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SHORT COMMUNICATION

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Anomalous enhanced mobility in a semicrystalline random poly(butylene isophthalate / butylene adipate) copolyester

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Abstract An anomalous enhancement of the segmental dynamics upon crystallization is observed by analyzing the dielectric relaxation of a random copolymer formed by stiff aromatic and flexible aliphatic co-monomeric units. The corresponding aliphatic homopolymer is characterized by a low glass transition temperature. The results show that the characteristic self-confinement inherent to semicrystalline polymer systems, which significantly slows down the segmental dynamics as compared to that of pure amorphous ones, is not only avoided but pushed in the opposite direction. Although the effect formally resembles that observed in liquids confined within non-interacting environments, X-ray measurements have shown that the origin in the present case must be sought in an enrichment of the amorphous phase with the most flexible co-monomer upon crystallization.

A great amount of experimental evidence has shown that the dynamics of small molecules and polymers under confined geometries is characterized by the existence of a retarded layer of surface interacting molecules and a bulk-like phase inside the confined space [1, 2, 3, 4, 5]. This effect is usually accompanied by a significant broadening of the relaxation time distribution function [5]. A special case of confined dynamics is that occurring in semicrystalline polymers. In general, crystallization can be envisioned as a first-order phase transition by which molecules self-assemble. In polymers, due to the inherent molecular connectivity, crystallization is kinetically hindered. For this reason, polymers may develop a characteristic folded chain crystalline lamellar morphology at the nanometer level, consisting of stacks of laminar crystals and amorphous regions intercalated between them [6, 7]. Characteristic of this morphology is the fact that a single polymer chain may have a part of it belonging to the crystalline phase and another part to the amorphous phase. Accordingly, at temperatures higher than the glass transition temperature, T_g, the fraction of polymer chain segments in the amorphous phase can be considered as self-confined by the crystalline regions. This self-confinement modifies significantly the segmental dynamics of semicrystalline polymers as compared to that of pure amorphous ones inducing a retardation of the segmental dynamics and a broadening of the relaxation function [8, 9, 10]. This effect resembles qualitatively the dynamical features of the retarded layer found in pore-confined molecules [2, 4, 5] and those found in thin films supported in strongly attractive surfaces [11, 12]. The similarity can be understood by considering that polymer segments located in the amorphous phase are anchored at the crystal surface. Therefore, the amorphous phase dynamics is slowed down by an enhancement of the intramolecular co-operativity which can be explained in terms of the Hall-Helfand equation [13, 14, 15]. The tremendous importance of semicrystalline polymers in our society, mainly polyolefins and polyesters, originates from the fact that they combine strength imparted by the crystalline phase with flexibility due to the amorphous one.

From this point of view, the restrictions in the amorphous phase dynamics imposed by the crystalline phase can be envisioned as a process undesirably tending to enhance brittleness and mechanical fragility of the material. In fact, as an example, broad commercial application of biodegradable bacterial poly(hydroxy alcanoates) has been in part prevented by physical aging-like behavior induced by secondary crystallization at ambient conditions [16]. Random copolymers offer the possibility of controlling the crystallization behavior by an adequate selection of the individual components.

In this study, we show that under certain conditions, in a random copolymer of an aromatic polyester and an aliphatic one of lower glass transition temperature, not only the dynamical retardation of the amorphous phase can be prevented upon crystallization but also that an enhancement of the amorphous phase mobility can even be achieved. A series of poly(butylene isophthalate/adipate) (PBABIP) random copolyesters were prepared by a two-stage polycondensation procedure as described elsewhere [17]. The chemical structure of the repeating units is illustrated in the inset of Fig. 1. In this work we present the results concerning PBIP ($Mw = 13\times10^3$ g/mol, $Tg = 296$ K), PBA ($Mw = 7.3\times10^3$ g/mol, $Tg = 210$ K) homopolymers and 50PBABIP copolymer with molar ratio 50/50($Mw = 8.9\times10^3$ g/mol, $Tg = 248$ K). The technique used to probe polymer dynamics was dielectric loss spectroscopy. Complex dielectric permittivity measurements ($\epsilon^* = \epsilon'' - i\epsilon''$) were performed over a frequency of $10^{-1} < F/Hz < 10^6$ in a temperature range $Tg \leq T \leq Tg + 70$ °C. A Novocontrol system integrating an ALPHA dielectric interface was employed. The temperature was controlled by means of a nitrogen gas jet (Quatro from Novocontrol) with a temperature error of ± 0.1 during every single sweep in frequency. The samples were prepared by melt pressing between two aluminium electrodes (20 mm in diameter) separated by 0.12 mm thick kapton spacers, and by subsequent fast quenching in ice-water. The kapton spacers were used in order to control the sample thickness and to avoid short circuit of the two electrodes. Semicrystalline samples were prepared from the previous amorphous ones by isothermal treatment at appropriated crystallization temperatures of 399 K and 303 K for the PBIP polymer and the 50PBABIP copolymer, respectively. Wide angle X-ray diffraction scattering (WAXS) experiments were conducted at room temperature by means of a Seifert (XRD 3000) symmetrical reflection q/2q scanning diffractometer with Ni-filtered CUKa wavelength. The crystallinity, was calculated as the ratio between the deconvoluted crystalline contribution, given by the crystal reflections and the total scattered intensity [18].

Figures 1a and b show the dielectric loss, ϵ'', values for the PBIP homopolymer and 50PBABIP samples ,respectively, as a function of frequency, both in the amorphous and in the semicrystalline state. In both cases, the main relaxation displayed corresponds to the α process which appears at $T > Tg$ due to segmental motions. Moreover, at higher frequencies a tail of the β-relaxation, due to local motions, is detectable. For the analysis of the dielectric data, ϵ'' values were fitted using a superposition of two relaxation Havrilak-Negami functions [19] with an additional conductivity term [2]. Continuous lines represent customary separation of the relaxation processes [20]. As it is shown, the α relaxation for the semicrystalline homopolymer ($X_c = 0.35$)appears at lower frequencies as compared with that of the amorphous sample, indicating the typical slowing down of the amorphous phase dynamics induced by the crystalline phase [8, 9, 10]. On the contrary, in the case of the 50PBABIP copolymer (Fig. 1b), measured at close thermal conditions ($T = Tg + 5$ K) as for the homopolymer, the α relaxation of the semicrystalline sample ($X_c = 0.1$), anomalously

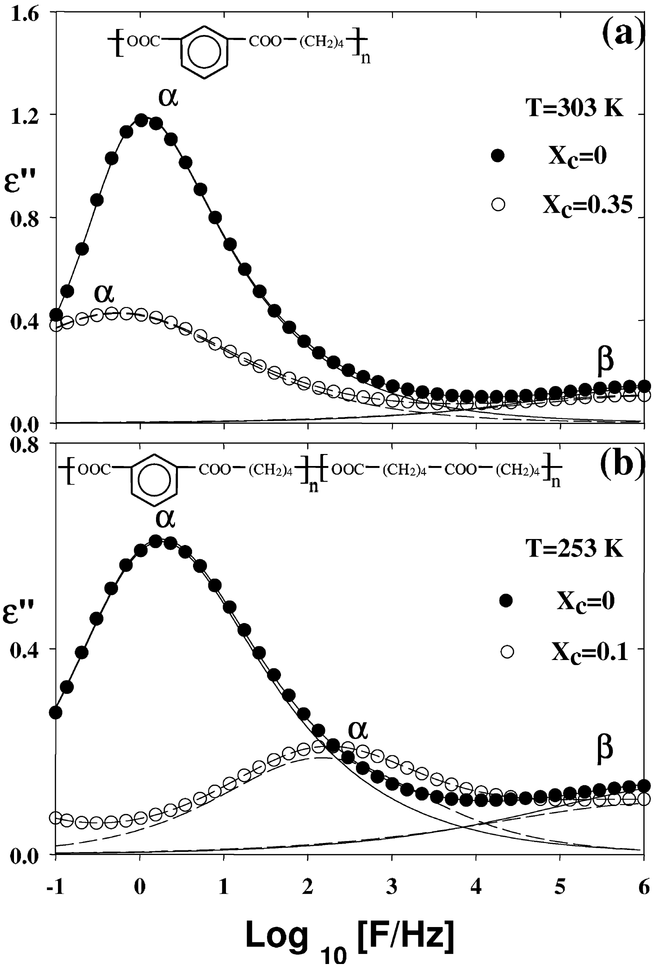

Fig. 1a, b Dielectric loss, ϵ'', of **a** PBIP and **b** 50PBABIP as a function of frequency. ● Amorphous specimens, ○ semicrystalline specimens. *Solid lines* for amporphous specimens and *dashed lines* for semicrystalline ones are fits according to a superposition of a conductivity term and two Havriliak-Negami functions corresponding to the α- and β-process appears to a frequency which is two orders of magnitude higher than the one corresponding to the amorphous specimen. As far as the intensities of the α-relaxation of the semicrystalline PBIP and 50PBABIP samples are concerned, these are comparatively weaker than those of the amorphous ones, as result of the reduction of relaxing fraction upon crystallization [8, 9, 10]. Figure 2 show the logarithmic mean frequency of the α-relaxation as a function of the reciprocal temperature for the homopolymer and the copolymer, both in the amorphous and in the semicrystalline state. For the sake of comparison, the corresponding values of the semicrystalline PBA homopolymer are also included. In the case of PBA homopolymer, the α-relaxation appears at lower temperatures than that of PBIP and 50/50 50PBABIP, emphasizing the higher flexibility of PBA in relation to the other systems. In all cases the α-process follows characteristic Vogel-Fulcher-Tamman (VFT)dependence:

$$F_{\max} = F_0 \exp[-D/(T - T_0)]$$

By fixing the pre-factor to $F_0 = (2\pi \times 10^{-14})^{-1}$ Hz in accordance with recent estimates [21], values for fragility strength, D, of 8.1 and 7.8 and for Vogel temperature, T_0, of 238.6 K and 242.3 K are found for the PBIP amorphous and semicrystalline specimens, respectively. Analogously, for the 50/50 copolymer, D values of 8.6 and 8.4 and T_0 values of 196.2 K and 190.2 K are obtained for the amorphous and semicrystalline specimens, respectively. Lastly, D values of 5.3 and T_0 values of 186.6 K for semicrystalline specimen PBA were obtained. Comparing the Vogel parameters of the amorphous and semicrystalline samples of PBIP and 50PBABIP, one can see that they are very similar in the case of the homopolymer, being, however, as expected [8, 9, 10], T_0 higher for the semicrystalline specimen than for the amorphous one. On the contrary, an opposite difference in T_0 is observed for the copolymer being smaller, the value corresponding to the semicrystalline specimen. Such a trend formally resembles those found in liquids confined within non-interacting environments [2]. In principle, this behavior can be considered as anomalous for a semicrystalline polymeric system taking into account that the segments located in the amorphous phase are pinned at the crystal surface. Accordingly, in the semicrystalline copolymer the amorphous phase dynamics should be slowed down as a consequence of increasing intramolecular co-operativity as compared with that of the completely amorphous sample [13, 14, 15]. In fact, studies carried out on a great number of polymeric system have proven this [8, 9, 10]. In order to better understand the anomalous behavior observed in 50PBABIP, it is essential to know more about the crystalline structure developed upon crystallization. Figure 3 shows the WAXS diffracted intensity as a function of the reciprocal lattice vector $s = (2/\lambda)\sin\theta$ (2θ being the scattering angle) for the semicrystalline PBIP and PBA homopolymer and 50PBABIP copolymer. As one can see, the crystalline structure of PBIP is very

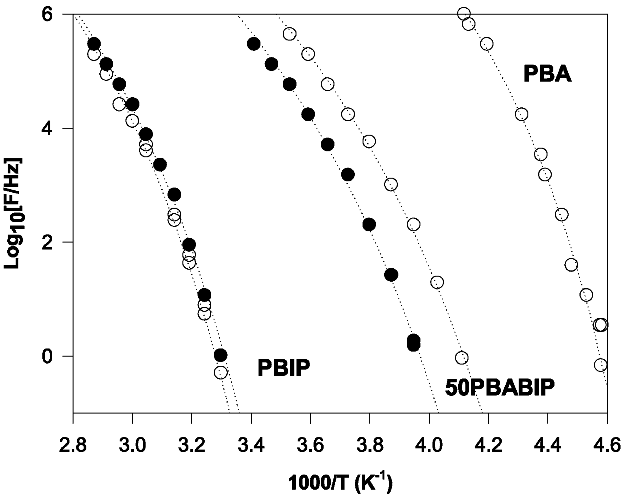

Fig. 2 Frequency of maximum loss as a function of inverse temperature for PBIP, 50PBABIP, and PBA. ● Amorphous specimens, ○ semicrystalline specimens. *Continuous lines* are fits according to the Vogel-Fulcher-Tamann equation

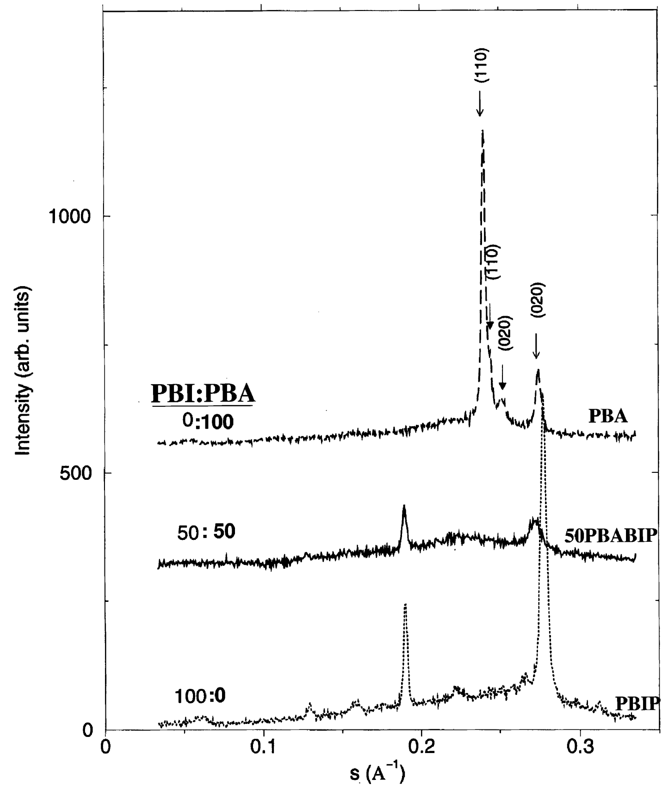

Fig. 3 Diffraction intensity as a function of reciprocal lattice vector $s = (2/\lambda)\sin\theta$, the scattering angle being 2θ, for PBI, 50PBABIP, and PBA. *Arrows* for PBA indicate spacings corresponding to the crystalline phases reported [22]

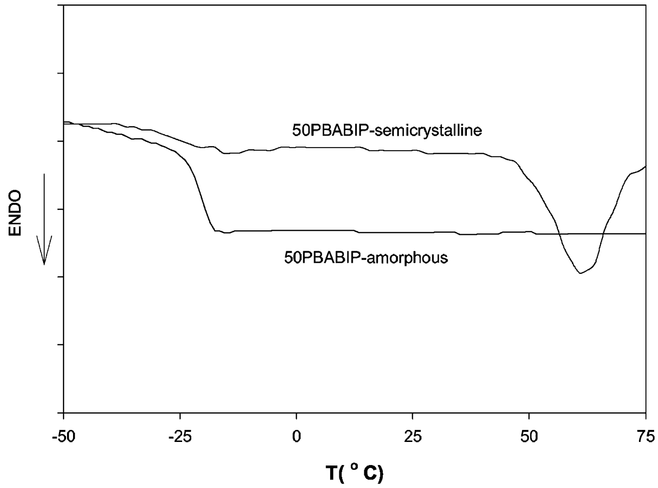

Fig. 4 DSC traces of semicrystalline and amorphous 50PBABIP as taken from ref. [24]

different from that of PBA. This latter exhibits an orthorhombic structure [22] whose spacings are indicated by arrows in Fig. 3. It was reported that this crystalline structure evolves towards a monoclinic one upon storage at room temperature [22]. In fact, traces of this structure are observed and marked by the filled arrow in Fig. 3. Concerning PBIP, its WAXS pattern is very different from that of PBA and agrees with previous reported data [23]. The diffraction pattern of 50PBABIP closely resembles that of the PBIP homopolymer indicating that the formed crystalline phase adopts a crystalline structure closer to that of PBIP. Therefore, it can be expected that the amorphous portion of the material is being progressively enriched in the butylene adipate co-monomeric units during crystallization. As pointed out above, PBA is a more flexible polymeric material than PBIP and therefore is characterized by an α-relaxation process which appears at lower temperatures (see Fig. 2). Consequently, the anomalous dynamic behavior shown by the semicrystalline copolymer can be explained as due to the enrichment of the amorphous phase in the more flexible butylene adipate co-monomer, being the more rigid butylene isophthalate comonomeric units subjected to crystallization. Further support of this explanation comes from previous calorimetric measurements [24]. As known for semicrystalline polymers, the confinement of the amorphous phase by the crystalline one provokes a broadening and a positive shift of the Tg as measured by differential scanning calorimetry(DSC) [25, 26]. Figure 4 shows DSC traces of amorphous and semicrystalline 50PBABIP. As seen, the semicrystalline specimen presents a negative shift of the calorimetric Tg as compared with the amorphous sample. This suggests that the anomalous enhancement of the segmental mobility has to be ascribed to an enrichment of the amorphous phase in the more flexible co-monomer.

In conclusion, these results show that by copolymerization of appropriated aromatic polyesters with aliphatic ones of higher flexibility it is possible to obtain semicrystalline polymeric systems in which the characteristic dynamical retardation of the amorphous phase upon crystallization can be precluded. In fact, an enhancement of the amorphous phase mobility can be achieved, formally similar to that observed in confined systems within non-interacting environments.

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