline PBT hard segment domains gives rise to the observed high temperature endotherms observed by DSC experiments (Fig. 3). The mul-

tiplex endothermic melting behavior exhibited by the 60/40/0 system has been attributed to different crystal populations which are highly dependent on thermal history [16]. As the PC soft segment amount increases a decrease of the crystallinity is observed (see Table 1). These results are in agreement with the WAXD patterns of Fig. 2, revealing a decrease in the intensity of the Bragg maxima as the amount of PC increases. The decrease in crystallinity might be connected with the different compatibility of PBT/PO4 segments and PBT/PC segments in the amorphous phase.

The existence of endothermic peaks between the glass and melting temperature shown in Fig. 3 has been observed in other copoly(ester-ether) systems. These endotherms are dependent on annealing conditions [2] and their origin has been attributed to a slow enthalpy relaxation, in the intercrystalline region, of PBT hard segments [2, 16, 18].

The β relaxation process

The dielectric relaxation of PEEC terpolymers in the investigated temperature range reveals in Figs. 4–7 the existence of two main relaxation processes β and γ in order of decreasing temperature. According to the DSC results (see Table 1), the β relaxation can be attributed to the large scale Brownian motions which appears above the glass transition temperature. The β process exhibits a Vogel–Fulcher type temperature dependence (Fig. 8) as observed for the relaxation associated to the glass transition temperature. The ν_{max} values for the β process corresponding to the two first systems (60/40/0 and 60/32/8) do not differ to much from each other. However, as the PC segment content further increases, a shift of the ν_{max} values towards higher temperatures is observed. The transition temperatures for the β process at 1 kHz are represented in Fig. 10 as a function of the PC hard segment content. For comparison, the glass transition temperatures measured by DSC experiments (Table 1) are also shown. Both transition temperatures increase with PC content. This behavior suggests, in agreement with other authors [23], that the amorphous phase in the terpolymers consists of a mixture of PO4, PC soft segments, and PBT hard segment, giving rise to a single T_g value. Consequently, the T_g value of the terpolymers lies between the corresponding ones of the two limiting copolymers.

Relaxation processes associated to local motions

Subglass relaxation processes are frequently associated to local motions of dipolar groups attached to the polymeric

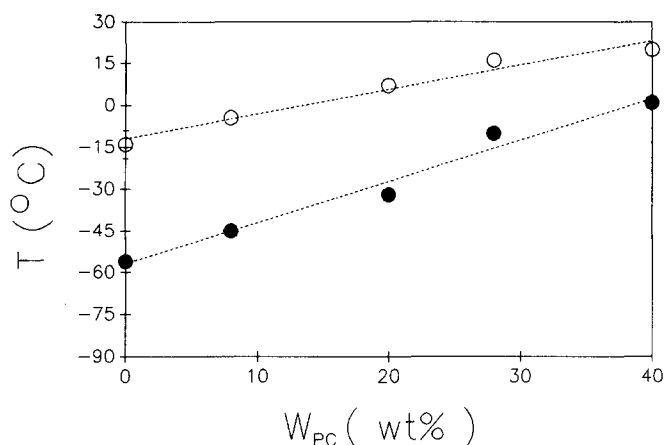


Fig. 10 Glass transition temperature measured by DSC (●) and transition temperature for the β relaxation process at 1 kHz (○) as a function of the weight percent of PC soft segments for PEEC terpolymers

chain. In PBT the γ relaxation has been related to the motions of the $-\text{COO}$ group in the noncrystalline regions [20]. In PBT-PO4 copolymers the γ process is expected to be a combination of local mode motions of both the ether groups present in the soft-segment units and the $-\text{COO}$ moiety of the PBT segments in the amorphous phase. In the latter case activation energies for the process of between 8 and 11 kcal/mol have been reported [20]. In our case, for the 60/40/0 system, the observed activation energy of 8.1 ± 1 kcal/mol suggests the existence of an ester-ether local relaxation process.

In the case of polycarbonates the γ process is associated with local motions of the $-\text{OCOO}$ groups giving rise to activation energies similar to those of polyesters [24]. With increasing amount of PC segments an increase of the contribution of the $-\text{OCOO}$ moiety present in the PC hard segments is expected. For the limiting case 60/0/40, the γ process is expected to be mainly due to the contribution of the $-\text{COO}$ groups from amorphous PBT and of the $-\text{OCOO}$ groups from the soft PC segments. The measured activation energy is higher for the 60/0/40 terpolymer ($E_A \approx 12$ kcal/mol) than the one observed for the 60/40/0 system and agrees with values observed in polyesters and polycarbonates [24]. These results reveal that the γ relaxation in PEEC terpolymers, as measured by dielectric measurements in our frequency range, detects a change from an ester-ether dominated γ process at low PC concentrations to a ester-carbonate γ process at higher PC soft segment content.

Havriliak Negami analysis

Concerning the Cole–Cole plots of Fig. 9, the large broadening of the β relaxation process for these systems

Table 3 b_γ , $\Delta\epsilon_\gamma$, and $\tau_{0\gamma}$ obtained from the fitting of Eq. (1) in the case of the γ relaxation process

SAMPLE	T(°C)	$\Delta\epsilon_\gamma$	b_γ	$\tau_{0\gamma}$
60/40/0	-84.8	0.54	0.28	$3.9 \cdot 10^{-6}$
60/32/8	-80.6	0.55	0.28	$4.7 \cdot 10^{-6}$
60/12/28	-47.8	0.77	0.26	$3.6 \cdot 10^{-6}$
60/0/40	-33.4	0.51	0.37	$2.2 \cdot 10^{-6}$

shown in Figs. 4–7 does not allow a systematic fitting of the experimental results in our frequency range using the following equation:

$$\epsilon^* = \Delta\epsilon^* + \epsilon_\infty, \quad (2)$$

with:

$$\Delta\epsilon^* = \frac{\epsilon_0 - \epsilon_\infty}{[1 + (i\omega\tau_0)^b]^c}, \quad (3)$$

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 [25]. On the other hand, the continuous lines in Fig. 9 represent the best fit to the Havriliak–Negami equation [25] for the γ relaxation of the terpolymers which appears as a broad and symmetric process as indicated by the low value of the b parameter. The fitting parameters corresponding to Fig. 9 are presented in Table 3. In the case of the 60/12/28, a conspicuous deviation from the calculated curves is observed at high frequencies (Fig. 9). Fittings of these data to Eq. (1) assuming that $c \neq 1$ (asymmetric broadening) give rise to unrealistic values of the c parameter. For this reason, we have fitted only the lower frequency data assuming $c = 1$. In accordance with the discussion above, we can consider the γ relaxation process of the 60/12/28 as consisting of a main contribution of OCOO groups from PC segments together with another one due to the ether groups from PO4 segments. The above-mentioned deviation observed at higher frequencies can be interpreted as being due to a separated influence of the ester groups in PO4 segments.

Conclusions

In summary, dielectric relaxation experiments of poly(ether-ester-carbonate) systems in the 10^3 – 10^6 Hz frequency range reveal the existence of two relaxation processes. The γ process, appearing at low temperatures, is due to local mode motions of the polar, ether, and carbonate groups attached to the soft segments and ester groups from PBT segments in the amorphous phase. For low poly(carbonate) concentrations the γ process is mainly

governed by the ether groups of poly(tetramethylene oxide) segments. As the amount of PC soft segments increases, a shift of the transition temperatures at fixed frequencies is observed and higher activation energies are measured. The β process, appearing at higher temperatures, is associated with long-range motions above the glass transition temperature. The dependence of T_g with PC concentration suggests the existence of good mixture

between PC and PO4 soft segments in the amorphous phase.

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