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# β-Relaxations in Phenylene Polymers

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ABSTRACT: Using dynamic mechanical and dielectric techniques, we have studied β-relaxations in a group of polymers having high concentrations of phenylene links in the main chain. These included polycarbonate, PEEK, and a series of polyarylates based on Bisphenol A and mixtures of terephthalic and isophthalic acids. In all cases, the maximum value of tan δ was larger in the mechanical data, the activation energy was larger, and the peak occurred at a higher temperature and a lower frequency than in the dielectric data. The activation entropies of the dielectric relaxations were close to zero, a condition that is attributed to a noncooperative motion of a small molecular fragment. It is concluded that the dielectric β-relaxation is the low-temperature, high-frequency component of a broader distribution of internal motions that are seen in the dynamic mechanical measurements.

The β-relaxation in polycarbonate has been studied extensively. Dielectric measurements[1,2] have indicated an activation energy of 7–8 kcal/mol. Reports of dynamic mechanical measurements[3,4] have included evidence for three overlapping loss peaks with the largest centered at −97 °C with an overall activation energy of 10.3 kcal/mol. On the other hand, the dielectric data do not show evidence for structure within the relaxation.[5] Dynamic mechanical studies on polycarbonate led Yee and Smith[6] to conclude that the relaxation, which they referred to as $\gamma$, involves the entire monomer unit. NMR studies on selectively deuterated polymers led Spiess[7] to conclude that the C–$CH_3$ bonds are fixed while the phenylene units undergo 180° flips in addition to small angle fluctuations. Since the β-relaxation is dielectrically active, it is reasonable to conclude that the carbonate groups are also moving.

We have previously found a class of simple, noncooperative relaxations for which the activation entropy is close to zero.[8,9] Examples of this class include methyl group rotations,[8] the β-relaxations in poly(methyl methyacrylate) and poly(vinyl acetate),[9] the crystalline α-relaxation in poly(oxymethylene),[10] and grain boundary relaxations in certain metals.[9] Local mode γ-relaxations also have this property when restricted to a short polymethylene sequence.[9]

The purpose of the present study was to examine the cooperative character of the secondary relaxations in polymers containing a high concentration of phenylene links in their main chains. Examples included polycarbonate, poly(ether ether ketone) (PEEK), and a series of polyesters derived from Bisphenol A and mixtures of isophthalic and terephthalic acids.

The dynamic mechanical measurements were made at frequencies from 0.033 to 90 Hz with a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA), and the dielectric measurements were made at frequencies from $10^2$ to $10^5$ Hz with a custom-built dielectric spectrometer employing a Hewlett-Packard LCR meter (Model 4274A). An Arrhenius plot based on the maxima in tan δ for the β-relaxation in polycarbonate is shown in Figure 1. The dielectric data are consistent with those reported by O'Gara and co-workers,[11] who calculated an activation energy of 11.5 ± 1.2 kcal/mol from a combination of dielectric, mechanical, and NMR data. Our dynamic mechanical loss peak is about 20 °C higher at a frequency of 1 Hz. This is thought to reflect a larger weighting of the higher temperature portions in the multicomponent relaxation discussed earlier.[3-5]

Similar plots for PEEK and the polyester BPA-I/T-(50/50) are shown in Figures 2 and 3, respectively. In each case, the apparent activation energy calculated from the dielectric data is 10–11 kcal/mol. At a given temperature, the dynamic mechanical peak occurs at a lower frequency and its apparent activation energy is larger, as indicated by a larger slope in the Arrhenius plot. A similar pattern has been reported for the β-relaxation in polyethylene terephthalate.[5,12] In contrast with this, the mechanical and dielectric data for the γ- and β-relaxations in dry Nylon 6I, the polyamide derived from hexamethylenediamine and isophthalic acid, follow the same temperature–frequency relationships (Figure 4).

Data of tan δ versus temperature in polycarbonate from dynamic mechanical measurements at 90 Hz and dielectric measurements at 100 Hz are compared in Figure 5. The 10% difference in frequency is thought to have little significance. The maximum value of tan δ is larger for the dynamic mechanical data and occurs at a higher temperature.

We do not know of a theoretical justification for comparing the magnitudes of tan δ values from dielectric and mechanical experiments. However, there are a number of secondary relaxations in polymers having high concentrations of dipoles for which the dielectric and dynamic mechanical maxima in tan δ are quite similar.[5]

Isothermal plots of tan δ versus log frequency were shifted along the horizontal axis to form master curves at a designated reference temperature.[5] The dynamic mechanical and dielectric master curves for polycarbonate are compared in Figure 6 using a reference temperature of −75 °C. The maximum for the dielectric data occurs at a higher frequency, and the two curves appear to approach each other in the limit of high frequencies. For the dielectric data, the temperature-dependent shift factors correspond to the same activation energy as was calculated from the data in Figure 1. The behavior of the β-relaxations in PEEK and the polyesters was similar.

From the patterns in Figures 5 and 6, we conclude that the dielectric β-relaxation in these polymers is the low-temperature, high-frequency component of a broader distribution of motions that are revealed in dynamic mechanical measurements. Further support for this view is found in the values of the activation energies. As stated above, we have previously found a class of simple, noncooperative relaxations for which the activation entropy is close to zero.[8-10]

If $\Delta S^{\ddagger} = 0$, the relationship between the Arrhenius activation energy, $E_a$, and the temperature of the relaxation at a frequency of 1 Hz, $T'$, is given by[1]

$$E_a = RT'[1 + \ln (k/2\pi h) + \ln T']$$

As shown in Figure 7, the activation energies for the dielectric relaxations are close to this relationship. This indicates that the dielectric technique is sensitive to the noninteracting motions of local groups. The activation

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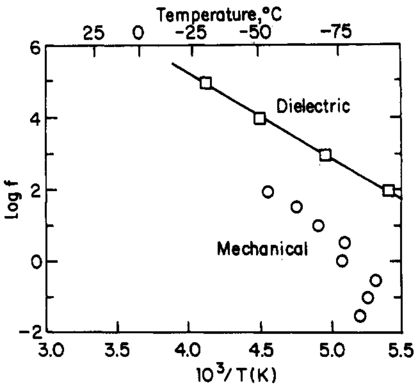

**Figure 1.** Arrhenius plot for the β-relaxation in polycarbonate.

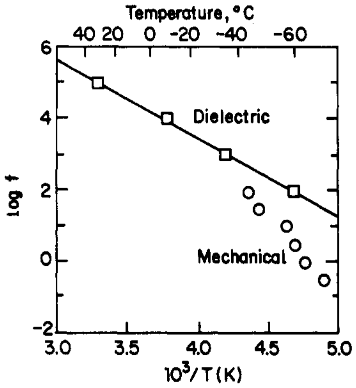

**Figure 2.** Arrhenius plot for the β-relaxation in PEEK.

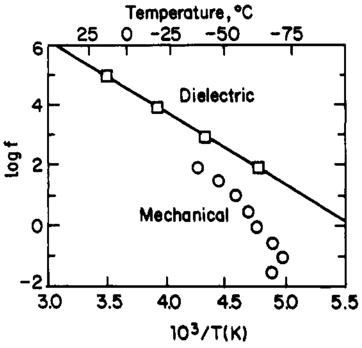

**Figure 3.** Arrhenius plot for the β-relaxation in BPA-I/T(50/50).

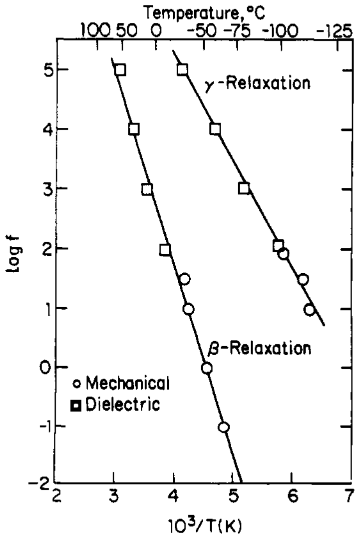

**Figure 4.** Arrhenius plot for the secondary relaxations in Nylon 6I.

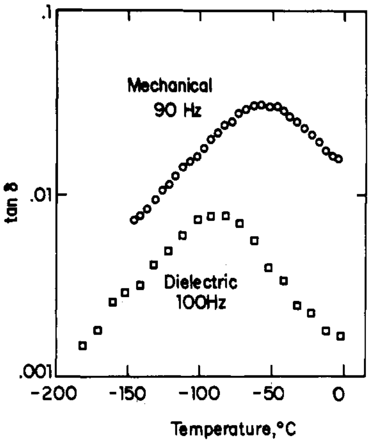

**Figure 5.** tan δ versus temperature for the β-relaxation in polycarbonate.

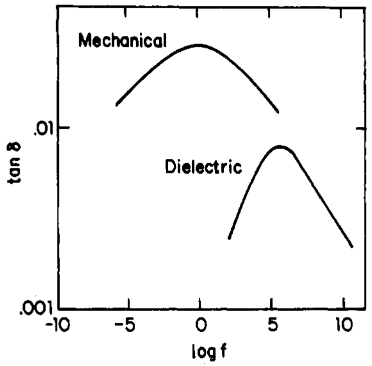

**Figure 6.** Comparison of the dynamic mechanical and dielectric master curves for the β-relaxation in polycarbonate. Reference temperature: −75 °C.

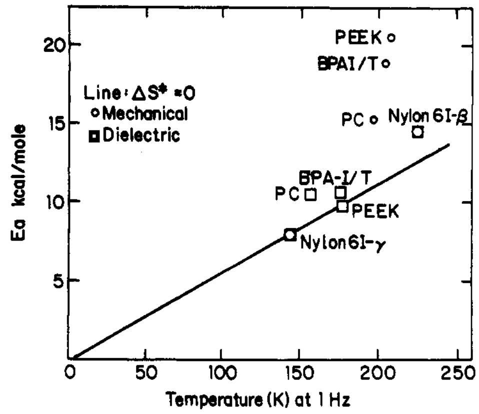

**Figure 7.** Activation energies for the β-relaxations in phenylene polymers.

energies calculated from dynamic mechanical data are considerably larger. The vertical distances between the points and the line in Figure 7 correspond to $T'\Delta S^{\ddagger}$. We conclude that the dynamic mechanical data reflect cooperative motions of a wider range of chain segments in addition to those that are dielectrically active.

Electric fields can interact directly with the dipoles within a sample in highly specific ways. Mechanical forces, on the other hand, must act from outside the sample, exciting all available internal motions, including those that are dielectrically active as well as others involving somewhat larger molecular fragments. Thus, it is not surprising that, in these highly aromatic polymers, the dielectric relaxation appears to be the low-temperature, high-frequency component of a broader mechanical relaxation. Moreover, as indicated in Figure 7, the mechanical relaxation has significant cooperative character, while the dielectric relaxation is essentially noncooperative.

Nylon 6I consists of alternating polymethylene and aromatic segments. Since similar segments are isolated from one another, they respond to mechanical and dielectric oscillations in a similar manner.

**Registry No.** PEEK, 31694-16-3; (bisphenol A)(isophthalic acid)(terephthalic acid) (copolymer), 26590-50-1; (bisphenol A)(isophthalic acid)(terephthalic acid) (SRU), 39281-59-9; (hexamethylenediamine)(isophthalic acid) (copolymer), 25722-07-0; (hexamethylenediamine)(isophthalic acid) (SRU), 25668-34-2.

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# Thermodynamic Characterization of Miscible Blends from Very Similar Polymers by Inverse Gas Chromatography. The Poly(ethyl acrylate)–Poly(vinyl propionate) System

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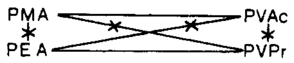
ABSTRACT: Thermodynamic interaction parameters for the interaction of poly(ethyl acrylate) (PEA) (component 2) and poly(vinyl propionate) (PVPr) (component 3) with themselves and separately with various probes (component 1), e.g., *n*-heptane, ethanol, benzene, toluene, methyl propionate (MP), acetone, ethyl acetate (EA), methyl ethyl ketone (MEK), ethyl propionate (EP), chloroform, 1,2-dichloroethane (EDC), and chlorobenzene, have been determined by the inverse gas chromatographic method (IGC) at four temperatures, 60, 80, 100, and 120 °C. The values of $\chi^*_H$ for the various polymer–probe interactions and their exchange interaction parameters ($X_{1i}/s_1$) as defined by the Flory–Prigogine theory have also been evaluated. These data have been analyzed to understand the nature of the interaction. $\chi^{*\prime}_{23}$ varies randomly with probes, assuming small positive or small negative values. The variation in sign is attributed to poor accuracy in the determination of a vanishingly small $\chi^{*\prime}_{23}$. The blends did not phase separate in the temperature region starting from the $T_g$'s to the decomposition temperatures of the blends.

## Introduction

Modern polymer solution theories[1-3] require that for a polymer–polymer system to be miscible in the absence of specific interactions not only should the exchange interaction energy be very close to zero but the differences in free volumes of the polymers must be very small also. In the absence of specific interactions, the exchange interaction energy would be positive. The exchange interaction energy or the $X_{ij}$ parameter of the Flory–Prigogine theory may be written in terms of contact energies $\eta_{ij}$ expressed per unit area of molecular contact[4]

$$X_{ij}/s_i = \tfrac{1}{2}(\eta_{ii} + \eta_{jj}) - \eta_{ij} \tag{1}$$

where $s_i$ is the molecular surface to volume ratio. The dispersion interaction $\eta_{ij}$ may be approximated as the geometric mean of $\eta_{ii}$ and $\eta_{jj}$, leading to a positive value for $X_{ij}$ (endothermic mixing) which is unfavorable for solution. $X_{ij}$ would be very small if the contact energies $\eta_{ii}$ and $\eta_{jj}$ are very close to each other, i.e., if the polymers are very similar. Recently, in our laboratory, several miscible polymer pairs have been discovered of which one component belongs to the polyacrylate family and the other to the poly(vinyl ester) family, viz., poly(methyl acrylate) (PMA) and poly(vinyl acetate) (PVAc),[5-7] poly(ethyl acrylate) (PEA) and poly(vinyl propionate) (PVPr),[8] and poly(phenyl acrylate) and poly(vinyl benzoate).[9] The degree of similarity required for miscibility could be anticipated from the following results. For example, six binary polymer pairs could be formed from the four polymers PMA, PEA, PVAc, and PVPr, as summarized in the following diagram



In the diagram the polymer pairs are linked by lines of which those not crossed turn out to be miscible. The components of the miscible pairs have one common feature; viz., their repeating units are isomeric esters differing only in the orientation of the COO group. The immiscible pairs differ only by one methylene group in their repeating units. The thermal expansion coefficients of the components of the miscible pairs are also very close to each other so that the equation-of-state effect contribution to $\Delta G_m$ remains very small.

Previously, the thermodynamic interaction for the PMA–PVAc system was studied in our laboratory by using the inverse gas chromatogrphic (IGC) method.[5] This paper is concerned with a similar study for the PEA–PVPr pair. The study also gave rise to the values of the thermodynamic interaction parameters of a number of probes with the neat polymers. These data are obtained at four temperatures, 60, 80, 100, and 120 °C, which allows the evaluation of $\chi^*_H$ used to interpret the polymer–probe interactions.

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