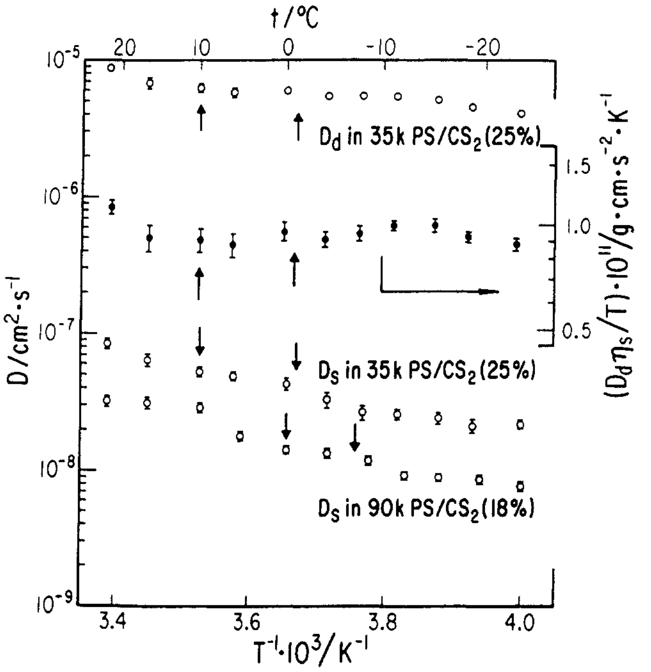

Figure 3. Temperature dependences of the diffusion coefficients are given by open circles. A pair of arrows on each sample run indicates $T_{\mathrm{gel,f}}$ and $T_{\mathrm{gel,m}}$, where $1/T_{\mathrm{gel,f}} > 1/T_{\mathrm{gel,m}}$: (top) probe dye (methyl yellow) diffusion coefficient D_d in 35K PS/CS$_2$ (25 wt %) matrix; (middle) the self-diffusion coefficient D_s of 35K PS/CS$_2$ (25 wt %); (bottom) the self-diffusion coefficient D_s of 90K PS/CS$_2$ (18 wt %). Solid circles of the second profile from the top represent the temperature-corrected and solvent viscosity corrected D_d, shown on the right-hand-side ordinate, indicating temperature invariance of the hydrodynamic radius of methyl yellow in the same matrix. Solvent viscosities at different temperatures η_s for evaluating $D_d\eta_s/T$ were obtained from ref 11.

to the coherent background; thus a constant B approximates the slow component. Therefore, $B/(A + B)$ reasonably represents the relative contribution of the slow component. An Arrhenius plot of the fast component together with the diffusion coefficient of a probe molecule, methyl yellow dye, is shown in Figure 3. The probe diffusion seems to have a monotonic temperature dependence and appears to be a simple hydrodynamic process (in Figure 3, solid circles) as exhibited by the constancy of solvent viscosity η_s and temperature-corrected diffusion coefficient (see the right ordinate scale). On the other hand, the self-diffusion has a minor indication of discontinuity at $T_{\mathrm{gel,f}}$ and $T_{\mathrm{gel,m}}$.

We conclude that most of the polymer chains still diffuse rather freely in the gel state and less than 20% of the chains is involved in "junctions" of the gel structure. Unfortunately, due to the limitation of the dye lifetime, we cannot be definite about whether the junctions are permanent or dynamic. If they are dynamic, then their time constant would be of the order of 10^{-11} cm^2/s or slower. If this were indeed the case, the rate of chain association and dissociation and the number of the junctions at a certain time scale should be considered as important factors in gelation.

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Registry No. CS$_2$, 75-15-0; polystyrene, 9003-53-6.

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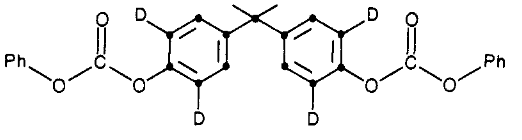
Ring Dynamics in a Crystalline Analogue of Bisphenol A Polycarbonate

Intermolecular interactions may control the rate at which ring flips occur in bisphenol A polycarbonate.[3,4] Intermolecular structure is ill-defined in the amorphous polymer, but a crystal structure for 4,4'-isopropylidenediphenylbis(phenyl carbonate) (I), a model for bisphenol A polycarbonate, has recently been reported.[5] We have prepared a deuteriated form of this material in the hope that ring flipping could be detected in a system related to polycarbonate for which the molecular conformation and the packing structure are well established. Characterization of motion in the model system may help to differentiate between alternate schemes for motion in the polymer.[5,6]



I

Unfortunately, the aromatic rings in the crystal structure of ref 5 are rigidly clamped. Even at 350 K, the deuterium spectrum is that of a rigid solid (Figure 1). The spectrum

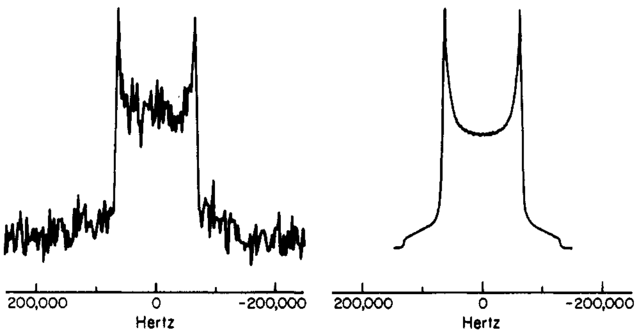


Figure 1. Experimental (left) and simulated (right) deuterium spectra at 41.445 MHz of rigid crystalline form of I at 350 K. A two-pulse sequence with 90° pulses of 3.2 μs, separated by 30 μs, and a relaxation delay of 40 s were used. The relatively low signal-to-noise ratio of the spectrum results from a very long deuterium spin-lattice relaxation time for this crystal form. The simulated spectrum was calculated with e^2qQ/h = 175 333 Hz and η = 0.034.

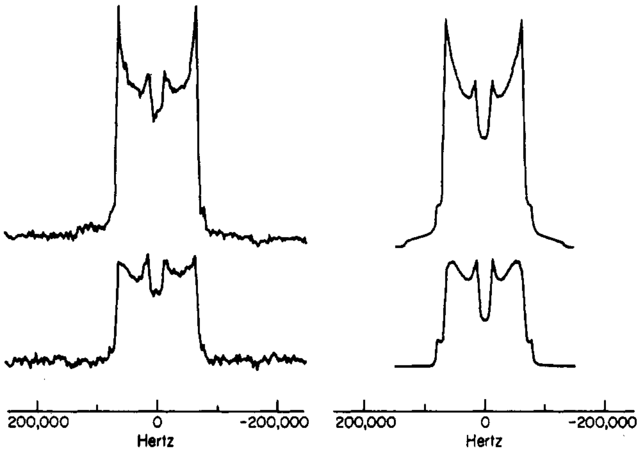


Figure 2. Experimental (left) and simulated (right) deuterium spectra of the mobile crystalline form of I at 305 K. The experimental spectrum on the bottom was accumulated with 4-s relaxation delay; the spectrum on the top was taken with 40-s delay. Other experimental parameters are the same as those used for Figure 1. The experimental spectrum on the bottom was simulated with the assumption that $e^2qQ/h = 169\,000$ and $\eta = 0.049$ and a ring-flipping rate of 1.4×10^6 s^{-1}. The spectrum on the top was simulated as a summation of the spectrum of rigid material (Figure 1) and that of the mobile species. Corrections for motion during the formation of the echo and the widths of the pulses were included in the simulations.

is best fit in terms of a slightly asymmetric quadrupole coupling interaction.

In a second crystal form, considerable averaging of the deuterium spectrum does occur, even at 305 K (Figure 2). Rather different spectra of this mobile crystal form were obtained at 305 K, however, depending on the length of the relaxation delay between data accumulations. In 40 s all the deuterium nuclei relax, but in 4 s only about half of the nuclei recover. There appear to be at least two flipping populations, one in which the rings are relatively rigid and another in which the rings flip with a rate constant of about 1.4×10^6 s^{-1}.

At 350 K, most of the rings flip rapidly on the time scale set by the deuterium spectral width (Figure 3). The experimental spectrum was fit reasonably well with the assumption of a single rate constant for ring flipping of 5.0×10^6 s^{-1}, although the sharp edges of the spectrum signal that some rigid material remains even at the elevated temperature. The spectrum is best fit with a quadrupole coupling interaction slightly reduced in magnitude from that of the rigid crystal form. In addition to ring flipping, there is a second, very fast motion in the mobile form which shrinks the coupling tensor from that for the rigid form. The second motion may be low-amplitude wobbling of the rings. Overall, the ring motion in the model compound is very similar to that in bisphenol A polycarbonate,[1-3] although higher temperatures are required to produce comparable ring-flipping rates.

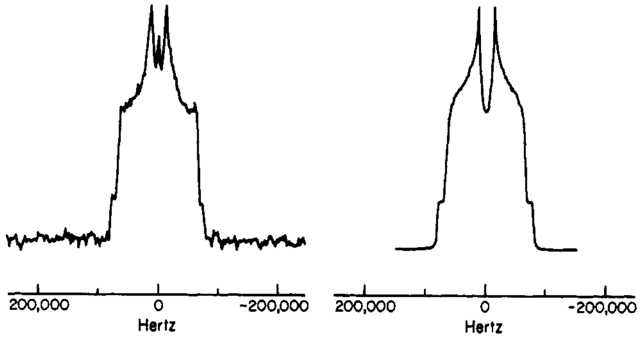


Figure 3. Experimental (left) and simulated (right) spectra of the mobile form of I at 350 K. The simulated spectrum was calculated with the tensor used for the bottom spectrum of Figure 2 and a rate constant for ring flipping of 5.0×10^6 s^{-1}.

The rigid form was obtained when crystals were grown by slow solvent evaporation, regardless of the particular solvent used and the temperature. It had a melting point of 102–105 °C. The mobile form resulted from rapid cooling of a saturated solution in methylene chloride. It had a melting point of 104–106 °C. Differential scanning calorimetry showed essentially equivalent areas under the melting peaks for each form. Mass spectrometry gave no indication of incorporated solvent, and X-ray structures found for each form showed no solvent.

The space group of the mobile form is *C*2. There are four molecules and two crystallographically independent half molecules per unit cell. Each molecule has a 2-fold axis of symmetry between the methyl groups. The molecules differ from each other in the direction of twist of the aromatic rings: one is right-handed and the other is left-handed. The carbonate groups are all in the trans-trans conformation and are oriented well away from the planes of the adjacent aromatic rings (Figure 4). The rings themselves are roughly aligned with the carbon–methyl bonds in the isopropylidene group.

A full characterization of the dynamic properties of the mobile crystal form will be reported later. We are in the

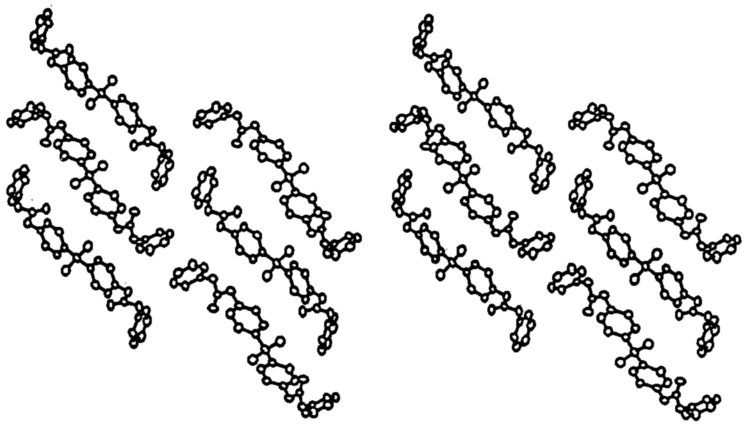


Figure 4. Stereoscopic view of the crystal structure of the mobile form of I in the (010) direction.

process of analyzing the structure of the mobile form in terms of how packing and overall molecular conformation affect the rate of ring flipping.

Registry No. I, 20325-64-8; I (copolymer), 25037-45-0; I (SRU), 24936-68-3.

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