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Origin of the Subglass Dynamics in Aromatic Polyesters by Labeling the Dielectric Relaxation with Ethero Atoms

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ABSTRACT: The dynamic behavior of a series of polymers based on 2,6-naphthalenedicarboxylic acid where the chemical structure of the monomer has been systematically modified was studied. The effect of the different chemical structure of the monomeric unit on the subglass dynamics has been evaluated. The β relaxation has a complex character. The slowest subglass relaxation, labeled as β^* relaxation, is directly related to motions of the naphthyl moiety. However, the observed variations of the position of this relaxation, compared with analogues' more rigid polymers, indicate a certain degree of cooperativity of the subglass dynamics.

Introduction

The α relaxation is the traditionally most studied relaxation process relating to the dynamic origin of the relaxation map of a polymer system. This process occurs at temperatures above the glass transition temperature, T_g, and it is attributed to the segmental motions of the chains.[1] However, below T_g, the dynamics of polymer systems can be quite complex. The microscopic origin of the secondary relaxation, β, has not been yet completely understood. In polymers, the β relaxation has been attributed to localized motions of pendant groups. If the β relaxation is investigated in a narrow frequency range, generally the temperature dependence of the corresponding relaxation time, τ_β, can be described by an Arrhenius behavior. However, the possibility of measuring in a wide dynamic range, offered by modern high-resolution relaxation techniques like dielectric spectroscopy,[2] has contributed extensively to a more precise description of the β or secondary relaxation. Recently, it has been possible to detect, in particular cases, that the β relaxation, i.e., the process that appears well below T_g, can be formed by more than one relaxation mode.[3–5] By means of simulation techniques, Boyd et al. tentatively assigned the different modes observed in the β relaxation of poly(ethylene terephthalate) (PET) to individual motions of different parts of the monomer unit.[3] Additionally, these authors studied modifications in the subglass relaxations induced by the presence of comonomer units of chemically related polymers, such as poly(ethylene naphthalate) (PEN).[3] They were able to identify up to three different modes in the β relaxation map, the slowest one being associated with motions of the carbonyl group in the monomer. In this study[3] it was pointed out that the slowest β mode, β_3, could have the same origin as the β^* relaxation of PEN.[6,7] Consequently, some degree of cooperativity in groups of bond rotations or conformational jumps was suggested for the β_3 mode.

A possibility to address the role of each monomer bond in the β relaxations is to study polymers where the chemical structure is modified systematically. In particular, in polymers with naphthyl moieties, the β^* relaxation appears well separated from the β relaxation.[8,9]

Recently, dynamic mechanical analysis measurements (DMTA) on a series of new polyesters, based on 2,6-naphthalenedicarboxylic acid in which the nature of the moiety between consecutive naphthalene rings has been systematically changed, have been reported.[7] The aim of the present paper is to progress in the general understanding of the role of the different groups in the β relaxation and to address whether cooperative dynamics starts at temperatures below T_g. The presence of the β^* relaxation was only observed by DMTA in one of the studied polymers. In this work we have studied by broadband dielectric spectroscopy the relaxation behavior of these novel polymers. By comparing their dynamics with that of PET and PEN, several conclusions are drawn, emphasizing the cooperative character of the $\beta^* \sim \beta_3$ relaxation.

Experimental Part

Poly(butylene naphthalate) (PBN), poly(diethylene naphthalate) (PDEN), and poly(thiodiethylene naphthalate) (PTDEN) were synthesized as described previously.[7] A summary of the molecular and thermal characterization data for these polymers is reported in Table 1. The chemical structures of the studied samples are shown in Figure 1. For dielectric spectroscopy experiments, the synthesis product was transformed as follows: the powder was dried for 1 day under vacuum at a temperature of 100 °C. The dried powder was mold-pressed 5 °C above the melting point of the polymer[7] and subsequently quenched into iced water. In this way 0.2 mm thick films were obtained. The films were amorphous except for PBN. For the dielectric experiments, circular gold electrodes, 2 cm in diameter, were deposited onto the film surfaces by sputtering. Measurements of the complex dielectric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, were performed over a frequency window of 10^{-1} Hz $< F < 10^7$ Hz in a temperature range of -150 °C $< T < +150$ °C. To cover the above frequency range, a Novocontrol system integrating an ALPHA dielectric interface was employed. The experimental accuracy of the measurements in $\tan(\delta) = 10^{-5}$ was $\tan(\delta) = \varepsilon''/\varepsilon'$. The temperature in these experiments was controlled by a nitrogen jet with a temperature error, during every single sweep in frequency, of 0.1 °C.

In the case of the initially amorphous samples (PDEN and PTDEN) the samples crystallized during the dielectric experiment. Therefore, further dielectric experiments were performed, the

Table 1. Molecular and Thermal Characterization Data[a]

polymer	M_n	M_w	D	T_m (°C)	T_g (°C)
PBN	23000	50000	2.1	240	79
PDEN	35000	41000	2.5	179	58
PTDEN	16000	66000	1.9	160	47

[a] M_n is the number-average molecular weight, M_w the weight-average molecular weight, D the polydispersity, T_m the melting temperature, and T_g the glass transition temperature.

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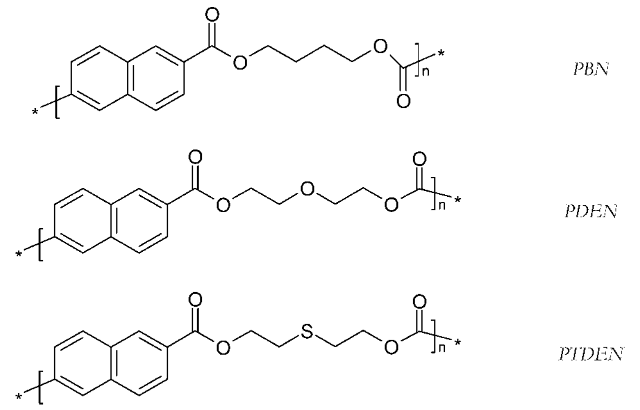

Figure 1. Chemical formulas of the studied samples.

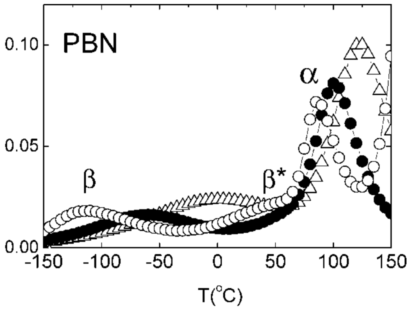

Figure 2. Isochronal ε'' for semicrystalline PBN as a function of temperature. Measuring frequencies: 10^1 (○), 10^3 (●), and 10^5 Hz (△).

sample being already semicrystalline from the beginning of the experiment.

Results

Isochronal Plots. Figure 2 presents the isochronal ε'' values obtained for the semicrystalline PBN at selected frequencies. PBN exhibits three relaxations labeled as β, β^*, and α in order of increasing temperature. At low temperatures, the β relaxation is observed as a broad maximum (centered on −120 °C at $F = 10$ Hz) that shifts toward higher temperatures as frequency increases. At intermediate temperatures (40 °C at $F = 10$ Hz) the β^* relaxation is observed as a shoulder. At high temperatures a sharper maximum in ε'' reveals the presence of the α relaxation. This dielectric relaxation behavior is in agreement with previous DMTA experiments.[7]

In the case of amorphous PDEN and PTDEN (Figure 3), the intensity of the α relaxation is considerably higher than that of the β. The α maximum of initially amorphous PTDEN at 1 Hz is accompanied by a broader shoulder at higher temperatures, provoked by the crystallization of the sample during the dielectric scan. The strong difference in intensities between the α and the β relaxation prevents the observation of fine structure that is easily observed in the dielectric spectrum of the semicrystalline samples (right panels in Figure 3). In these cases, the intensities of the α and β relaxation are closer. Thus, the β relaxation is very broad and even for PDEN exhibits clearly two maxima, which indicate the existence of more than one mode in the low-temperature relaxations. In the isochronal plots it is difficult to detect the presence of any extra processes between the β and the α relaxations in PDEN and PTDEN. However, because of the chemical nature of these two polymers, a β^* relaxation associated with the relaxation of the naphthalene group has to be expected.[3,6,10–12]

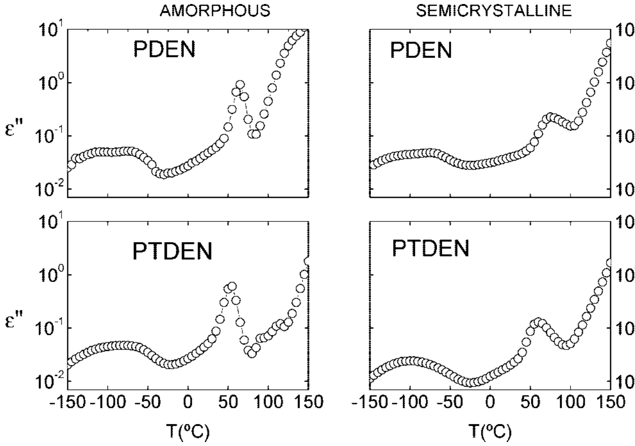

Figure 3. Isochronal ε'' for the PDEN and PTDEN samples, initially amorphous (left panels) and semicrystalline (right panels), as a function of temperature measured at 10^1 Hz.

Amorphous Samples. To describe in more detail the complexity of the observed dielectric spectrum of PBN, PDEN, and PTDEN, careful analysis of the dependence of ε'' with frequency has been performed in different temperature regions. In correspondence with what is observed in the case of the isochronal plots, for the amorphous samples (PDEN and PTDEN), only the β and α relaxations can be resolved. The dielectric loss in the region of low temperature has been described by the combination of different Cole–Cole contributions[13] by using the equation

$$\varepsilon'' = \sum_n \operatorname{Im}\left(\frac{\Delta\varepsilon_n}{1 + (i\omega\tau_n)^{b_n}}\right) \tag{1}$$

where n takes values of 1 or 2, depending on the sample, $\Delta\varepsilon_n$ is the dielectric strength associated with the n component of the β relaxation, $\omega = 2\pi F$ is the angular frequency, τ_n is the average relaxation time, and b_n is the symmetric broadening factor that may take values between 0 and 1. To estimate the accuracy of the fitting parameters, their values have been varied. We found that the maximum possible variation without provoking a significant deviation between the measured and calculated curves was less than ≈5% for b_n and $\Delta\varepsilon_n$ and ≈10% for τ_n. Figure 4 shows as an example the obtained fits for selected temperatures for amorphous PDEN and PTDEN. The low-temperature spectra of these two polymers clearly show that the β relaxation has two main contributions.

For the α relaxation, at high temperatures, dielectric loss values as a function of frequency can be described by a Havriliak−Negami equation[13]

$$\varepsilon'' = \operatorname{Im}\left(\frac{\Delta\varepsilon_\alpha}{(1 + (i\omega\tau_\alpha)^{b_\alpha})^{c_\alpha}}\right) \tag{2}$$

where $\Delta\varepsilon_\alpha$ is the dielectric strength, τ_α is the average relaxation time, and b_α and c_α are the symmetric and asymmetric broadening factors, respectively, taking values between 0 and 1. When the c_α parameter takes a value of 1, the Havriliak−Negami equation becomes a Cole–Cole equation. To analyze the shape and temperature evolution of the α relaxation at low frequencies, a conduction term was added to ε'':

$$\varepsilon''_{\text{cond}} = \frac{\sigma}{\varepsilon_{\text{vac}}\omega^s} \tag{3}$$

where σ is related to the direct current electrical conductivity, ε_{vac} is the vacuum dielectric constant, and s is related to the nature of the conduction mechanism.[13] In addition to that, in the α relaxation region, it is necessary to include the extrapolated tail for the high-frequency processes (β relaxation). An example

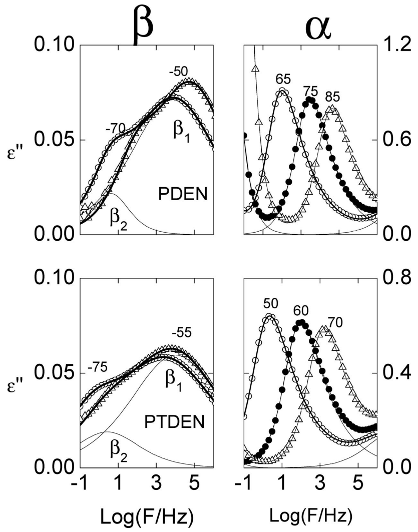

Figure 4. ε'' values as a function of frequency for amorphous PDEN and PTDEN samples at selected temperatures, corresponding to the temperature region where the β relaxation (left panels) and the α relaxation (right panels) appear. Thick continuous lines represent the best fit of the superposition of several HN curves (see text). Different contributions are represented by thinner lines. In the case of the α relaxation, thin lines represent the separated contributions of the conductivity, the α relaxation and the subglass relaxations.

on how all these contributions are separated is presented in Figure 4, right panel, for selected temperatures. For the studied amorphous polymers, the α relaxation is asymmetric ($c_\alpha < 1$). It appears at lower temperatures for PTDEN than for PDEN, which correlates with the glass transition temperature (T_g) measured by differential scanning calorimetry (DSC).[7]

Semicrystalline Samples. As observed in the isochronal plots (Figure 3), the dielectric spectrum of the semicrystalline samples becomes more complex, partly because the decrease of the more intense relaxation, the α process, reveals an extra contribution appearing in the intermediate temperature region between the α and the β relaxations, the β^* relaxation. However, the β^* relaxation is only detectable in the isothermal plots shown in Figure 5. The better resolution of the β^* relaxation in the case of the semicrystalline samples is due to two factors: On one hand, the decrease in intensity of the α relaxation, due to the amount of dipoles that were mobile in the amorphous sample and that do not contribute to the relaxation processes in the case of the semicrystalline one. On the other hand, it is known that crystallinity induces in the α relaxation of polymers a shift toward lower frequencies (or higher temperatures).[10,14,15] As a consequence, a splitting of the β^* with respect to the α relaxation in the semicrystalline samples is observed. The β^* relaxation is characteristic of systems with a naphthalene group in the chain.[3,6,10–12] Figure 5 shows selected dielectric curves at the three temperature regions where the different processes appear. In the left column, the β relaxation of PBN, PDEN, and PTDEN has been presented. In the case of PBN and PTDEN, the β relaxation of the semicrystalline system can be represented by a single Cole–Cole contribution. The reason why one of the contributions of the β process disappears in these two semicrystalline polymers can be related to the sensitivity of the equipment, since, as observed in Figure 5, ε'' values are very small at low temperatures. The right column of Figure 5 presents the ε'' values in the region of the α relaxation which can be described by a symmetric Havriliak−Negami equation, i.e., a Cole–Cole equation. The main difference between the dielectric spectrum of the amorphous and semicrystalline samples is the observation of a shoulder in ε'' values at temperatures around 50 °C, corresponding to the β^* contribution. To describe this process, the fitting procedure was accomplished as follows: first, the β region was fitted. The obtained parameters were extrapolated toward high temperatures; second, the α relaxation was fitted. The parameters were extrapolated toward lower temperatures. Considering these two extrapolations, the intermediate region (β^* region) was fitted by using a Cole–Cole equation and the tails describing the α and β contribution, respectively. Examples of fittings obtained by this procedure are presented in Figure 5, central column.

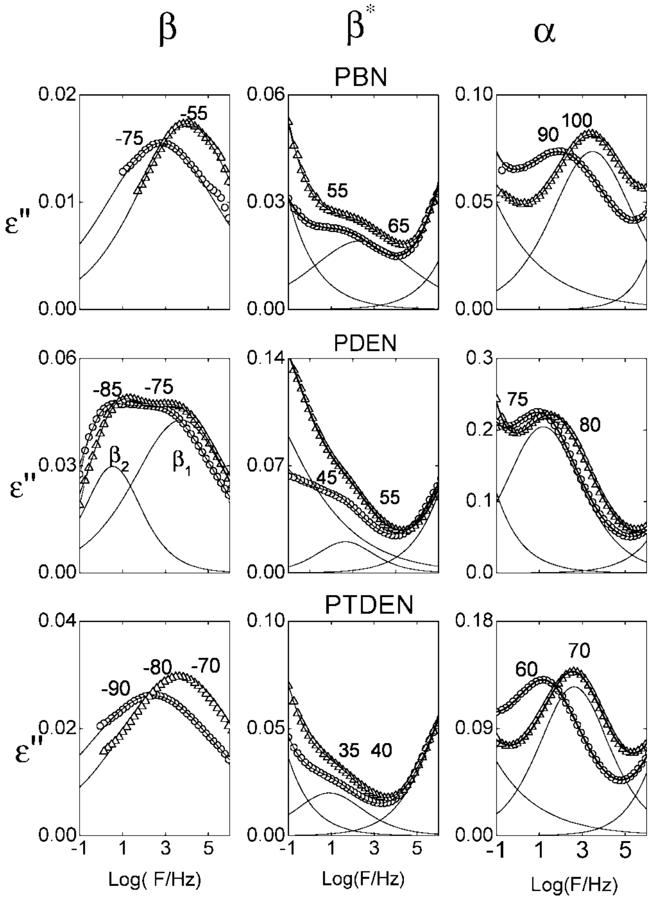

Figure 5. ε'' values as a function of frequency for semicrystalline PBN, PDEN, and PTDEN samples at selected temperatures, corresponding to the temperature region where the β relaxation (left panels), the β^* relaxation (central panels), and the α relaxation (right panels) appear. Thick continuous lines represent the best fit of the superposition of several HN curves (see text). Different contributions are represented by thinner lines.

From the analysis described above, it is possible to obtain the relaxation map of the amorphous and the semicrystalline samples. This map is presented in Figure 6. Here, the dependence of the frequency of maximum loss ($F_{\max}$) for each relaxation is plotted as a function of the reciprocal temperature. In the case of amorphous PDEN and PTDEN the two low-temperature process (labeled as β_1 and β_2) exhibit an Arrhenius-like behavior, with a linear dependence of $\log(F_{\max})$ vs $1/T$. From this plot, the activation energy of these processes can be calculated. They are presented in Table 2. As observed in this table, the lower the temperature range at which the relaxation appears, the lower the activation energy is. In close analogy to what has been reported for PEN, the polymers studied here present a complex low-temperature behavior including the presence of a β^* relaxation. These results are also in good agreement with those obtained previously by DMTA.[7]

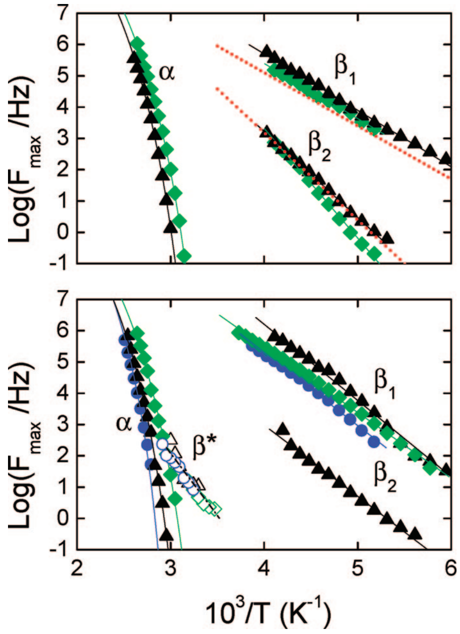

Figure 6. Dependence of the frequency of maximum loss (F_{max}) with the reciprocal temperature for the relaxations in the studied samples, in the amorphous state (top panel) and in the semicrystalline state (bottom panel) (PBN, blue; PDEN, black; PTDEN, green). Continuous lines represent Arrhenius fits for the β relaxations and Vogel–Fulcher–Tamann fits for the α relaxation. In the upper panel dotted lines correspond to the dependence of the β_1 and β_2 relaxation found for PET and PEN from ref 3.

Table 2. Activation Energies (kJ/mol) of the Different Subglass Processes

	β_1 amorphous	β_1 semicryst	β_2 amorphous	β_2 semicryst	β* amorphous	β* semicryst
PBN		42				76
PDEN	35	45	49	40		75
PTDEN	34	42	67			74

Discussion

Molecular Origin of the Different β Modes. The dielectric spectra of aromatic polyesters can be roughly described by the presence of two major relaxation processes associated both with motions in the amorphous phase of the system. However, close inspection to the subglass regime reveals that the traditionally called β relaxation is the composition of more than one relaxation processes. Bravard et al.[3] were able to identify up to three different components of the β relaxation in PET. By studying the variations observed in these different modes in PET/PEN copolymers, they interpreted that the third and lowest frequency component has the same origin as the β* process in PEN, and it was assigned to the motion of the aromatic group. The higher frequency β modes were tentatively associated to motions of the aliphatic CH_2 bonds and the ester bonds.[3] The dependence of these two relaxations in the case of PET and PEN has been plotted in Figure 6 for the sake of comparison. In our case, the β relaxation of the three studied polyesters presents some interesting features.

For the two amorphous polymers, PDEN and PTDEN, one may observe two different modes in the β relaxation (labeled as β_1 and β_2). The activation energies and the temperature position of these two modes are similar to those reported by Bravard et al. for PET and PEN.[3] By analogy to PET and PEN, the dielectrically active groups in our polymers are the aromatic ring carbon to ester carbon bond, (CA–C bond), an ether oxygen (O) to aliphatic carbon (C) (O–C bond), and the aliphatic carbon–carbon bond (C–C bond). In addition to that, for PDEN and PTDEN, two extra active bond are found, i.e., the aliphatic carbon adjacent to the heteroatom bond (C–O bond in the case of PDEN and C–S bond for PTDEN). Several comments need to be made regarding the β relaxation of the studied samples when compared with PET and PEN.

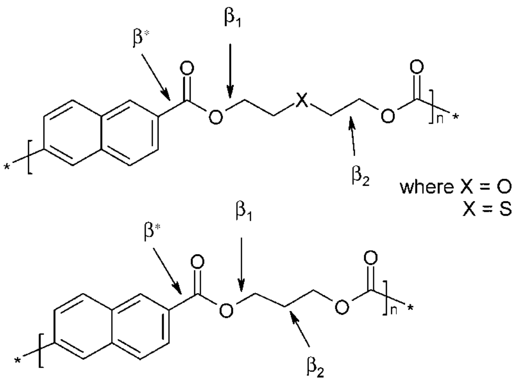

Figure 7. Schematic representation of the active bonds in each of the observed β modes.

β_1 Relaxation. This process is observed in all the studied samples. This observation is compatible with the idea of this mode being associated with the O–C bond of the ether oxygen to aliphatic carbon, as proposed by Bravard et al.[3] Moreover, on the basis of the fact that, along the monomer unit of PDEN there are three O–C bonds, one may understand why the β_1 relaxation is more intense in this polymer than in PTDEN (see Figure 4). For this latter case, the C–S bond may contribute also to the β_1 process, but with a lower dielectric moment.

β_2 Relaxation. This process is only present in amorphous and semicrystalline PDEN and in amorphous PTDEN. The activation energy and the position of this relaxation are exactly those observed in the case of PET and PEN. Following again Bravard et al. interpretation,[3] this mode can be related to the C–C aliphatic bond. It is known that the motions of this sort of bonds are not accompanied by changes in the dipolar moment. However, it is reasonable to think that any conformational transition of the aliphatic bonds in the case of PET or PEN, where the aliphatic segment is formed with only two carbons, could be affected by the presence of the adjacent polar ether atom, which is detectable by dielectric spectroscopy. In the case of PBN, since the aliphatic segment is formed by four carbons, conformational transitions in this portion of the monomer are less affected by the neighboring ether oxygen. This interpretation can explain why the β_2 mode is not detected in the case of PBN whereas it is observed in PEN.[3,5] On the other hand, the fact that the β_2 relaxation is observed in amorphous PDEN and PTDEN and in semicrystalline PDEN corroborates this interpretation. In fact, in PDEN and PTDEN, the ethero atom constitutes a break in the aliphatic segment. Moreover, the polarity of the ethero atom affects further the characteristic of the β_2 relaxation. This latter is indeed evidenced only in semicrystalline PDEN, the polarity of the sulfur etheroatom being much lower than that of the oxygen one. The general interpretation of the different modes observed in the studied polymers is presented in Figure 7 where the active bond in each of the detected β modes is labeled.

Cooperative Character of the β* Relaxation. The β* relaxation is characteristic of polymers including a naphthalene group in the monomer.[8,9] Therefore, it is reasonable to expect such a relaxation in the polymers studied here. At a first glance, the β* relaxation is not found in the amorphous PDEN and PTDEN samples. However, the β* relaxation is observed in the three studied semicrystalline polymers (see Figure 5). The dependence of the frequency of maximum loss for the β* process as a function of the reciprocal temperature is presented

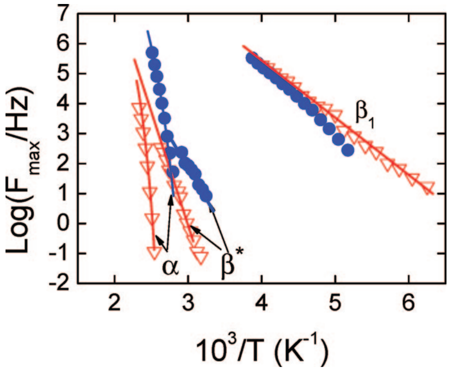

Figure 8. Comparison between the high-temperature relaxation map of PEN, from ref 3 (▽) and that of PBN (●). Continuous lines represent Arrhenius fits for the β* and β relaxations and Vogel−Fulcher−Tamann fits for the α relaxation.

in Figure 6. The position of this relaxation is nearly independent of the chemical structure of the polymer analyzed. This may led to conclude that this relaxation lacks a cooperative character. However, it is interesting to compare this behavior with that of the more studied PEN. In Figure 8 the relaxation map at high temperatures of the two chemically related polymers PEN and PBN has been presented (PEN data taken from refs 3 and 7). The β_1 and β_2 values in the relaxation map corresponding to PEN and taken from ref 3 are also included in Figure 8. Because of the highest rigidity imposed by the shortest aliphatic chain in the monomer, PEN exhibits a higher glass transition temperature (110 °C in PEN[3,7] and 79 °C in PBN[7]). The α relaxation follows a similar behavior, appearing at higher temperatures in the case of PEN. In the context of the low-temperature relaxation β* the most striking fact is that this difference in temperature is also present. This observation might imply that the β* relaxation possesses a certain degree of intramolecular cooperativity in the case of PBN, as recently proposed for PEN.[5] The difference in the position of the β* relaxation between PEN and PBN nearly mimics that of the α relaxation, whereas the position of β_1 mode is nearly the same as in PEN. Therefore, the β* relaxation, although associated with the presence of naphthalene group, cannot be exclusively related to it. Our experiments indicate that the β* relaxation have some cooperativity character which is related to the rigidity of the polymer chain.

Conclusions

The β relaxation in a series of polymers based on 2,6-naphthalenedicarboxylic acid presents at least two modes that coincide exactly with the β_1 and β_2 reported for PET and PEN. At higher temperatures, the β* relaxation is also observed analogously to PEN. The β* can be attributed to the motions of the naphthyl moiety. However, in contrast to β_1 and β_2, the β* relaxation is not completely insensitive to the rest of the monomer unit; i.e., it appears at lower temperatures in the case of PBN than in the case of PEN. This variation is nearly parallel to that exhibited by the α relaxation. This is a clear indication that the β* relaxation is, to a certain degree, a cooperative motion. Also, the introduction of ethero atoms of different polarity along the polymeric chain can be used as a label to follow the different components of the β relaxation. Our results based on this fact are in agreement with the assignation made by Boyd on the origin of the different observed motions below T_g and clearly demonstrate the existence of cooperativity in this temperature range.

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