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Sub-T_g Dynamic Processes in Amorphous Solids: A Deuterium and ^{13}C NMR Study of Poly(phenylene sulfide)

P. Mark Henrichs*,[†]

Corporate Research Laboratories, Eastman Kodak Company, Rochester, New York 14650-2021

V. A. Nicely and David R. Fagerburg

Research Laboratories, Eastman Chemical Company, Eastman Kodak Company, Kingsport, Tennessee 37662

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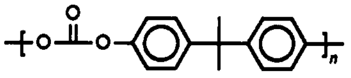
ABSTRACT: Deuterium NMR spectroscopy shows that the aromatic rings in deuterated amorphous poly(phenylene sulfide) (PPS) undergo rapid 180° flips at room temperature. Detailed analysis of the deuterium NMR spectrum shows that any subsidiary motion that accompanies ring flipping involves ring reorientation of no more than 20°. There is a distribution in the natural logarithm of the flipping rates of 6.8 at 205 K and 3.9 at 350 K. The distribution of flipping rates corresponds to a distribution of activation energies centered about 11.0 kcal/mol. The signals in the ^{13}C NMR spectrum of amorphous PPS are exceptionally broad, reflecting a wide range of local conformations for the polymer chains that are imposed by the local packing of the chains. The range of local packing environments presumably accounts for the distribution of activation energies.

The relation between low-temperature mechanical and dielectric relaxation processes of synthetic polymers and localized conformational processes is not well understood.[1-3] Bisphenol A polycarbonate (BPAPC) is a case in point.

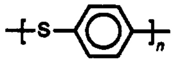


Bisphenol A polycarbonate (BPAPC)

The phenylene rings of BPAPC undergo facile 180° flips at temperatures well below the glass transition temperature,[4-6] and the frequency of ring flipping at a given temperature determined with NMR spectroscopy lies close to the curve describing the temperature and frequency dependence of the dielectric and mechanical secondary transitions.[6] Nevertheless, ring flipping by itself can account for neither the mechanical nor the dielectric transitions of BPAPC since after each flip of a ring the polymer chain is in a conformation equivalent to that before the flip. No net reorientation of dipoles or absorption of mechanical energy takes place during ring flipping.

The apparent relation between ring flipping and mechanical and dielectric activity in BPAPC probably results from tight coupling of the flipping to other processes that play a direct mechanical and dielectric role. There are several possibilities for these processes. The NMR spectrum of the methyl groups shows evidence of wagging of the chain transverse to its long axis through as much as 20°.[5] The presence of dielectric relaxation also suggests that the dipolar carbonate group is mobile. Coupling of ring flipping to conformational changes of the carbonate group is possible. Furthermore, there could be mechanically active rearrangements of the lattice surrounding each polymer chain that are associated with ring flipping.[7] Finally, coupling of ring flipping to diffusion of defects along the polymer chain has been proposed.[8]

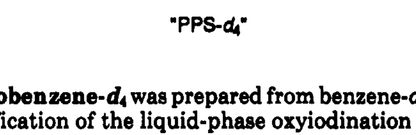
We report here that the aromatic rings in amorphous poly(phenylene sulfide) (PPS) undergo 180° flips almost as readily as do the rings in BPAPC. The structural simplicity of PPS limits the types of mechanically active motions that could be coupled to ring flipping. Facile ring flipping occurs without much secondary motion. Because the low-temperature mechanical transition for PPS is small[9] or nonexistent,[10] it appears that the secondary motions, rather than ring flipping, correlate to mechanical activity.



poly(phenylene sulfide) (PPS)

Experimental Section

Poly(phenylene sulfide). Commercial samples of PPS are partially crystalline. Although individual samples can be quenched from the melt into an amorphous form, inorganic impurities readily induce recrystallization of the initially amorphous materials at elevated temperature. We have chosen to examine samples prepared by a process that results in very little inorganic impurity. The presence of 16% disulfide linkages in the deuterated sample and 5% biphenylene sulfide units in the undeuterated sample further inhibits crystallization in variable-temperature experiments. We operate under the assumption that these levels of "impurities" do not significantly perturb the dynamic properties of the samples. For convenience we will refer to the deuterated copolymer simply as PPS-*d*.



"PPS-d_4"

p-Diiodobenzene-d_4 was prepared from benzene-d_6 (Aldrich) via a modification of the liquid-phase oxyiodination of benzene with molecular iodine.[11] Nitric acid was substituted for potassium iodate as the oxidant, and the product was purified by recrystallization from glacial acetic acid.[12] The exact mass, measured with a ZAB mass spectrometer, was 333.8646 (theoretical, 333.8658; experimental error, 3.6 ppm), and the ^{13}C NMR spectrum consisted of a singlet at 93.04 ppm for the ipso carbons and a triplet of equal intensity at 138.85 ppm for the β-carbons. The integrated intensity ratio of the two regions was 1:2.

[†] Present address: Exxon Chemical Co., Baytown Polymers Center, 5200 Bayway Drive, Baytown, TX 77522-5200.

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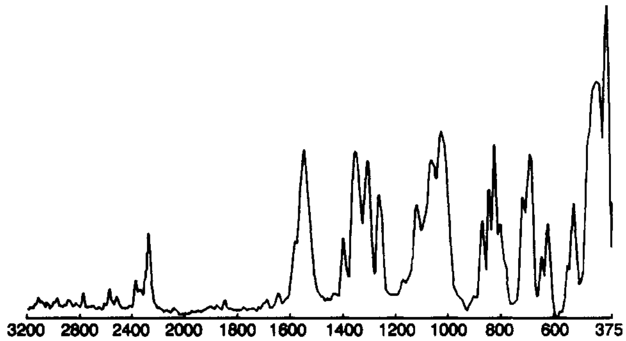

Figure 1. Infrared spectrum (absorbance vs cm^{-1}) of PPS-d_4.

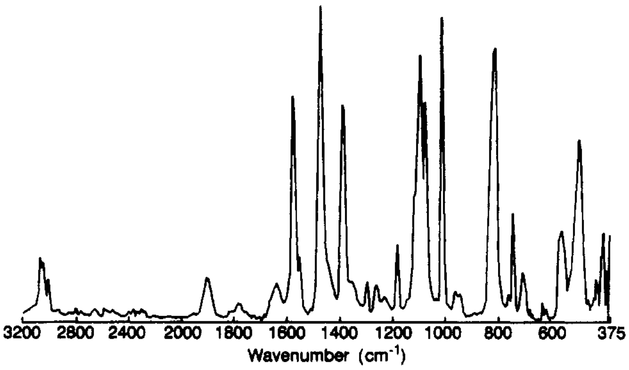

Figure 2. Infrared spectrum (absorbance vs cm^{-1}) of PPS.

Deuterated poly(phenylene sulfide) was made by the method reported for preparation of the hydrogenous material.[13-15] Into a 500-mL three-neck round-bottom flask were weighed 34.0 g of sulfur (1.06 mol, sublimed grade; Mallinckrodt) and 410 g of *p*-iodobenzene-d_4 (1.23 mol, 16 mol % excess). The flask was fitted with a 350-mm Vigreux column, a mechanical stirrer through the center joint, and an inlet tube for a slow air sweep. The column, which was wrapped with heating tape covered with glass tape and was heated to about 100 °C, was attached via a distillation head and a takeoff tube to a distillation receiver cooled in dry ice and connected to a vacuum source. The flask was maintained at 200 Torr with immersion in a metal bath controlled to 230 °C for 2.5 h, during which time iodine distilled; the bath temperature was then raised to 240 °C for 2.5 h. The pressure was reduced to 120 Torr for 0.5 h, then 60 Torr for 0.5 h, then 30 Torr for 0.5 h, and finally 0.5 Torr for 1.5 h. Simultaneously with the last pressure drop the bath temperature was raised to 250 °C. The reaction flask was then removed from the bath, repressurized with nitrogen, and allowed to cool under nitrogen, during which time the prepolymer solidified. The intermediate product was dark tan and opaque. The melt had very low viscosity. The cooled solid was granulated and heated in 30-g quantities in a 32-mm glass tube that was closed at one end and fitted with an 8-mm glass tube for nitrogen inlet and a gas outlet. The tube was inserted into a heated metal bath held at 240 °C, and nitrogen was passed over the sample at 1.0 ft^3/min for 24 h. The viscosity of the resulting polymer melt was measured at 23 200 P at 300 °C on a Rheometrics mechanical spectrometer at a shear rate of 25 rad/s. The infrared spectrum of the deuterated polymer, measured on a Nicolet 5DX spectrometer (Figure 1), was consistent with that of authentic hydrogenous material[13-15] (Figure 2). The C–D stretching and bending vibrations are shifted to lower wavenumbers while the C–C vibrations for both materials are at almost the same frequencies.

Amorphous Films. The samples were pressed under 6000 psi pressure at 300 °C into molten films prior to quenching in ice water into the amorphous solid.

Deuterium NMR spectra were measured at 41.445 MHz with a home-built probe in a narrow-bore magnet having a proton NMR frequency of 100 MHz. The sample size was 7 mm, and a 90° pulse typically was 3.6 μs. Temperatures are believed to be accurate to within 1°, as determined by calibration of the nominal probe temperature against the temperature of a thermocouple in a dummy sample. The console was a Bruker CXP-100 equipped with a Bruker Aspect 3000 computer.

All spectra were generated by Fourier transformation of the second half of the quadrupolar echo generated by a pair of 90° pulses. The pulse spacing was 25 μs. Generally the signal was stored in 2K data points that were expanded to 4K by zero filling before Fourier transformation. Exponential weighting equivalent to 1000 Hz of Lorentzian broadening was applied before transformation; each spectrum spanned 1.67 MHz.

For measurement of peak positions the number of data points was expanded to 8K before Fourier transformation to give digital resolution of 407 Hz. The measured peak positions are rounded to the nearest 500 Hz. The spectra were transferred to a Macintosh IIx computer for preparation of the figures.

Deuterium spin–lattice relaxation times were measured by monitoring the recovery of longitudinal magnetization following a saturating train of 90° pulses. The actual measurement was of the initial intensity of a spin-echo generated after each relaxation period by a pair of 90° pulses. The longest recovery time was 8 s, and the shortest recovery time was 0.001 s. The decay curves were fitted with routines written for the statistical package SAS on an IBM 3040 computer.

Simulated deuterium NMR spectra were calculated with a program written in Pascal for the Aspect computer. Powder spectra were calculated by sampling all possible orientations of the magnetic field with respect to a flipping ring of fixed orientation. This procedure is equivalent to consideration of all possible orientations of the ring with respect to a fixed magnetic field direction. The azimuthal angle was increased in steps of 2°. At each step the longitudinal angle was incremented through steps that were scaled to the sine of the azimuthal angle. The spectra were convoluted with a Lorentzian line shape having a width at half-height of 3000 Hz and were corrected for the finite value of the pulse power in the actual experiment.[16] Illustrations were created from calculated spectra that were digitized with a scanner for a Macintosh computer.

Spin–lattice relaxation times were calculated with a computer program written in Pascal based on the formulas of Torchia and Szabo.[17] The program performed a powder average over all possible orientations of the flipping ring and allowed for the presence of a distribution of ring-flipping rates.

Carbon NMR spectra were measured with magic-angle spinning and the cross-polarization technique with a probe from Doty Scientific operating at 25 MHz. The 90° pulse typically was 4.0 μs. The console was the same as that used for deuterium NMR spectroscopy.

Results

Deuterium NMR Spectroscopy. The spectrum acquired for PPS-d_4 at 360 K (Figure 3) is typical of that from deuterium nuclei attached to aromatic rings undergoing rapid 180° flips. The spectra taken at progressively lower sample temperatures show a gradual conversion toward the pattern expected for a rigid solid. Even for a sample temperature of 230 K, however, there is evidence for some molecular motion in the form of peaks in the center of the spectrum corresponding to the maxima in the high-temperature spectrum.

The recovery of deuterium longitudinal magnetization following a saturating pulse train was highly nonexponential. At 305 K the recovery curve could be approximated as the sum of two exponentials having weights of 0.49 and 0.51 and relaxation times of 0.015 and 1.29 s. Most likely, however, the curves are actually the sum of very many exponential terms resulting from a variation in flipping rate from site to site in the amorphous polymer. Recovery of magnetization was essentially complete after 10 s so that there appeared to be no sites having relaxation times greater than a few seconds. So as to be assured that there was no saturation of the magnetization, we acquired the spectra shown in Figure 3 with delay times ranging from 100 s at 205 K to 30 s at 360 K.

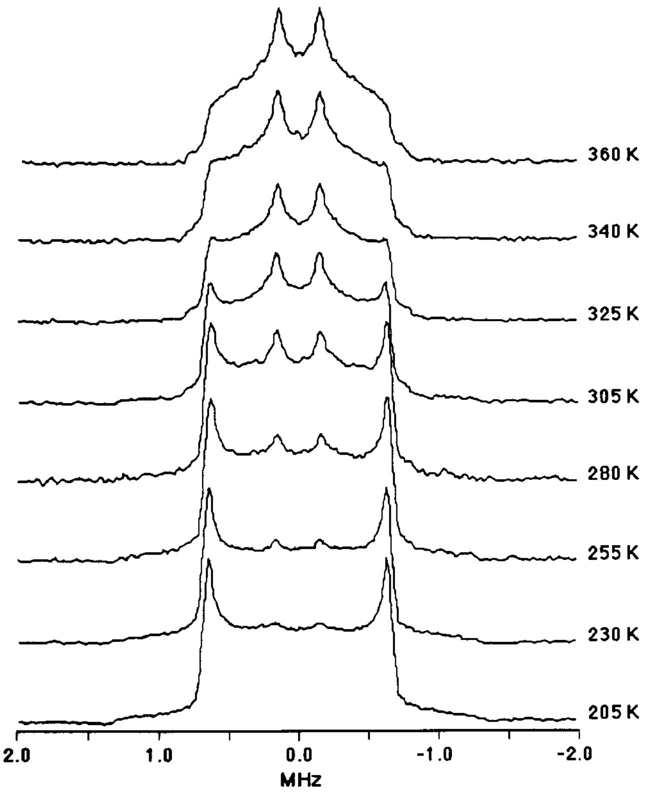

Figure 3. Deuterium NMR spectra of amorphous poly(phenylene sulfide) in which approximately 16% of the linkages are disulfide units.

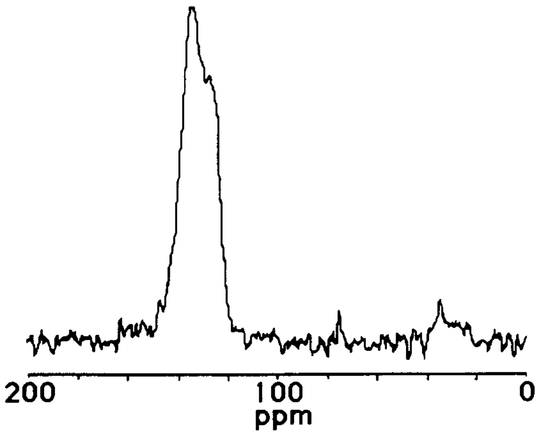

Figure 4. ^{13}C NMR spectrum of an amorphous copolymer of 95% phenylene sulfide and 5% biphenylene sulfide, taken at 305 K with magic-angle spinning and high-power decoupling.

The maxima in the spectrum recorded at 360 K are at ±14 500 Hz. The spectral edges are at about ±64 000 and ±79 000 Hz. For the spectrum recorded at 305 K the spectral maxima from the rigid portions of the sample are at ±62 500 Hz. The edges of the rigid spectrum are at about ±129 500 Hz.

^{13}C NMR Spectroscopy. As may be seen in Figure 4, the room-temperature ^{13}C NMR spectrum of PPS consists of surprisingly broad signals. Each of the two resonances contributing to the observed signal has a width of more than 10 ppm. By contrast, the width of the protonated aromatic signals of BPAPC at room temperature is only about 4 ppm. Furthermore, the ^{13}C NMR signals of crystalline PPS are sharp. The ^{13}C spectrum of partially crystalline PPS contains signals with a width less than 5 ppm from the crystalline portion of the sample on top of the broad signals from the amorphous part.[18-20] The signal broadening in the spectrum of the amorphous polymer is very inhomogeneous. After it has fully decayed, the time-domain NMR signal of PPS is readily refocused into a spin echo by a 180° pulse.

The sample used for the ^{13}C NMR spectrum was a copolymer containing 5% biphenylene units, but this is not believed to be the source of the broad signals. Observation of a variety of various copolymers of PPS has indicated that the presence of comonomer at the 5% has negligible effect on the spectrum.

Discussion

Ring Motion in Amorphous PPS. The deuterium NMR spectrum acquired from amorphous PPS-d_4 at 360 K is that expected for deuterium nuclei attached to aromatic rings undergoing rapid 180° flips. Initial analysis of the spectra was made in terms of ring flipping as the only reorientational motion. Spectral simulations were made with assumed principal elements of the quadrupole coupling tensor of $-67000/2\pi$, $-62500/2\pi$, and $129500/2\pi$ rad/s. These elements were chosen because they gave the most satisfactory fit to the rigid portion of the spectrum acquired at 305 K. Note that the quadrupole coupling tensor for deuterium attached to an aromatic ring need not be strictly axially symmetric. We assumed further that the x axis of the PAS is perpendicular to the aromatic ring and that the z axis is colinear to the C–D bond.

Best fit of the averaged spectra resulted when it was assumed that the rings at different sites in the amorphous polymer flip at different rates. A similar distribution of ring-flipping rates is found for BPAPC.[6,7,21-25] In the calculations we assumed that there was a Gaussian distribution in the natural logarithm of the ring-flipping rate that decreased in width from 6.8 at 205 K to 3.9 at 360 K (see Figure 5). A Gaussian distribution in the logarithm of rates corresponds to a Gaussian distribution in activation energies, and the Arrhenius equation shows that, if there is a temperature-independent distribution of activation energies, there should be a temperature-dependent distribution of flipping rates.

The temperature dependence of the central rate in the distributions led, with the Arrhenius equation, to an activation energy of 11.0 kcal/mol. This value is slightly higher than the 9.1 kcal/mol calculated for ring flipping in deuterated BPAPC.[26] The width of the distribution of flipping rates for PPS is also larger than that for BPAPC.[4]

Secondary Ring Motions in PPS. The aromatic rings of BPAPC undergo a librational motion in addition to ring flipping.[6,21-25] It is reasonable to expect that similar secondary motion might also occur in PPS. However, the frequencies of the maxima and edges in the high-temperature spectrum place limits on the amplitude that any such motion could have. To determine what these limits are, one needs to know the elements of the quadrupole coupling tensor for a perfectly rigid ring. The elements that were used for calculation of the spectra in Figure 5 are unsatisfactory because they may already be partially averaged by librational motion of the rings. A more satisfactory set of reference values comes from a crystalline form of the bis(phenyl carbonate) of Bisphenol A for which motion of the aromatic rings is known to be very restricted.[28] From the measured quadrupole coupling tensor for this model compound, one calculates that the maxima in a spectrum that is averaged by ring flipping alone should occur at ±14 750 Hz. Experimentally we find that the maxima in the high-temperature spectra of PPS-d_4 are at ±14 500 Hz. The close agreement between the calculated and experimental values is one indication that secondary motion in PPS is very restricted.

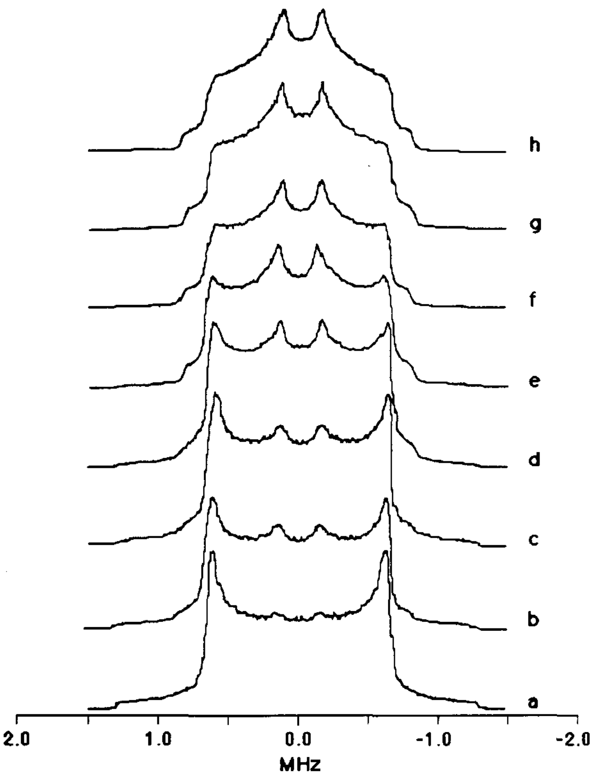

Figure 5. Calculated deuterium NMR spectra matching the experimental spectra in Figure 3. The rates of ring flipping, standard deviations of the distribution of the logarithm of the rates, and temperatures are (a) $k = 1.52 \times 10^2$, $\sigma = 6.8$, and $T = 205$ K; (b) $k = 2.80 \times 10^3$, $\sigma = 6.1$, and $T = 230$ K; (c) $k = 2.92 \times 10^4$, $\sigma = 5.5$, and $T = 255$ K; (d) $k = 2.00 \times 10^5$, $\sigma = 5.0$, and $T = 280$ K; (e) $k = 1.0 \times 10^6$, $\sigma = 4.6$, and $T = 305$ K; (f) $k = 3.00 \times 10^6$, $\sigma = 4.3$, and $T = 325$ K; (g) $k = 6.40 \times 10^6$, $\sigma = 4.1$, and $T = 340$ K; and (h) $k = 1.58 \times 10^7$, $\sigma = 3.9$, and $T = 360$ K.

A second indication of the limited nature of secondary motion in PPS can be obtained by comparison of the high-temperature spectra of PPS-d_4 with those of other compounds for which ring flipping occurs readily. One such material is a second crystalline form of the model compound for BPAPC. The maxima in its high-temperature spectrum were at ±13 000 Hz at 350 K. The spectral maxima in deuterated BPAPC occur at the same frequencies at a corresponding temperature. The fact that the frequency separation of the spectral maxima for PPS-d_4 is greater than that for either the model compound or BPAPC suggests that the amplitude of the secondary motion for PPS is smaller than that for the other materials. Analysis of the spectra frequencies for the model compound indicated that the amplitude of any secondary motion that primarily involves rotation about a single axis in that material is less than 20° (±10°).[28] This is an upper limit on the amplitude of any secondary motion that may occur in PPS.

Still, it should not be concluded that there is no secondary ring motion in PPS at all. The fact that the principal elements of the quadrupole coupling tensor that gave best fit to the experimental spectra ($-67000/2\pi$, $-62500/2\pi$, and $129500/2\pi$ rad/s) are somewhat smaller than those found for the rigid form of the model ($-68000/2\pi$, $-63500/2\pi$, and $131500/2\pi$ rad/s) does suggest that some secondary averaging takes place. Furthermore, there is a contribution to spin–lattice relaxation of the deuterons in PPS-d_4 that cannot be accounted for by ring flipping alone. The observed rate of recovery of magnetization in PPS-d_4 at 305 K following a saturating pulse train at 305 K is less than that calculated from the distribution of flipping rates that gives the best spectral shape. The extra spin–lattice relaxation results from some motion other than ring flipping, even though this motion apparently has an amplitude less than 20°.

Mechanical and Dielectric Relaxation in Amorphous PPS. The dynamic mechanical spectrum of amorphous PPS, measured at a frequency of 0.5 Hz by Eisenberg and co-workers,[9] shows a relaxation peak at 165 K. Measurements of the temperature of the peak at multiple observation frequencies yielded an activation energy of 11 ± 2 kcal. The agreement of the activation energy with that determined by deuterium NMR spectroscopy for ring flipping suggests that ring flipping and the process responsible for low-temperature mechanical relaxation are related. Nevertheless, recent measurements in Schaefer's group with a torsional pendulum have failed to detect the low-temperature mechanical transition.[10] If it exists, it is small compared with that for BPAPC.

Likewise the dielectric spectrum of PPS provides little evidence for significant low-temperature reorientation of the local electric dipoles in PPS. There is only very weak dielectric relaxation for PPS between 193 and 260 K for observation frequencies between 62 and 100 kHz.[29]

Relation between Ring Flipping and Mechanical Activity. Schaefer and co-workers proposed that the barrier to ring flipping in BPAPC is largely imposed by intermolecular constraints.[7,30,31] In fact, conformational calculations have consistently shown that internal restraints alone provide little hindrance to ring flipping in either BPAPC or PPS.[32-42]

The similarity of the measured activation energies for ring flipping in both BPAPC and PPS in spite of the differences in their internal structure supports the idea that the barriers in these polymers result from external forces. Similar ring-flipping barriers were also observed in the phenoxy resin of Bisphenol A and epichlorohydrin.[30] A slightly lower barrier was found for the aromatic rings in the amorphous portion of poly(butylene terephthalate).[43]

Nevertheless, an external source of the ring-flipping barrier by itself does not account for mechanical activity. Schaefer and co-workers postulated that the polymer chains in BPAPC form "bundles" in which the chains are locally parallel.[7,30] Within the bundles motion of the centers of gravity of the aromatic rings modulates the constraints on ring flipping such that each ring can turn over as sufficient space opens up. It is the motion within the lattice that leads to mechanical activity. Interestingly, there is evidence from wide-angle X-ray scattering to suggest a degree of nonrandomness in the chain packing of BPAPC that would be consistent with the bundle model.[44]

Some perturbation of the lattice around each aromatic ring in PPS probably does take place as the ring turns over. Translations of the centers of gravity of the rings with respect to each other would help to open up sufficient space for ring reorientation, for example. However, only minor changes in the lattice remain after the completion of each ring flip; the ring undergoes a total rotation very close to 180°. Furthermore, the lattice motions that do take place do not result in significant mechanical activity of PPS.

The similarity of the activation energies in PPS and BPAPC argues strongly against the Jones model for ring flipping in BPAPC, which involves interconversions of cis and trans conformations of the carbonate.[8] These interconversions are not possible for PPS. At least as originally stated, the Jones model does not directly lead to ring flipping in BPAPC anyway. Each aromatic ring adjacent to a carbonate group in a cis conformation is restored to its original orientation when that carbonate group returns to the trans conformation. Only if the rate of ring flipping of aromatic rings adjacent to a cis carbonate group is assumed to be much faster than the rate of ring flipping of rings adjacent to the more abundant trans linkages or if the passage of a cis "defect" down the chain is allowed progressively to turn the entire chain over does the presence of cis conformations lead to ring flipping. Complete reversal of a chain as bulky as that in BPAPC is unlikely.

On the Distribution of Local Structure in Amorphous PPS. The broad resonances in the ^{13}C NMR spectrum of an amorphous PPS point are rather curious. Other amorphous aromatic polymers, such as BPAPC, do not give such broad ^{13}C signals. The signal widths probably reflect a distribution of local chain conformations. That is, there are many different values for the dihedral angle describing the relative orientation of adjacent rings. Intermolecular shieldings could account for signal widths of only 1 or 2 ppm.

The presence of a wide range of local conformations in amorphous PPS indicates that internal forces are relatively ineffective in determining the local conformation. In fact, the minimum in the plot of potential energy versus the dihedral angles at the bonds on either side of the sulfur group in PPS is extremely broad.[45] Although the value chosen for the energy of conjugation of the electron pairs of the sulfur into the aromatic rings does affect the calculated width of the minimum, the calculations indicate that concerted rotation of adjacent aromatic rings can occur with an internal energy cost of only about 1 kcal/mol. Thus the relative orientation of each ring in the amorphous polymer is dictated by the particular packing arrangement in which these rings are found. Internal constraints on the conformation are relatively unimportant. External control of the local conformation of PPS corresponds to external control of the ring-flipping barrier, and the distribution of local conformations corresponds to the distribution of activation energies observed for the ring-flipping barrier.

Conclusions

The barrier to ring flipping in PPS, as in BPAPC, originates largely from intermolecular interactions. However, in PPS ring flipping takes place with little secondary motion. The low-temperature mechanical activity of PPS is much less than that of BPAPC. Thus the mechanical activity may require the presence of secondary motion even though ring flipping does not.

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