A Comparative Dielectric Study on the Molecular Dynamics of the Liquid Crystalline and the Isotropic State of Copolyesters.

O. Ahumada¹, T.A. Ezquerro*, A. Nogales, F.J. Baltà-Calleja.

Instituto de Estructura de la Materia, C.S.I.C. Serrano 119, Madrid 28006,
Spain.

H.G. Zachmann

Institut für Technische und Makromolekulare Chemie.

University of Hamburg. Bundesstrasse 45, D-2000 Hamburg, Germany

Abstract

The complex dielectric permittivity has been measured in the 10^3 - 10^6 Hz frequency range for selected random copolyesters of poly(ethylene terephthalate)(PET). The variation of the dielectric properties with temperature has been qualitatively related mainly to two processes. The α relaxation, which is associated to the glass transition, has been shown to be dependent on the molecular order of the systems. It is shown that copolymers with frozen-in liquid crystalline order exhibit an α relaxation process occurring at lower temperatures than the isotropic ones. In particular, PET-co-PHB with a molar ratio of 60/40 shows the occurrence of two maxima in the region of the α relaxation suggesting the coexistence in this copolymer of the liquid crystalline and the isotropic phase. The β relaxation process has been assigned to a local motion of the ester groups attached to both sides of the aromatic rings. The β process is also shown to exhibit a dependence on molecular order.

¹Present address: Institut für Polymere, ETH Zürich, Switzerland.

Introduction

Mesophases are considered to be intermediate states between the isotropic liquid and the ordered solid state [1]. Molecular mobility in mesophases is restricted as compared with that of the liquid state in which a high degree of translational and rotational molecular motions is allowed [1,2]. Main chain liquid crystalline polymers (MCLCP) are semirigid systems in which rigid mesogenic groups and flexible segments alternate along the same polymer chain giving rise to the existence of thermotropic mesophases [2]. Upon cooling from the isotropic liquid (melt), a MCLCP typically exhibits a phase transition to a liquid crystalline state. By further cooling to even lower temperatures the mesophase can be frozen in rendering a liquid crystalline glass [1,3]. The existence of a frozen liquid crystalline order affects the chain dynamics of MCLCP [1].

Random binary copolymers of poly(ethylene terephthalate) (PET) and poly(p-hydroxybenzoic acid) (PHB) exhibit thermotropic liquid crystalline properties provided the PHB amount is higher than 30 % [3,4]. Experiments performed on PET-co-PHB copolymers suggest that the glass transition of the liquid crystalline state occurs at lower temperatures than that of the isotropic state [3]. In particular, dynamic mechanical analysis of the PET-co-PHB (PET:PHB = 60:40) copolymer, in the temperature region where segmental motions are expected, shows the occurrence of two maxima pointing towards the coexistence of the liquid crystalline and the isotropic phase [3]. The presence of two maxima has been also been interpreted as due to regions with different PET content [5]. The aim of the present short-communication is to compare the segmental dynamics of the isotropic and of the liquid crystalline state by performing dielectric spectroscopy measurements on selected PET-co-PHB copolymers.

Experimental

In the present study, PET-co-PHB copolyesters having PET:PHB molar ratios of 30:70, 60:40 and 70:30 were investigated. The copolymers were synthesized in Hamburg as described previously [3]. Amorphous films were obtained by melt pressing in vacuo for 1 minute at a temperature lying 10°C above the individual melting point of each polymer and after quenching in ice water. Measurements of the complex dielectric permittivity ($\epsilon^* = \epsilon' - i\epsilon''$) were carried out in the frequency range of 10^3 - 10^6 Hz by using a Hewlett-Packard impedance analyzer HP 4192A. Films with thicknesses of approximately $100\text{ }\mu\text{m}$ were prepared. Circular gold electrodes, having diameters of 1-3 cm. were brought onto the sample surfaces by sputtering. The dielectric cell was introduced in a home-made furnace operating at a temperature controlled nitrogen atmosphere. Dielectric measurements were made at constant temperature from -150°C up to 150°C in 5°C steps. The error involved during measurement was estimated to be $\pm 0.1^{\circ}\text{C}$. The thickness inhomogeneity of the samples controls the error in the absolute value of ϵ'' which can be estimated to be below 15 %.

Results and Discussion

Fig. 1 shows the ϵ'' values as a function of temperature and frequency for PET-co-PHB 60:40. Three dielectric relaxations in the investigated temperature range labeled as α , α_{Lc} and β in order of decreasing temperature, are observed. At the highest measured temperatures a conduction process is detected, as revealed by the dramatic increase of ϵ'' at low frequencies. Calorimetric experiments in the 60/40 PET-co-PHB system show the coexistence of amorphous and liquid crystalline phases with well differentiated glass transition temperatures [3]. Both phases contribute to different maxima associated

to the α relaxation in the dynamic mechanical experiments [3]. In accordance with these findings, the high temperature relaxation observed in our study for the 60/40 PET-co-PHB copolyester (fig. 1) can be associated to the α process occurring in the amorphous phase. The second relaxation, in order of decreasing temperature, can be assigned to the corresponding α process of the liquid crystalline phase (α_{Lc}). To give additional support to this assignment, the dielectric relaxation of PET-co-PHB 30:70 and 70:30 which are liquid crystalline and isotropic specimens respectively [3] have been investigated. Fig. 2 shows the plot of ϵ'' as a function of the temperature measured at different frequencies for the samples 30:70, 60:40 and 70:30. Two main relaxation processes are found in the investigated temperature range for the 30:70 and 70:30 specimens. Since the 30:70 and 70:30 samples at room temperature are in a frozen-in liquid crystalline and glassy isotropic state respectively we shall refer to them as α_{Lc} and α , indicating the higher temperature process in each case. The 70:30 copolyester exhibits a reproducible peak in ϵ'' around 100°C which disappears in subsequent heating cycles and is thought to be due to local inhomogeneities in the sample [9].

The temperature activated character of the α and β relaxation processes is illustrated in fig 3. Here we show the plot of the measured values of the maximum loss frequency (ν_{max}) obtained from the isochronal plots as a function of the reciprocal temperature for the three molar ratios investigated. The β process observed in the three PET-co-PHB copolymers can be associated, as in most of copolyesters, to the local motion of the ester groups attached to the polymeric chain [8,10,11]. The frequency of the maximum loss allows one to define an average relaxation time $\langle \tau \rangle = (2\pi\nu_{max})^{-1}$ which, for subglass relaxation processes, usually follows a temperature dependence of the type:

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

where ΔS and ΔH are the molar entropy and molar enthalpy of activation respectively [7]. The temperature dependence of the relaxation time is led by the exponential factors. If we neglect the influence of the entropy factor eq. 1 leads to the well known Arrhenius law, where ΔH is identified with the activation energy of the process. By fitting straight lines to the experimental points corresponding to the β process in fig. 3, activation energies E_A of about 53 kJ/mol are obtained. This value is in the range of what is expected for the local motion of the ester groups [8,10,11].

From fig. 3 one sees that the transition temperatures of the β relaxation at different frequencies for the liquid crystalline sample (30:70) are higher than for the isotropic one (70:30). According to eq. 1 the entropic exponential factor may shift the straight lines of the plot parallel to the reciprocal temperature axis depending on the value of ΔS . Thus, our results could be explained by assuming that the variation in the activation entropy for the liquid crystalline samples due to the β relaxation process ($[\Delta S]_{LC}$) is smaller than the one corresponding to the isotropic samples ($[\Delta S]_i$). This result is in agreement with the fact that liquid crystalline polymers are characterized by the existence of mainly nematic order in contrast to the absence of it in amorphous systems. This observation reveals that in spite of the local character of the motion associated to the β process, the state of molecular order in polymeric systems may affect the dynamics of the process.

The α relaxation appears, as a consequence of segmental motions of the polymeric chain at temperatures above the glass transition temperature. Our results of fig. 3 clearly show that the glass transition temperature of the liquid crystalline phase is smaller than that of the amorphous phase. This finding

sheds light about the nature of the two α maxima observed in the 60:40 PET-co-PHB sample. As shown in fig. 3, the values of ν_{max} corresponding to α_{Lc} in 60:40 are close to the corresponding ones of the liquid crystalline sample (30:70). Similarly, the ν_{max} values for the α relaxation are closer to those of the isotropic sample (70:30). This result unambiguously indicates that the two observed α maxima in the 60:40 sample can be attributed to an isotropic and to a liquid crystalline phase respectively where the transition temperature T_α is larger than $T_{\alpha_{Lc}}$.

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. At the glass transition temperature the free volume of the polymer assumes just the smallest value which is necessary for the molecules to perform those motions which makes 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. In the liquid crystalline state, the motions occurring close to T_g can be due to rotations of the elongated chain around their axes, translational motions of the chain, and to some other motions of small atomic groups. The free volume required in the latter kinds of motion is considerably smaller than that involving a segmental motion in the amorphous isotropic case.

Conclusions

In conclusion, dielectric relaxation of binary copolymers of PET and PHB exhibit mainly two relaxation processes in the investigated temperature range: The α relaxation process, associated to the glass transition of the copolyesters, which depends on the state of molecular ordering of the copolymers. Lower T_α values are observed for systems exhibiting liquid crystalline order than for

the isotropic ones. This effect has been 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 state. The free volume required to perform such localized motions in the liquid crystalline state is smaller, and can be reached at a lower temperature than, the free volume necessary for more extended segmental motions in the isotropic state.

The β process, assigned to a local motion of the ester groups, also depends on molecular order. Higher values of $T_\beta(1\text{kHz})$ are observed for the liquid crystalline sample than for the isotropic one. Such an effect can be explained by assuming that the variation in the activation entropy of the β process for the liquid crystalline samples, due to the existence of nematic order, is smaller than the corresponding process in the amorphous samples.

References

- [1] J.K. Moscicki, Liquid crystal polymers: From Structures to Applications, Ed. by A.A. Collyer, Elsevier London 1992, p. 143
- [2] G. Williams, Materials Science and Technology (Ed. by R.W. Cahn, P. Haasen, E.J. Kramer) VCH Weinheim **12** 472 (1993).
- [3] D. Chen, H.G. Zachmann, Polymer **32**(9) (1991) 1612.
- [4] H.G. Zachmann, C. Spies, S. Thiel, Physica Scripta **T49** 247 (1993).
- [5] U.W. Gedde, D. Buerger, R.H. Boyd, Macromolecules **20** (1987) 988.
- [6] A.R. Blythe "Electrical Properties of Polymers" Cambridge University Press 1980.
- [7] J.C. Coburn, R.H. Boyd, Macromolecules **19**, 2238 (1986).

- [8] O. Ahumada, T.A. Ezquerro, A. Nogales, F.J. Baltá-Calleja, H.G. Zachmann. (In preparation).
- [9] T.A. Ezquerro, F.J. Baltá-Calleja, H.G. Zachmann, *Acta Polymer.* **44** (1993) 18.
- [10] P. Hedvig, *Dielectric Spectroscopy of Polymers*. Adam Hilger Ltd., Bristol 1977.

Legends to the figures.

Figure 1: Dielectric loss, ϵ'' , as a function of temperature and frequency for PET-co-PHB (60:40) copolymer .

Figure 2: Isochronal dielectric loss ϵ'' as a function of temperature for PET-co-PHB (PET:PHB = 30:70, 60:40 and 70:30) copolymers at $10^3(\circ)$, $10^4(\bullet)$, $10^5(\triangle)$, $10^6(\blacktriangle)$ Hz.

Figure 3: $\text{Log}[\nu_{max}]$ as a function of the reciprocal temperature for PET-co-PHB copolymers with different PET:PHB molar ratios: 70:30($\blacktriangle$), 60:40($\blacklozenge$), 30:70($\circ$)

fig. 1

PET-co-PHB

fig. 3