Molecular Mechanism of the Ring-Flip Process in Polycarbonate
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ABSTRACT: Calculations of the conformational preferences of isolated single chains of poly(2,6-dimethylphenylene oxide) (PPO) and bisphenol-A polycarbonate (PC) predict that the rings of both chains are nearly free rotors at room temperature. However, experimental dipolar rotational spin-echo 13C NMR shows that in the glass, the rings of PPO execute only small-amplitude motions while those of PC undergo primarily 180° ring flips (a hindered rotation) superimposed on some wiggles. Geometrical considerations of the dense packing of chains in the glass suggest that the rings of adjacent chains block rotational freedom. We propose that the mobility of the PC main chain results in lattice distortions which allow ring flips not permitted by the stiffer PPO main chain.

Introduction
Polycarbonates undergo a variety of large-amplitude molecular motions, some of which have been characterized recently by the collapse of deuterium quadrupolar,1 carbon chemical shift,2 and dipolar3 tensors. The dominant motion for bisphenol-A polycarbonate (PC) is 180° flips about the aromatic-ring C2 symmetry axis. These flips occur over a broad range of frequencies centered about 300 kHz at room temperature. The flips are superimposed on 30° ring oscillations about the same axis. Other main-chain motions are also significant; amplitudes of these wiggling motions are of the order of 20° (root mean square).3

In this paper we demonstrate experimentally that poly(2,6-dimethylphenylene oxide) (PPO) and its methyl-brominated analogue have no large-amplitude motions in the glass at room temperature. We then relate the differences between microscopic molecular motions in PC and PPO to the differences in their anelastic mechanical loss behavior. This connection aids in the identification of a mechanically active lattice distortion in PC which we claim is ultimately responsible for its ring flips.

Experiments
Carbon dipolar tensors were characterized by using dipolar rotational spin-echo 13C NMR at 15.1 MHz with magic-angle spinning,4 usually at 1894 Hz. This is a two-dimensional experiment in which, during the additional time dimension, carbon magnetization is allowed to evolve under the influence of C-H coupling while H-H coupling is suppressed by homonuclear multiple-pulse (WAHUHA) decoupling.5,6 For singly protonated carbons whose resonances are well resolved in the chemical shift dimension, a Fourier transform of the intensity at the peak maximum vs. evolution time yields a dipolar spectrum consisting of a 13C–H Pake doublet, scaled by the WAHUHA decoupling, and broken up into sidebands by the magic-angle spinning.7

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Table I
Carbon-13 Relaxation Parameters for Some Polycarbonates and Poly(phenylene oxides)

<table>
<thead>
<tr>
<th>polymer</th>
<th>$\langle T_1(C) \rangle$, ms ($H_1(C) = 44$ kHz)</th>
<th>$n_2/n_1$, aromatic dipolar sideband ratio (MAS = 1894 Hz)</th>
<th>$n_2/n_1$, methyl dipolar sideband ratio (MAS = 947 Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>aromatic</td>
<td>methyl</td>
<td></td>
</tr>
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</tbody>
</table>

Figure 1. Dipolar rotational spin-echo 15.1-MHz $^{13}$C NMR spectra of a methyl-brominated poly(phenylene oxide) as a function of the number of WAHUHA cycles used during $^1$H-$^{13}$C dipolar evolution.

Figure 2. Dipolar Pake patterns for the aromatic CH and methyl CH$_3$ for dimethoxybenzene (top, polyphenylene oxide) (middle), and methyl-brominated poly(phenylene oxide) (bottom). These patterns are the result of 16-point Fourier transforms of absorption-mode data, examples of which are shown in Figure 1. Magic-angle spinning was at 1894 Hz for the patterns on the left and 947 Hz for those on the right.

so that 16 WAHUHA cycles fit in one rotor period. After one rotor revolution, all CH vectors have been restored to the orientations they had following the end of the matched, spin-lock, cross-polarization preparation of the carbon magnetization. Thus, all dephasing of carbon magnetization due to CH coupling has been reversed and a dipolar echo results. The intensity of this echo should match that of the signal before any dephasing (zero WAHUHA cycles). The observed echo is only about half as big with losses due primarily to imperfect H-H decoupling.

Dipolar sideband patterns for the CH and CH$_3$ groups in the methyl-brominated PPO, in PPO itself, and in a crystalline model compound for PPO, dimethoxybenzene, are shown in Figure 2. The aromatic-carbon dipolar-

spectra on the left are all Pake doublets broken up into spinning sidebands separated by 1894 kHz (the inverse of 16 times the WAHUHA cycle time). Each sideband is represented by a single point in the dipolar frequency dimension. Intensities of the sidebands can be reliably compared so long as sideband widths are all equal, an assumption we will make here.

The fact that the PPO and methyl-brominated PPO protonated aromatic-carbon dipolar pattern are indistinguishable from that of a nominally rigid crystalline material (Figure 2, left) means the rings in the two PPOs have no large-amplitude motions. This conclusion is supported by the similarity of the methyl-carbon dipolar patterns for PPO, the methyl-brominated PPO, and dimethoxybenzene (Figure 2, right).

PPO and methyl-brominated PPO have few low-frequency small-amplitude wiggles. Both protonated-aromatic and methyl-carbon $T_1$'s are an order of magnitude
Table II

Dipolar Rotational Sideband Intensities for a CH Pair Undergoing Molecular Motion and Magic-Angle Spinning at 1894 Hz

<table>
<thead>
<tr>
<th>sideband no.</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>expt or motional model</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>expt (polycarbonate)</td>
<td>0.247</td>
<td>0.214</td>
<td>0.101</td>
<td>0.037</td>
<td>0.013</td>
<td>0.007</td>
</tr>
<tr>
<td>static</td>
<td>0.120</td>
<td>0.124</td>
<td>0.185</td>
<td>0.075</td>
<td>0.058</td>
<td>0.013</td>
</tr>
<tr>
<td>180° flips</td>
<td>0.217</td>
<td>0.235</td>
<td>0.111</td>
<td>0.036</td>
<td>0.008</td>
<td>0.002</td>
</tr>
<tr>
<td>half static and half flipsa</td>
<td>0.189</td>
<td>0.180</td>
<td>0.148</td>
<td>0.056</td>
<td>0.023</td>
<td>0.008</td>
</tr>
<tr>
<td>wiggles (15° rms CH reorientation on a 120° cone)</td>
<td>0.126</td>
<td>0.136</td>
<td>0.154</td>
<td>0.069</td>
<td>0.053</td>
<td>0.011</td>
</tr>
<tr>
<td>half wiggles and half flipsa + wiggles</td>
<td>0.198</td>
<td>0.188</td>
<td>0.140</td>
<td>0.048</td>
<td>0.019</td>
<td>0.006</td>
</tr>
<tr>
<td>flipsa + wiggles</td>
<td>0.269</td>
<td>0.255</td>
<td>0.095</td>
<td>0.026</td>
<td>0.005</td>
<td>0.001</td>
</tr>
</tbody>
</table>

*aThis designation means half the rings in the sample are static and the other half are undergoing 180° flips. bExact 180° flips independent of the random wiggles.

Table III

Ratio of Intensities of Second to First Aromatic CH Dipolar Rotational Sidebands with MAS = 1894 Hz

<table>
<thead>
<tr>
<th>13C rotating frame</th>
<th>n2/n1</th>
<th>poly(BPA-formal)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>spin lock, ms</td>
<td>polycarbonate</td>
<td>poly(BPA-formal)</td>
</tr>
<tr>
<td>0.05</td>
<td>0.47</td>
<td>0.75</td>
</tr>
<tr>
<td>3.00</td>
<td>0.44</td>
<td>0.87</td>
</tr>
<tr>
<td>8.00</td>
<td>0.47</td>
<td>0.95</td>
</tr>
<tr>
<td>16.00</td>
<td>0.44</td>
<td>1.06</td>
</tr>
<tr>
<td>20.00</td>
<td>0.45</td>
<td>1.28</td>
</tr>
</tbody>
</table>

*a 50% of the protonated-aromatic carbon magnetization decayed after 20 ms with H1(C) = 60 kHz. bAnnealed material; ref 3.

patterns between those rings with slow and those with fast rotating-frame relaxation (Table III, middle column). Such differences are readily apparent in polycarbonate-like polymers with multiple populations (Table III, right column).

The flexibility of the polycarbonate main chain can be inferred either from the short methyl-carbon T2, or from the methyl-carbon n2/n1 dipolar sideband intensity ratio (Table I). The latter is significantly less than that of either of the PPOs or of tetrachloropolycarbonate (Table I). Both PC parameters are unaffected by ring motions but are direct measures of main-chain wiggling. The weak H1(C) dependence3 of the methyl-carbon T2 means the frequency of the main-chain wiggling is of the order of 100 kHz. This result may explain the inability of deuterium spin alignment experiments to detect main-chain motion. Such experiments are insensitive to motions with correlation times between 10 and 100 μs. In addition, the relatively small difference between the observed methyl-carbon n2/n1 ratio and the rigid-lattice value suggests a weak temperature dependence for the deuterium quadrupolar splitting of methyl-deuterated polycarbonates. This is especially true in view of the broadly distributed motions characteristic of PC. A 7% decrease in quadrupolar splitting has been observed by Smith12 between +100 and -100 °C. Smith compared splittings from spectra taken at 10 °C intervals over the entire temperature range to confirm this weak dependence.

Discussion

Molecular Motion in PC and PPO. We begin with a summary of the features of the molecular motion in PC and PPO that any successful model of the dynamics must encompass.1-3 Poly carbonate undergoes 30° ring oscillations over a broad frequency range plus 180° ring flips between apparent rotational potential minima, with an average flipping rate greater than 100 kHz. The dipolar spinning sideband patterns are inconsistent with a 180° ring flip plus any small-angle oscillation that permits ratcheting around the C2 aromatic axis and produces motion equivalent to that of a free rotor. On the NMR time scale there is only a single dynamic population at

Figure 3. Anelastic mechanical shear loss spectra of polycarbonate and poly(phenylene oxide) taken from the work of Yee.9,10

longer than those of PC at 44 kHz (Table I). In fact, the PPO relaxation times are comparable to those of a ring-substituted chloro polycarbonate, the rigidity of whose ring and main chain are documented by dipolar sideband intensity ratios comparable to those of crystalline materials (Table I).

With neither large- nor small-amplitude ring motions active at room temperature, it is not surprising the anelastic mechanical loss spectrum of PPO is featureless10 (Figure 3). By contrast, the PC loss spectrum11 shows a broad intense peak, centered near -100 °C (at 1 Hz). The activation energy associated with this loss peak is of the order of 10 kcal/mol,11 which translates to a frequency of about 200 kHz at room temperature, the same average frequency as that of the ring flips.3

PC has large-amplitude ring motions which significantly change its sideband pattern from that expected for a static system (Table II, rows 1 and 2). The form of the collapse of chemical shift tensors has been used to prove that the large-amplitude motion predominantly involves 180° flips.23 To match the observed dipolar sideband intensities requires all the rings to flip (Table II, comparisons of rows 1, 4, 6, and 7). This means there is only one dynamic ring population at room temperature, not one undergoing flips and another static.

Even using a carbon rotating-frame spin lock for 20 ms as part of the carbon spin-system preparation prior to the dipolar evolution period reveals no differences in dipolar
Figure 4. Calculated conformational preference maps for poly(phenylene oxide) (left) and polycarbonate (right). The maps were produced by rotating the chain rigidly about the angles $\phi_1$ and $\phi_2$ and evaluating the relative potential due to intramolecular interactions. Energy maxima occur in both maps near $\phi_1 = \phi_2 = 180^\circ$. An energy minimum exists for poly(phenylene oxide) with $\phi_1 = \phi_2$ and each slightly displaced from $\pi/2$, while a minimum exists for polycarbonate with $\phi_1 = \pi$ and $\phi_2 = \pi/2$. Contours decreasing in relative energy are represented by the sequence solid line, dashed line, dotted line, and increasing in energy by the reverse sequence.

If more than one ring population exists, it must interconvert at a rate substantially greater than 100 kHz. Superimposed on ring flips and oscillations are main-chain wiggles indicating that the PC main chain is flexible in the glass. Finally, PC has a broad mechanical loss peak consistent with 200-kHz motion at room temperature, the same frequency regime as the ring flipping. The mechanical loss necessarily involves cooperative motion of the rings. For PPO, there are no large-amplitude motions such as ring flips, and few low-frequency, small-amplitude wiggles. Furthermore, PPO possesses a featureless low-temperature mechanical loss spectrum.

Intramolecular Potential. Tonelli has calculated the conformational preferences for isolated PC and PPO chains and found the rings in both cases are essentially free rotors at room temperature. We have confirmed these predictions using a calculational approach based on a Gaussian overlap model, with range and strength parameters chosen to match Tonelli's calculated energy minima. Conformational energy maps for both PPO and PC are shown in Figure 4 at higher resolution than those calculated by Tonelli. The rings in both polymers have little difficulty in executing motions about the $C_2$ axis, with only a few special conformations on these maps forbidden by steric interactions. If $\phi_1$ in PPO or in PC is set equal to $90^\circ$, then Figure 4 shows a broad flat valley with low peaks and shallow valleys for full rotation about $\phi_2$. This motion about $\phi_2$ is essentially free. As shown by Tonelli, the absolute barriers are only of the order of 1–2 kcal/mol. This is not the situation if $\phi_2$ is fixed near $0^\circ$ (or $180^\circ$) and $\phi_1$ varied. There is a sizable steric repulsion between CH$_2$ (H) and H (H) groups in PPO (PC) when $\phi_1$ and $\phi_2$ are each near $n \times 180^\circ$. Hence, the two phenyl rings in adjacent monomer units in PPO, and within a monomer unit of PC, are not strictly equivalent. Depending on orientation, constraints can be imagined such that one of the rings can undergo free rotation and the other cannot. However, if the rings rotate cooperatively, they can both behave as free rotors.

Vacuum rotational potentials are useful in that motions which are strongly prohibited (due to steric effects) in the absence of chain–chain interactions will remain prohibited when intermolecular interactions are turned on. However, such a potential energy surface provides no clue as to what additional motions are prohibited when chain–chain packing is taken into account.

Packing in the Glass. We know from the experimental dipolar sideband patterns that the rings in PC and PPO in the glass are not free rotors. The deficiency in the potential energy maps of Figure 4 is a result of the omission of the effects of packing in the solid state. If we represent the two rings of the repeat unit of PC (with their slight...
The rings in the PC glass are not free rotors because of the steric constraints imposed by neighboring chains. Ring flips are a hindered motion allowed by the intermolecular constraints. Suppose we assume that the rings are allowed to flip because random packing creates "holes" within which rings are less burdened by steric interactions. These static holes might be interspersed throughout the glass allowing some fraction of the rings freedom. The holes would presumably be big enough to allow a monomer-unit pair to move together to avoid intrachain prohibited conformations.

This static description of the glass is not, however, consistent with all the facts. First, a static-hole description of the ring motion in PC predicts two classes of dynamic rings in PC: those that move in the holes, and those that form the holes. Experiment shows only one population (Tables II and III). If we insist that all the rings are part of the hole boundaries as well as move in them, we are faced with the dilemma of a rather airy structure for PC not at all consistent with the notion of a glass with a density close to that of crystalline material.

In addition, a ring-flip mechanism which involved static holes formed by neighboring chains could yield only a weak mechanical loss peak. Without distortion or dilation of the lattice, mechanical energy cannot be dissipated by internal frictional losses. In fact, using a dynamic Poisson ratio experiment, Yee\textsuperscript{16} has shown that both shear and bulk low-temperature loss peaks occur in PC. Assignment of the ring flips to static holes would therefore lead to the implausible situation that the only large-amplitude motion in PC (and a motion not available to PPO) could not be associated with the low-temperature loss peak which so clearly distinguishes PC from PPO (Figure 3).

**No Wiggles, No Flips.** Instead, we propose a dynamic description of the lattice during the flip process. Rings are indeed constrained from large-amplitude excursions by the rings of neighboring chains. When lattice distortions occur, these constraints are relaxed (Figure 6, top). As the lattice closes up, the rings must either return to their original orientation or have flipped by 180° since these are the only orientations which do not require a lattice distortion. The mechanism of the lattice distortion may include motions such as synchronous rotation\textsuperscript{11} or cis/trans isomerization about the carbonate linkage,\textsuperscript{17} as well as torsional oscillations. Eventually, all rings participate in both flipping and blocking as lattice breathing moves up and down the chain. The rate of flipping varies across the sample due to local variations in packing. The flip marks an important volume or shape change in the glass, and so flags a mechanically active process. PC rings can flip and PPO rings cannot because of the inherent differences in the mobilities of their lattices.

This description of ring flips in polycarbonate is similar to that proposed by McCammon et al. for tyrosine-ring flips in bovine pancreatic trypsin inhibitor.\textsuperscript{18} For this protein, computer simulations of molecular dynamics show that ring flips are occasionally gated on by cooperative displacements of nearby groups. The displacements create local cavities or defects in the protein interior, and these lattice distortions are sufficient to permit ring flips. The complete ring-flip process (rings plus lattice) is a restricted motion, but the flip part of the process need not be. During the picosecond (or fraction of a nanosecond) the ring takes to flip, it is almost a free rotor. This motion is too fast to lead to significant NMR relaxation. Most of the time the ring is clamped undergoing only small-amplitude wiggles. Thus, the time important for NMR relaxation due to flipping is the period between flips. This period is the same for both ring and lattice and leads to \(T_1\) and \(T_2\) as a function of \(H_0\) and \(H_1\), respectively, which are comparable for both ring and main chain.\textsuperscript{3}

When the lattice distorts, the ring can flip. When the lattice closes again the ring assumes the original position \(\pm n \times 180°\). The flip is viewed as an exact 180° flip which occurs in mid-wiggle without interrupting the course of the wiggle (Figure 7). The wiggle is the result of cooperative motion of another kind. The flips of Table II are exact 180° flips. If wiggles could continue during the flips (Figure 7, bottom), the combination would result in averaging close to that of a free rotor.\textsuperscript{3}

**Cooperative Flips and Mechanical Properties.** We do not know the correlation range of the ring-flip process in PC. Flipping must involve at least two rings down the chain and four or five other rings on other chains. The cooperativity could involve much more.\textsuperscript{15} On the other hand, it is also possible that once the lattice distorts, independent wiggles and flips are superimposed on the cooperative flips. Only some of the ring motion need be cooperative.\textsuperscript{3}

What we have attempted in this paper is a description of the salient features of the ring-flip mechanism in PC:
Influence of Polydispersity on Polymer Self-Diffusion Measurements by Pulsed Field Gradient Nuclear Magnetic Resonance

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ABSTRACT: The effects of finite polymer polydispersity on the pulsed field gradient nuclear magnetic resonance (PFGNMR) measurement of polymer self-diffusion coefficients is considered both theoretically and experimentally. It is found that polystyrene solutions characterized by a polydispersity $M_c / M_a < 1.10$ present little difficulty in the interpretation of PFGNMR data. Single-exponential echo decays are observed down to attenuations in excess of 0.05 and the ensemble self-diffusion coefficient obtained lies between $M_c$ and $M_a$. Polymer blends have been studied and the use of deuterated polystyrene has enabled determination of the component self-diffusion coefficients. We observe considerable microscopic averaging of molecular diffusion rates, with the greatest perturbation being suffered by the higher molar mass components. An investigation of the relative importance of reptation and tube renewal as relaxation mechanisms for random coil polymers in semidilute solution reveals that tube renewal is a weak process.

Introduction

In all experiments dealing with polymer dynamics the influence of finite polydispersity presents a conundrum. In some cases discrepancies are attributed to small polydispersity effects ($M_c / M_a < 1.10$), while in others theories are supported by data obtained where molar mass variations are larger by 1 order of magnitude. A notable example of this is the classic self-diffusion study of Klein1 in which the reptative scaling law $D \sim M^{-2}$ was exhibited in polyethylene melts whose $M_c / M_a$ ratios ranged between 1.3 and 3.4. We have used pulsed field gradient nuclear magnetic resonance (PFGNMR) to measure polymer self-diffusion. It has been recently suggested by von Meerwall2 on theo-