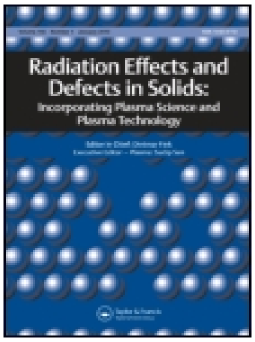

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DIELECTRIC RELAXATIONS IN STRUCTURALLY DISORDERED MATERIALS

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Chain mobility in multiphase polymeric materials is studied by thermally stimulated depolarization currents and dielectric spectroscopy in poly(styrene)-*b*-poly(butadiene)-*b*-poly(ε-caprolactone) triblock copolymers and poly(carbonate)/poly(ε-caprolactone) blends. The variation in the relaxation time distribution of the dielectrically active components and in the number of orientable dipoles in the amorphous phases of these materials is interpreted as the result of the existence of a rigid amorphous phase constrained by the crystalline regions or in the case of the blends by a phase segregation which takes place when the crystallization process of the blend components advances. The mean relaxation times for the secondary and segmental motions are not affected when the phases are segregated.

Keywords: TSDC; Dielectric relaxations; Glass transition; Segregated copolymers; Polymer blends

INTRODUCTION

The dynamics and the relative molecular arrangement are responsible for the properties of materials together with their chemical composition. Semicrystalline polymers are interesting multiphase materials where disordered and ordered phases coexist upon cooling. The amorphous phase changes from an irregular high-viscosity liquid-like structure with highly mobile molecular entities at high temperature, to a rigid glassy state below the glass-transition temperature, T_g, where the molecular dynamics become sluggish; additionally, some of the macromolecules are arranged with a 3 dimensional order forming crystalline lamellae by successive folding, whose melting temperature is above T_g. The orientable dipoles in a polar polymer are usually molecular segments perpendicular to the main chain, located in the mobile amorphous phase. The absence of translational symmetry results in differences in the microscopic environments felt by dipoles of the same type. These dipoles are immersed in a very complex energy landscape due to the combined effect of inter and intramolecular interactions in the disordered regions. The existence of constraints on the amorphous regions may cause the appearance of a rigid amorphous phase where the mobility of the electric dipoles is limited [1]. Dielectric relaxation techniques such as Thermally Stimulated

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Depolarization Currents, TSDC, or Broad Band Dieletric Spectroscopy, BBDS, allow one to study the response of the dielectrically active material to perturbations caused by dc or ac electric fields. Several types of relaxations characterized by different relaxation times, can be identified with increasing temperature: secondary relaxations (γ, β modes) due to local dipolar motions, a primary relaxation (α), which is the dielectric manifestation of the glass-rubber transition and which has a cooperative character and a Maxwell-Wagner-Sillars, MWS, peak (α') caused by the motion and accumulation of ionic and free defects at the interfaces. The profile of the relaxation peaks is always much wider than that predicted by Debye, characterized by a single preexponential factor and activation energy, due to the heterogeneous environment surrounding the reorienting dipole. A relaxation time distribution has to be introduced in the analysis of results and its characteristic parameters (profile, width and mean relaxation time) determined. In the interpretation of BBDS, either empirical distribution functions can be used in the fitting of the isothermal $\varepsilon''(\omega, T)$ curves or if the SADSA computer procedure is applied, no assumption is needed on the profile of the distribution [2].

The molecular dynamics can be studied either as a function of the angular frequency or temperature by measuring the real, $\varepsilon'(\omega, T)$, and imaginary part, $\varepsilon''(\omega, T)$, of the isothermal or isochronal complex dielectric constant. From the fitting of each isothermal run the relaxation time distribution at each temperature is extracted. The variation of the mean relaxation time as a function of the reciprocal temperature shows very distinct behaviors. Vogel-Tammann-Fulcher, VTF, dependence for cooperative rearrangements at and above the T_g of the polymer and Arrhenius dependence for the more localized motions, at lower temperatures is given by:

$$\tau_{VTF}(T) = \tau_0' \exp\left(\frac{E_{VTF}}{k(T - T_{VTF})}\right) = \tau_0' \exp\left(\frac{B}{T - T_{VTF}}\right), \quad \tau(T) = \tau_0 \exp\left(\frac{E_a}{kT}\right), \qquad (1)$$

The temperature T_{VTF}, where the relaxation time diverges, is found experimentally several tens of K below T_g and is taken as the temperature where all motions are frozen. When using thermally stimulated depolarization currents the equivalent frequency is in the range of mHz and the TSDC spectrum can provide information on the 2D relaxation time distribution for each mode.

EXPERIMENTAL

Materials

Two kinds of multiphase materials are used. Triblock copolymers poly(styrene)-*b*-poly(butadiene)-*b*-poly(ε-caprolactone), $S_{09}B_{14}C_{77}$ ($M_n = 181000$ g/mol), were prepared by sequential anionic polarization in benzene [3]; here the subscripts indicate the weight percentage of each component of the triblock copolymer. The poly(carbonate)/poly(ε-caprolactone) blends, PC/PCL, 60/40 in weight, were prepared by melt extrusion with dry homopolymers. The TSDC samples were disk shaped, 20 mm in diameter and 300 μm thick, cut from compression-molded films. Several thermal treatments were performed in order to follow the changes in the relaxation modes as the crystallinity of each component varies.

Thermally Stimulated Depolarization Currents

Our TSDC measuring system has been already described [3]. Its sensitivity is better than 10^{-16} A, and the experiments were performed with a heating rate of 0.07 K/s. The temperature range explored here is from 85 to 300 K in order to avoid changes in the crystallinity of the films. The crystallinity degree, *i.e.* the weight percentage of crystalline phase in the corresponding component, was determined by wide angle X-ray scattering, WAXS, based on a decomposition of the experimental trace into the PCL crystal reflections and the amorphous halos of each homopolymer, PS, PB and PCL.

BBDS

Measurements in frequency domain, $10^{-2} \leq f \leq 3 \times 10^{6}$ Hz, of the real and imaginary part of the dielectric function were performed with a Novocontrol Concept Twelve system. The samples were 30 mm in diameter and 0.3 mm thick with gold sputtered electrodes. The temperature interval ranged from 133 to 313 K and an isothermal run as a function of frequency was performed every 2 K.

Analysis

In such complex materials the assumption that the relaxation times for a given mode must be distributed around a mean value is necessary to explain the recorded experimental profiles. The analysis of the TSDC curves is performed by adding the contributions of elementary Debye processes, either Arrhenius or VTF, with a 2D distribution, both in the preexponential factor, τ_0, and in the activation energy, E_a. The decompositions are performed with computer procedures based on a Direct Signal Analysis, DSA, or a MonteCarlo algorithm that has the advantage of being independent of the starting parameters and uses the Simulated Annealing, SADSA, to randomly explore the parameter space [2]. For the fit of the dielectric absorption spectra the experimental profile is decomposed in Cole-Cole distributions corresponding to each of the overlapping relaxations observed at each temperature in frequency domain.

RESULTS AND DISCUSSION

$S_{09}B_{14}C_{77}$ Triblock Copolymer

In this PCL rich triblock copolymer the morphology consists of a PCL matrix with embedded PS cylinders with an ellipsoidal cross section surrounded by a PB shell, as represented schematically on the inset of Figure 1. The PCL crystalline regions, in a proportion of 53%, form undulated lamellae (dotted regions), while the amorphous PCL regions are located in the space left between the core-shell cylinders [4]. In the original samples the interfaces are rather diffuse but the morphology is clearly observed by Transmission Electron Microscopy if the samples are annealed at 413 K for 3 hours under nitrogen atmosphere and slowly cooled to 318 K and kept at this temperature for another 3 hours before cooling them to room temperature. The crystallinity determined by X-ray diffraction in this case decreases to 23%. In Figure 1 the TSDC results for the original and annealed $S_{09}B_{14}C_{77}$ material are shown. The low temperature part of the spectrum shows the γ and β secondary transitions as a very broad peak. The application of the DSA analysis for decomposing the peak in Arrhenius Debye modes show that the elementary modes can be grouped in 3 distributed relaxations located at 106 K, 129 K and 148 K with mean energies of 0.298 eV, 0.449 eV and 0.572 eV, respectively. After annealing the spectrum is less intense showing a reduction in the number of orientable dipoles, but the relaxation parameters given above for the original samples remain the same within the experimental error. This result implies that the dynamics of the short-range motions involved in these secondary relaxations are

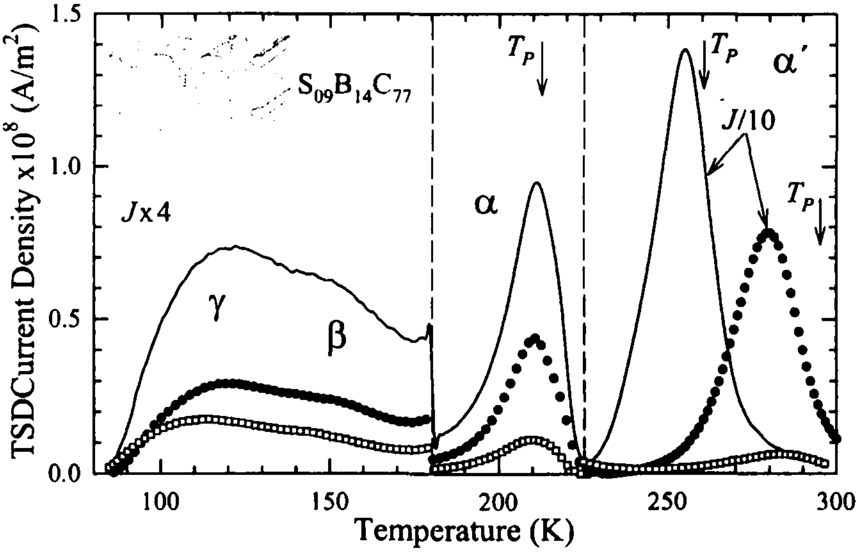

FIGURE 1 TSDC spectra of PCL ($M_n = 93000$ g/mol) (—) and $S_{09}B_{14}C_{77}$: original (•) and annealed (□). The polarization field is 1 MV/m. The morphology is represented schematically in the inset: PB dark grey, PS grey, amorphous PCL white, crystalline PCL dotted regions.

not affected by the better definition of the segregated microstructures. What is significantly affected by the thermal treatment is the number of the molecular entities participating in the total polarization caused by these local motions of the polar segments. On going to higher temperatures, the α relaxation is found and the peak is analyzed with the SADSA procedure. In Figure 2 the SADSA method is illustrated for the α mode of the annealed sample whose

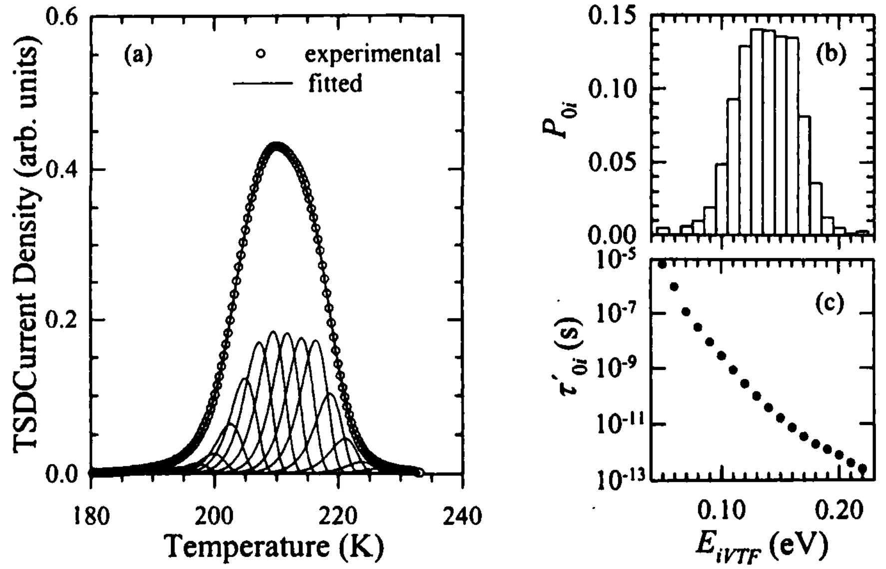

FIGURE 2 SADSA results for the partially discharged α mode of the annealed $S_{09}B_{14}C_{77}$: (a) experimental data and fitted profile, the elementary contributions are also drawn. (b) Energy histogram showing the contribution of each Debye process; (c) variation of τ_{0i}' with the VTF energy.

low temperature tail has been partially discharged in order to minimize the Arrhenius contributions. This decomposition in VTF Debye processes shows that in the original and annealed samples the mean E_{VTF} varies from 0.15 to 0.14 eV, the VTF temperature equals 152.5 K, and the position of the peak shifts from 210.5 K to 210.0 K. Again, no significant changes in the relaxation time distribution, but an important reduction in the α peak intensity shows in the global spectrum. If the intensity of the α PCL peak in the copolymer is compared to that of the homopolymers with different crystallinities, one finds that the intensity of the α peak in the original sample is already too small if scaled with its crystallinity. This effect is enhanced for the annealed material where the amount of crystalline regions is still lower. The lamellar morphology described above (a PCL matrix made of alternating crystalline and amorphous lamellae with core-shell cylinders embedded in the amorphous regions) is the key for the explanation of this behavior. The amount of amorphous phase that is not detected by its contribution to the relaxation spectra is constrained or rigidized. Poly(styrene) chains cannot be invoked here as for this composition there are no PS-PCL interfaces, the rigid poly(styrene) mesophase being segregated in the core of the deformed cylinders with the poly(butadiene) soft shells around them. However, the topological constrains produced by the PCL matrix, which are strong enough to deform the cylinders and to segregate the crystalline PCL zones in undulated lamellae, may be originated by the rigid amorphous phase that is enhanced when the morphology is better defined. The better segregation of the mesophases observed after annealing in the transmission electron micrographs is accompanied by the growth of this rigid amorphous phase. The observed variation in the highest temperature peak confirms this interpretation. This peak, which in neat PCL and in the original sample is very intense, is attributed to an interfacial polarization due to the free carriers present in the sample. It is located at different temperatures, 254 K for the homopolymer and 280 K for the triblock. This shift is due to the difference of free carriers present in the samples after the polymerization process. The huge loss of intensity in the annealed sample is also understood if the presence of the rigid amorphous phase is assumed. This rigid PCL phase should disappear after the melting of the crystals, *i.e.* above 325 K. The interfacial peak always occurs at $T > T_g$ when the material is in its rubber-like state. If in the annealed material there is only a small fraction of the chains whose mobility is increased then the free carriers remain mostly trapped in a motion-constrained environment.

The BBDS results are presented in Figure 3 for the original copolymer. At low frequencies the secondary and primary relaxations are clearly separated in wide bands and the steep rise due to the conductivity is observed at high temperatures. As the frequency is increased the $\epsilon''(T)$ peaks shift to higher temperatures and their relative separation becomes narrower as a merging of the α and β relaxation modes is gradually occurring [5]. The fitting of the $\epsilon''(\omega)$ curves at each temperature is achieved with 3 relaxations, each of them obeying a Cole-Cole relaxation time distribution. The results of these fittings are reported in Figure 4 as the variation of the average relaxation time of each mode as a function of T^{-1}. The dependence of the α mode is obviously not Arrhenius as evidenced by the non linear dependence of this curve in the relaxation plot. The continuous line is the fitting to a VTF dependence and the results of the fitting are $E_{VTF} = 0.14$ eV, $\tau_0{}' = 2 \times 10^{-12}$ s, and $T_{VTF} = 156$ K. The linear variation found for the variation of τ_γ and τ_β in the relaxation plot also allows the determination of the dynamic parameters for the β and γ modes, *i.e.* $E_{a\beta} = 0.51$ eV, $\tau_{0\beta} = 2 \times 10^{-16}$ s, and $E_{a\gamma} = 0.34$ eV, $\tau_{0\gamma} = 5 \times 10^{-15}$ s, respectively. These values are in excellent agreement with those found after TSDC experiments. The BBDS results on the annealed sample are very similar to those obtained for the original triblock except that the intensity of the spectrum is lower by a factor of ten. The decrease observed in the intensity of the TSDC modes is thus confirmed by the dynamic experiments.

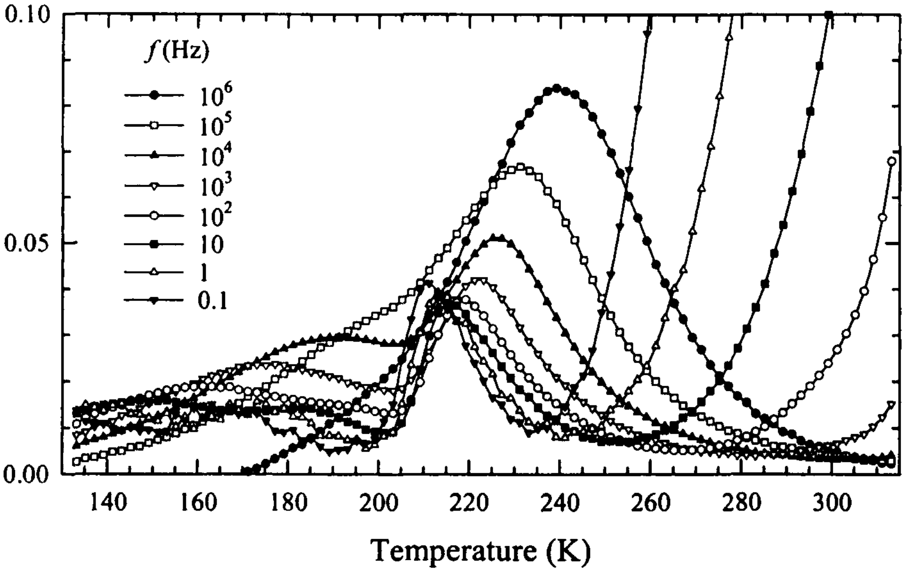

FIGURE 3 Dielectric absorption, $\epsilon''(T)$ of $S_{09}B_{14}C_{77}$ original sample for different frequencies.

Poly(carbonate)/Poly(ε-caprolactone) Blends

PC/PCL blends have been reported as an example of mixtures where an homogeneous phase exists in the molten state or in the amorphous phase [6, 7]. A single and intermediate glass transition temperature has been reported from calorimetric results. In the case of the 60/40 PC/PCL blend the samples were studied after 18 months of its extrusion [8]. The (A) samples were quenched from 523 K, the annealed (B) samples were slowly cooled from 523 K to room temperature, in the molding press and a third batch, (C), is the same sample as in (A)

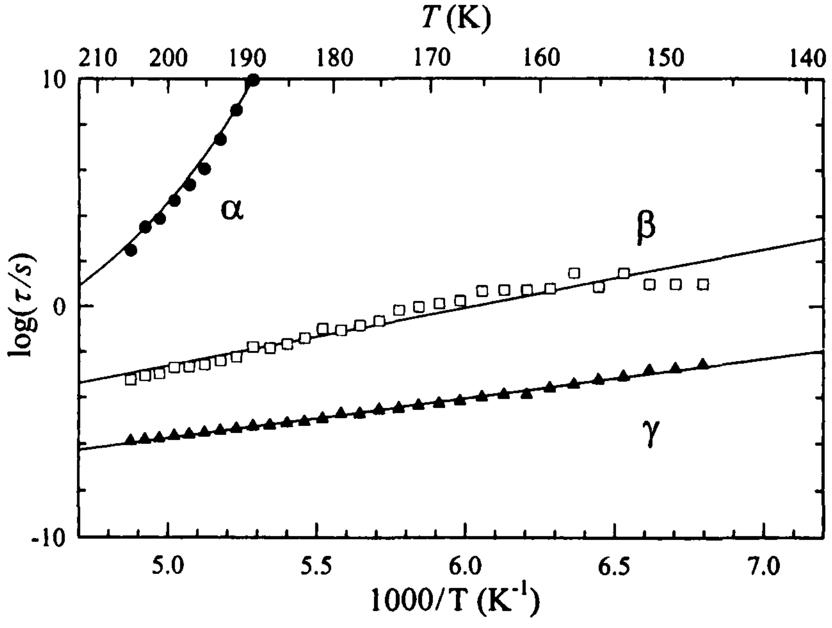

FIGURE 4 Relaxation plot from the BBDS experiments on $S_{09}B_{14}C_{77}$ original triblock.

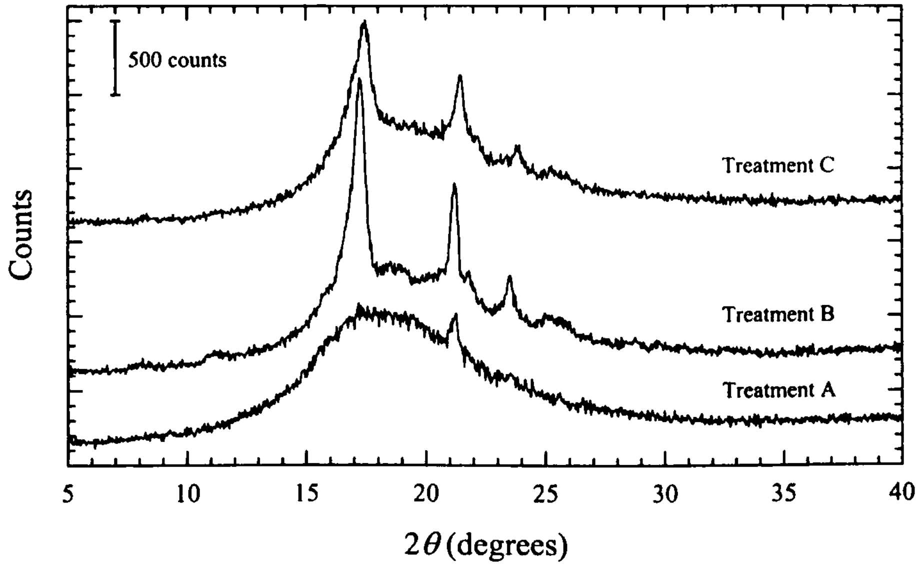

FIGURE 5 Wide-angle X-ray scattering (λCuKαNi-filtered radiation) spectra for the PC/PCL 60/40 blend: (A) quenched from 523 K; (B) slowly cooled from 523 K; (C) cooled from 423 K.

but heated to 423 K only. The X-ray diffraction spectra are drawn in Figure 5 and show an increase in crystallinity of both components, on going from the sample with treatment A (almost amorphous) to sample B. The heated sample is intermediate. The TSDC spectra are shown in Figure 6. For the A sample there is a broad band that covers the interval from 190 to 300 K, which is the α relaxation of the blend. The width of this peak shows that the amorphous state is far from being homogeneous and that there is a wide concentration distribution evidenced by the broad variation of the glass transition temperature of the blend which shifts gradually from that of neat PCL ($T_{gPCL} = 208$ K) to that of the homoge-

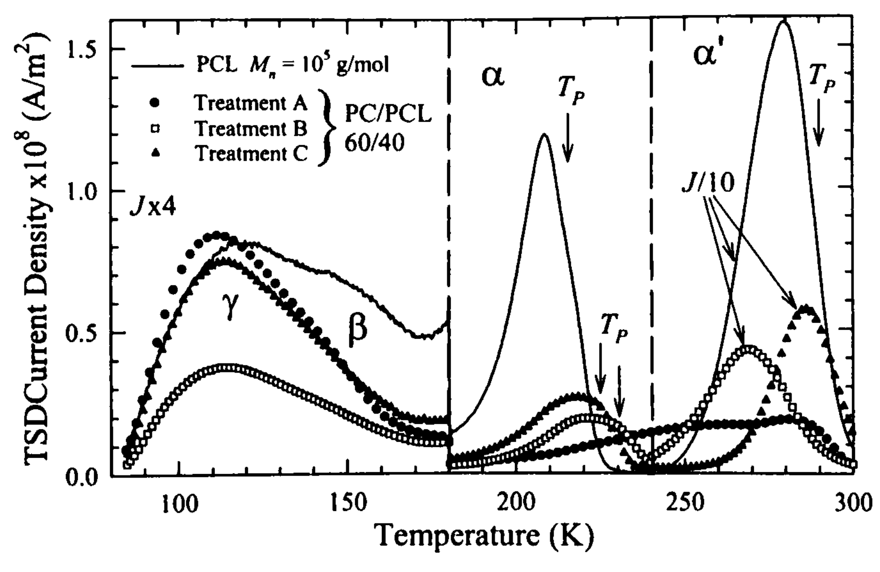

FIGURE 6 TSDC spectra of the poly(ϵ-caprolactone) and PC/PCL 60/40 blend with different thermal treatments; the polarization field is 1 MV/m.

neous blend as predicted by the Fox equation [8, 9]. These concentration fluctuations in the disordered phase which is the predominant one, show a rather poor blend miscibility. If now we focus on the thermally treated samples B and C, the blends show an α peak near the temperature of the α peak of neat PCL, in addition to a huge α' mode of interfacial origin. The calorimetric study of these same B samples, show a heat capacity step near the $T_g = 418\,\mathrm{K}$ of the poly(carbonate) [8]. These results are interpreted as indicative of the existence of two amorphous phases: a PCL very rich phase (as the α segmental mode has only shifted by 7 K), and a PC rich phase. The partial miscibility observed for A samples is destroyed and after treatments B and C phase separation is promoted. The high intensity α' peak observed in these samples due to the trapping at the interfaces confirms the existence of a segregated system after B and C treatments. The local relaxations are also affected by these changes in the miscibility state. The rigidity of the PC chains affects the longest-range modes, which are included in the high temperature side of the β relaxation.

CONCLUSION

With these two examples of disordered multiphase systems coexisting with one or two phases with 3 D order (PCL or PC and PCL crystalline lamellae) it has been shown that relaxation techniques combined with morphology and X-ray diffraction experiments are decisive to understand the mobility of the macromolecules. This mobility in the disordered phases leads to microphase segregation and within these mesophases there still can exist rigid regions due to the presence of crystalline zones. Also the miscibility of PC/PCL blends considered until now as miscible has been shown to depend on storage time, and development of crystallinity after different kinds of thermal treatments.

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