

# A dynamic n.m.r. study of dissolved and solid cyclohexyl polycarbonate

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The conformational dynamics both in the solution state and in the bulk in the structurally modified polycarbonate of Bisphenol-A (BPAPC) with a cyclohexyl moiety in place of the isopropylidene group has been examined using n.m.r. The solution <sup>13</sup>C spectra allow the identification of the intramolecular dynamics at the repeat unit level and the consequences of the existence of microstructure. The cyclohexyl ring dynamics suggest that the ground state conformation is considerably strained relative to a pure chair form. This leads to a lower barrier for the ring inversion in agreement with modeling conclusions. In the solid state this phenylene mobility is further restricted and at low temperatures the bridgehead carbon C5 shows doublet character. As the temperature is raised, motion increases along with the free volume and this follows the onset of motion of the phenylene rings. The differential dynamics of the two phenylenes results in a broadening of the mechanical relaxation which correlates with their dynamics. The position and breadth of the shear mechanical relaxation corresponding to the dynamics monitored by the collapse of the C5 carbon can be obtained from the n.m.r. data. The conclusion indicated is that the more restricted (axial) phenylene ring is the one whose motion correlates with the high temperature side of the mechanical loss and it is the phenylene ring dynamics which correlates with the unusual shift in the low temperature loss characteristic of the cyclohexyl substitution and the increased breadth of the relaxation relative to BPAPC. © 1997 Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

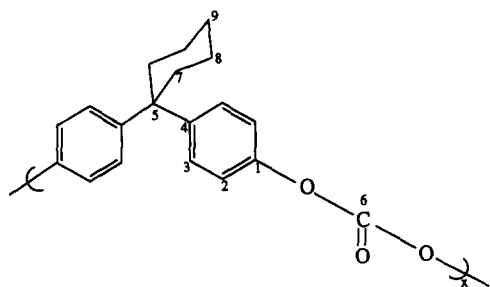
Numerous studies exist on the polycarbonate of bisphenol-A (BPAPC) and related structural analogues<sup>1–5</sup>. The n.m.r. investigations<sup>6–10</sup> have tended to focus on the relationship between the molecular dynamics, as determined by both solid and solution state n.m.r., and the bulk mechanical properties which have been used to characterise these materials and are also the basis for their value as engineering materials. We have recently carried out a solution spin-lattice relaxation study<sup>11</sup> on the analogue in which the isopropylidene group of bisphenol-A is substituted with a cyclohexyl ring (the repeat unit structure is shown in *Figure 1*). The interest in this cyclohexyl polycarbonate (CBPC) is a consequence of its rather unusual bulk properties relative to other analogues. The low temperature mechanical response of CBPC occurs at a higher temperature ( $\approx 50^\circ$ ) relative to BPAPC where the loss peak is at  $-100^\circ\text{C}$  at 1 Hz.<sup>3</sup> This is atypical of a substitution on the isopropylidene unit<sup>12</sup>. Usually substitution on the phenylene units is observed to shift the low temperature loss peak to a higher temperature while on the other hand even when a norbornyl group is substituted onto the isopropylidene unit the low temperature response is largely unaffected. It has been suggested<sup>3</sup> the lower free volume of CBPC, as demonstrated by the gas transport properties, is a contributing factor in this behaviour. This lower free volume is attributed to the flexibility of the cyclohexyl substituent which leads to better intermolecular packing.

In view of the influence of the cyclohexyl substituent on

these important mechanical and transport properties, the chain dynamics including the local motion of the cyclohexyl ring and the phenylene rings merit study. The previous n.m.r. solution spin-lattice relaxation results which included molecular modeling calculations on the repeat unit showed that the segmental motion of the chain backbone can be characterised using the Hall–Helfand model<sup>13</sup> and the local rotational dynamics of the two phenylene groups are inequivalent according to whether they have an axial or an equatorial orientation as defined by the cyclohexyl ring geometry. The axial or more hindered phenylene ring undergoes restricted anisotropic rotational diffusion whereas the equatorial ring undergoes complete anisotropic internal rotation.

The motion of the cyclohexyl ring is slow on the spin-lattice relaxation timescale and was not studied in the earlier report based on spin-lattice relaxation. However, conformational interchange of the cyclohexyl groups can be monitored by variable temperature lineshape collapse in a suitable solvent thus permitting a more complete elucidation of the intramolecular factors governing the conformational dynamics. This is the purpose of this investigation. In addition a similar examination of the high resolution solid state spectrum will address the issue of intermolecular constraints and will yield a quantitative description of the dynamics which will be matched to the mechanical response. There has been considerable discussion of the molecular origin of the low temperature relaxation (or  $\gamma$  transition) in polycarbonates<sup>2,3,14,15</sup>. Though there is no ultimate consensus it is accepted that the motion of the phenylene rings is a determining factor. The effect of

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**Figure 1** CBPC structure (the carbons are labelled in accordance with the assignments in Table 1)

substitution and its concomitant effect on dynamics of the individual structural moieties has been a useful probe of the link between molecular and bulk behaviours. In this regard CBPC is of considerable interest since, as has been mentioned, substitution at the isopropylidene group though changing the temperature of the glass transition ( $\alpha$  transition) normally has little or no effect on the  $\gamma$  transition except in this case. It is thus the intent of this study to provide further insight into the origin of the  $\gamma$  transition and explain the effects of the cyclohexyl unit on the dynamics.

#### EXPERIMENTAL

High molecular weight samples of CBPC were supplied by General Electric. For the low temperature solution spectra ( $-10^{\circ}\text{C}$  to  $-130^{\circ}\text{C}$ ) the sample was dissolved in dichlorofluoromethane (Freon21, b.p.  $8.9^{\circ}\text{C}$ , Aldrich Chemicals).

The samples were degassed and flame sealed in 5 mm NMR tubes. This solvent offers the potential of resolving conformational isomers in solution where most solvents would freeze or cause dissolution at the requisite temperatures.

The  $^{13}\text{C}$  solution spectra were obtained at 125.7 MHz with broad band decoupling on a Varian Unity 500. The  $^{13}\text{C}$  solid state spectra as a function of temperature were obtained at 75.4 MHz on a Bruker MSL 300 using standard cross polarization magic angle spinning (CPMAS) techniques with a CP contact time of 3 ms and a  $5\ \mu\text{s}\ \pi/2$  pulse width.

#### RESULTS

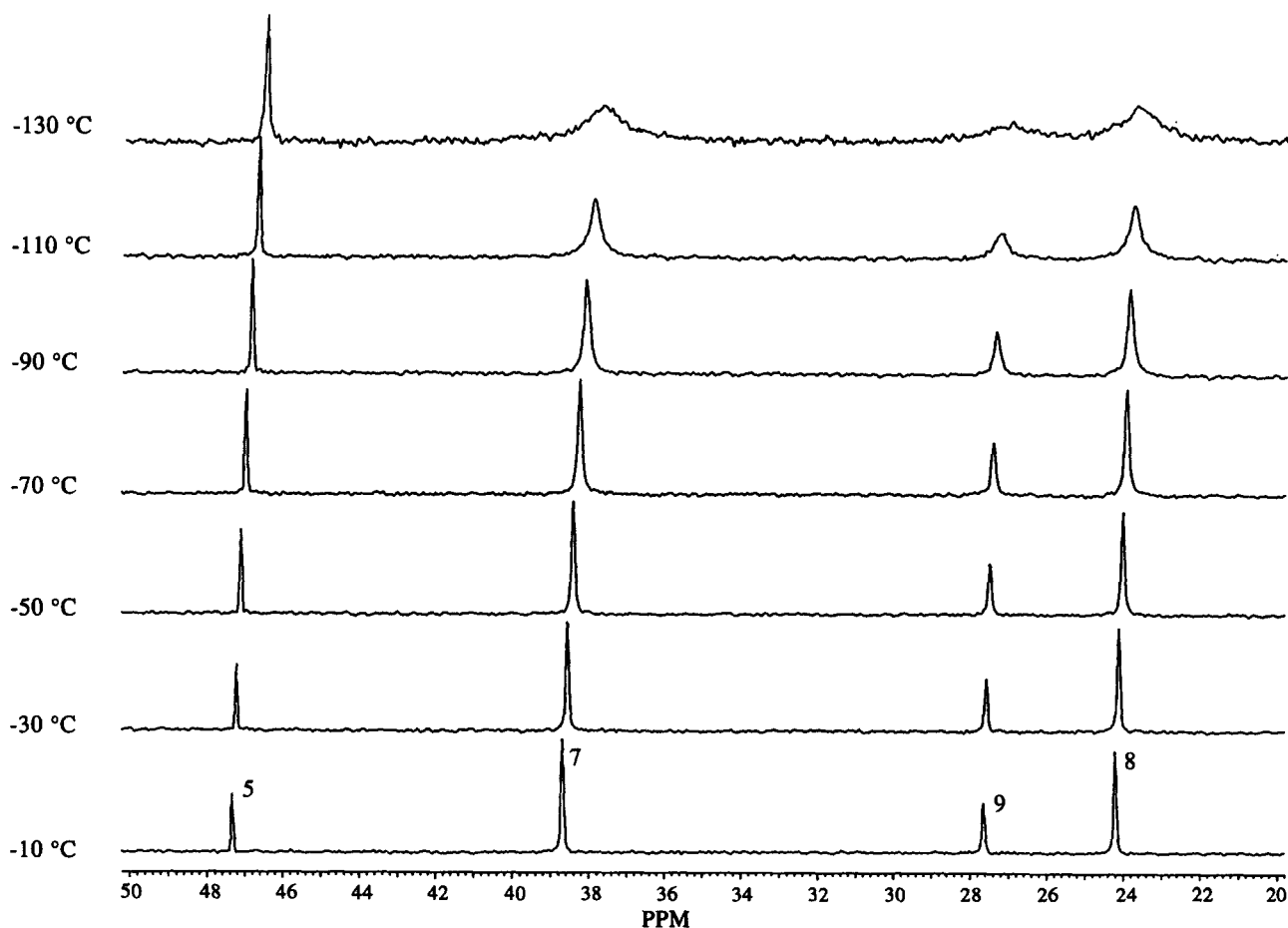
The variable temperature ( $-10^{\circ}\text{C}$  to  $-130^{\circ}\text{C}$ ) solution  $^{13}\text{C}$  spectra of CBPC for the aliphatic and aromatic regions are shown in Figures 2 and 3 respectively. The chemical shift assignments according to the structure shown in Figure 1 are given in Table 1.

The variable temperature ( $-100^{\circ}\text{C}$  to  $+104^{\circ}\text{C}$ ) solid state  $^{13}\text{C}$  spectra of CBPC are shown in Figure 4. The assignments can be compared with the solution  $^{13}\text{C}$  chemical shifts and are discussed in detail below.

#### INTERPRETATION.

##### *The variable temperature solution $^{13}\text{C}$ spectra*

The aromatic region shown in Figure 3 clearly shows the effect of the cyclohexyl ring dynamics on the exchange of



**Figure 2**  $^{13}\text{C}$  variable temperature spectra of CBPC: aliphatic region. Resonances are labelled in accord with assignments in Table 1

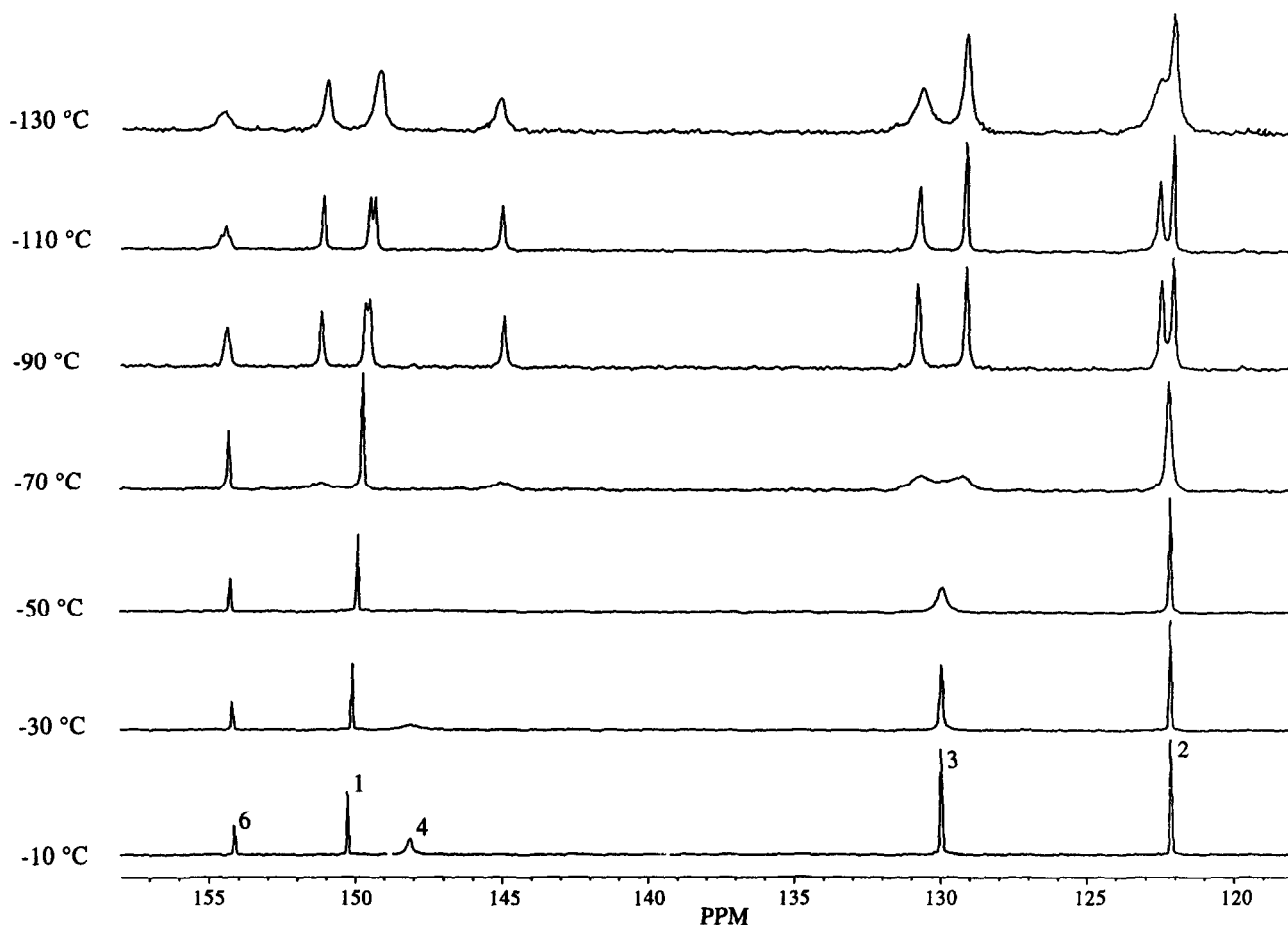


Figure 3  $^{13}\text{C}$  variable temperature spectra of CBPC: aromatic region. Resonances are labelled in accord with assignments in Table 1

the axial-equatorial carbons. This is most evident on the carbon 4 resonance, which appears as a single exchange averaged resonance at 148 ppm at  $-10^\circ\text{C}$  and as two peaks below  $-70^\circ\text{C}$  at 145 ppm and 151 ppm. The chemical shift of *ca.* 6 ppm is within the range of an axial-equatorial  $^{13}\text{C}$  shift for carbons directly bonded to a cyclohexyl ring<sup>16</sup>. The assignment of the high field line at 145 ppm to the equatorial carbon is verified by the differential broadening observed below  $-110^\circ\text{C}$  due to the freezing of the axial phenylene ring rotational motion relative to the equatorial ring<sup>11</sup>. The C4e thus sees more than one environment corresponding to the different conformers of the axial phenylene ring. Whereas the C4a is not affected by the different phenylene conformers of the equatorial or the axial conformation. The other phenylene carbons 3, 2, and 1 show similar behaviour with a decreasing value for the axial-equatorial shift in order with distance from the bridgehead carbon 5 of the cyclohexyl. The differential broadening of the axial and equatorial sites is also observed for C1, C2 and C3 though for C1 the effect is difficult to discern due to the small ax.

Table 1 Carbon-13 chemical shift assignments in CBPC (ppm rel. to TMS)

C1	150.04
C2	122.17
C3	129.89
C4	147.80
C5	47.34
C6	153.86
C7	38.82
C8	24.38
C9	27.78

eq. shift (0.18 ppm). For C2 and C3 the axial (downfield resonance) is broader in contrast to the C4 situation. This is a consequence of the axial phenylene conformers causing C2 and C2' on the axial ring to have different chemical shifts with a similar occurrence for C3 and C3'. As the axial ring undergoes restricted motional averaging the C2 and C2' carbons on the same ring become inequivalent producing differential broadening for the axial carbons.

The exchange lineshape collapse of C1, C2, C3 and C4 can be analysed using conventional means<sup>17</sup> and the results of simulations of the lineshape collapse are shown in Figure 5 for all four carbons. The rate parameters so obtained for all four carbons lie on a common Arrhenius plot yielding an activation energy of 28 kJ/mol. and  $\tau_\infty$  of  $6.5 \times 10^{-11}$  s for the cyclohexyl ring conformational inversion (a  $\leftrightarrow$  e). The dynamic coincidence of the data from four different resonances is convincing and the activation energy compares with other data<sup>18</sup>.

This can be compared with the results of a molecular mechanics calculation on 1,1 diphenyl cyclohexane (DPCH). The molecular mechanics estimate (MM2)<sup>19</sup> was carried out using the CAChe modelling system, version 3.8 using MM2 parameters. Figure 6 shows the conformational energies calculated using molecular mechanics for cyclohexane and 1,1-diphenyl cyclohexane as a function of the aliphatic ring C5-C7-C8-C9 dihedral angle. As the dihedral varies between  $-60^\circ$  and  $+60^\circ$  the cyclohexyl ring passes from a chair conformation to a twisted boat. From Figure 6 it is seen that the barrier is smaller for DPCH than is observed for the unsubstituted cyclohexane, 32 kJ/mol versus 41 kJ/mol. Steric strain is significant in the chair form

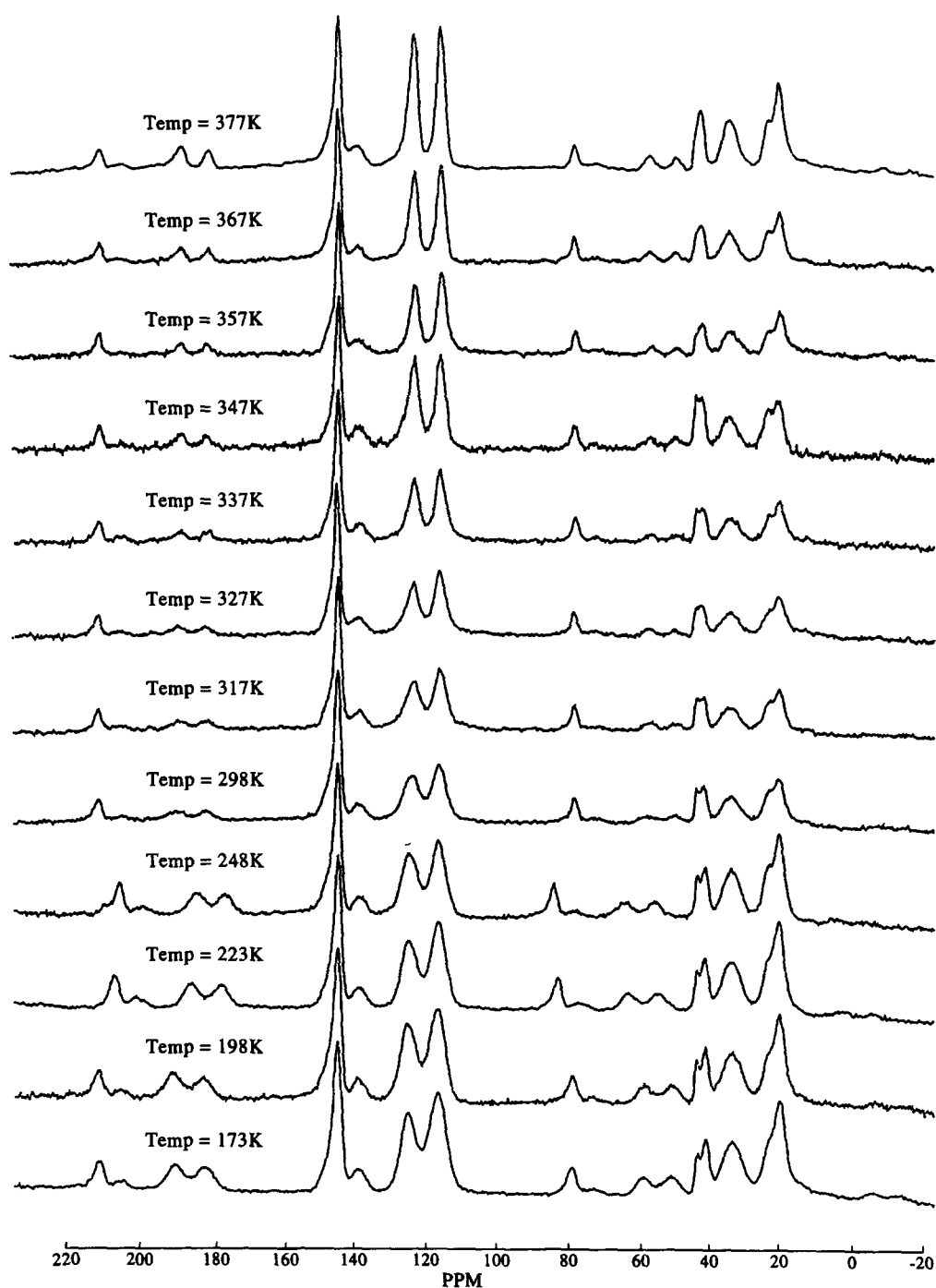


Figure 4  $^{13}\text{C}$  variable temperature, solid state spectra of CBPC using CPMAS

of DPCH, as can be seen from the change in the C–C–C bond angle at the bridge head carbon (C5) from  $110.9^\circ$  for DPCH relative to  $104.5^\circ$  for the unsubstituted cyclohexane. This extra strain in the substituted ring destabilises the chair, and leads to a smaller barrier. Low barriers for highly substituted cyclohexanes<sup>20</sup> have previously been ascribed to high ground state strain energies due to steric constraints. This implies that the cyclohexyl moiety in CBPC may not exist in a pure chair configuration in the ground state.

The carbonate resonance C6 also shows the effect of the cyclohexyl ring inversion though the situation is more complex. The C6 resonance has three potential chemical environments, namely, one in which the carbonate is adjacent to two axial phenylene rings, one with two equatorial rings adjacent and two degenerate forms with

one axial and one equatorial ring adjacent. This microstructure gives rise to the triplet pattern observed for C6 at  $-110^\circ\text{C}$  with the intensities determined by the population of the diad structures as described. Axial–equatorial exchange by ring inversion will average the triplet structure as observed and this can be analysed as before except that the data is limited compared to the phenylene carbons due to the small chemical shifts between the diad structures. However we are able to verify the timescale of this process is coincident with the other data on Figure 5 as shown. The effects of the existence of this type of microstructure on n.m.r. have been reported by other workers<sup>21</sup>.

The aliphatic region corresponding to the cyclohexyl carbons shown in Figure 2 is less informative. The C5

resonance is essentially unaffected by temperature change in the range studied whereas the protonated carbons: C7, C8, C9 show a slight broadening with decreasing temperature. This probably reflects a combination of minor dynamic effects and inefficient decoupling at the low temperatures.

#### The variable temperature solid state $^{13}\text{C}$ CPMAS spectra

The  $^{13}\text{C}$  CPMAS spectrum as a function of temperature in Figure 4 can be compared with the solution spectrum for the purpose of assignment. Two features are readily apparent. The resonance at 143 ppm is the 4e carbon, the 4a carbon being obscured by the C1 resonance at 150 ppm, thus indicating that in the solid state the cyclohexyl ring does not invert on the ms timescale over the temperature range studied ( $-100^\circ\text{C}$  to  $+100^\circ\text{C}$ ).

The more informative feature of the solid state spectrum is the doublet nature (ca. 226 Hz) of the C5 resonance at 47 ppm. This lineshape collapses slowly over the  $200^\circ$  temperature range studied and is shown in detail in Figure 7. This lineshape collapse can only be simulated with a broad

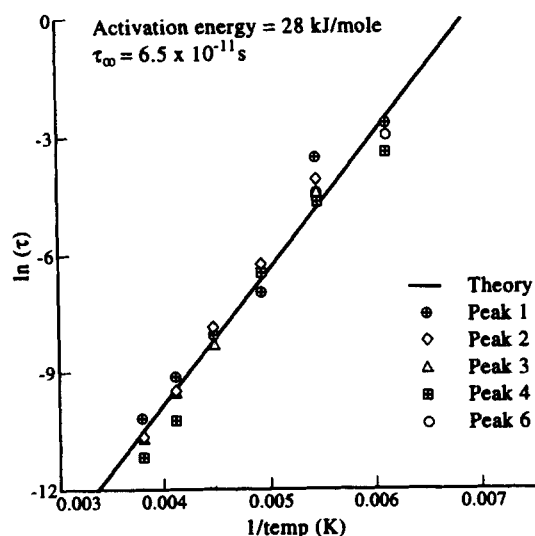


Figure 5 Activation energy plot for cyclohexyl ring inversion in solution in CBPC. Data from all carbons are fit to a common Arrhenius dependence

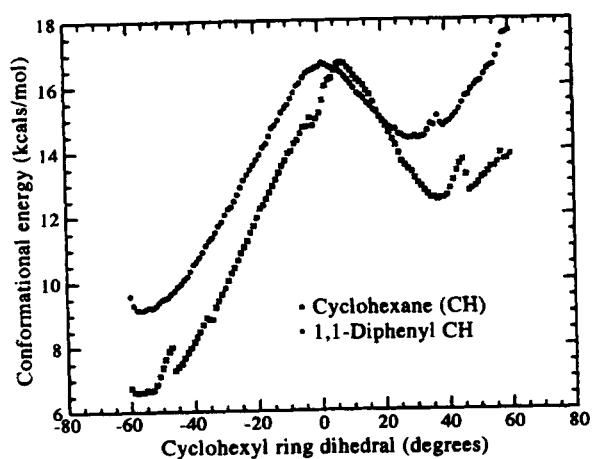


Figure 6 Conformational energies for the cyclohexyl ring inversion for cyclohexane (x) and 1,1-diphenyl cyclohexane (●) calculated using molecular mechanics. A difference of ca. 2.1 Kcal/mol in the barriers to ring inversion is evident

distribution of rates. The distribution chosen here is described by the stretched exponential, William-Watts form <sup>22</sup>:

$$\phi(t) = \exp(t/\tau_p)^\alpha \quad (1)$$

where the exponent  $\alpha$  describes the width of the distribution and  $\tau_p$  is the characteristic correlation time which is assumed to have an Arrhenius temperature dependence. This inhomogeneous distribution of rates is common in polymer dynamics in the solid state and lineshape collapse of this type has been treated in a similar fashion in the past <sup>14,23</sup>. The simulation is also shown in Figure 7 and yields an activation energy of 54 kJ/mol with a distributional width given by  $\alpha = 0.26$ . The origin of this conformational

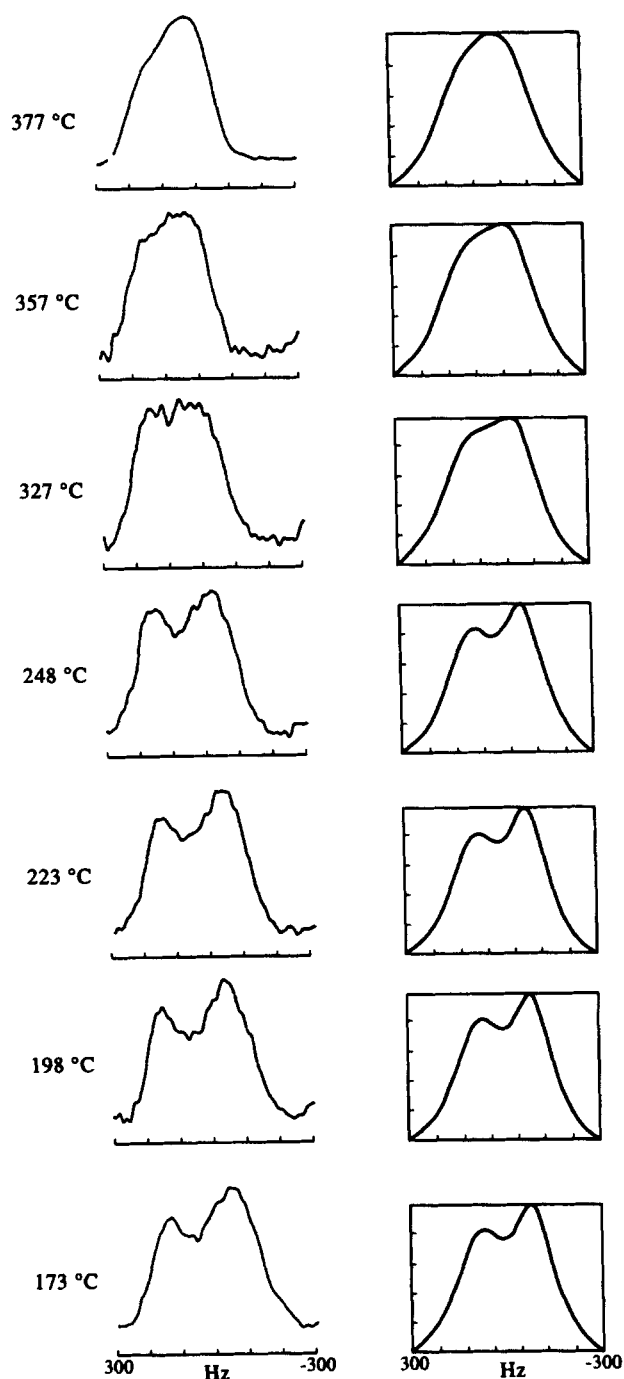


Figure 7  $^{13}\text{C}$  lineshape collapse of C5 (43 ppm) as a function of temperature in the solid state, experiment (right) and simulation (left) as described in the text

averaging is thought to be due to intermolecular constraints on the axial phenylene motion. In solution, the phenylene rings in polycarbonate undergo rotation in four-fold or higher intramolecular potentials which are typically reduced to two-fold potentials in the solid state by the effects of intermolecular interactions.

## DISCUSSION

The replacement of the isopropylidene group in BPAPC with a cyclohexyl moiety has been shown to alter the dynamic behaviours both in the solution state and in the bulk in a unique manner relative to other substitutions at this position. This characteristic seems to reflect the existence of conformational dynamics of the cyclohexyl ring. The solution  $^{13}\text{C}$  spectra allow one to identify the intramolecular dynamics at the repeat unit level and the consequences of the existence of microstructure. The cyclohexyl ring dynamics suggest that the ground state conformation is considerably strained relative to a pure chair form. This leads to a lower barrier for the ring inversion in agreement with the modeling conclusions. The inequivalence of the two phenylene rings, established previously<sup>11</sup>, is revealed in the low temperature regime where the effects of restricted mobility of the axial phenylene can be directly observed.

In the solid state this phenylene mobility is further restricted and at low temperatures the bridgehead carbon C5 shows doublet character at the lower temperatures. The origin of this doublet as two chemically shifted sites cannot be explicitly defined. Presumably two distinct sites exist as a consequence of different packing geometries in the solid. As the temperature is raised, motion increases along with the free volume and this follows the onset of motion of the phenylene rings. The differential dynamics of the two phenylenes will result in a broadening of the mechanical relaxation which correlates with their dynamics, the slower (axial) ring producing relaxation at a higher temperature and the faster (equatorial) ring at a lower temperature.

The position and breadth of the shear mechanical relaxation corresponding to the dynamics monitored by the collapse of the C5 carbon can be obtained as before<sup>2,14</sup> using:

$$G_{\gamma}(\omega)^{\text{loss}} = \frac{\langle \sigma_{\gamma}(0)^2 \rangle}{k_{\beta}t} \int_0^{\infty} \sin(\omega t) [-\phi(t)] dt \quad (2)$$

where  $G_{\gamma}(\omega)^{\text{loss}}$  is the imaginary part of the Fourier transform of the derivative of the correlation function  $\phi(t)$ . The value of  $\langle \sigma_{\gamma}(0)^2 \rangle^{\text{loss}}$  controls the magnitude of  $G_{\gamma}(\omega)^{\text{loss}}$  and is used to normalise the intensity.  $G_{\gamma}(\omega)^{\text{loss}}$  is readily computed using  $E_a = 54$  kJ/mol and  $\alpha = 0.26$  obtained from the n.m.r. data.

The experimental mechanical loss<sup>3</sup> and the loss peaks calculated from n.m.r. data and equation (2) are compared in Figure 8. It can be seen from Figure 8 that the relaxation calculated from the C5 collapse corresponds to the high temperature side of the experimental loss. Included on Figure 8 is the loss calculated from n.m.r. data on BPAPC<sup>14</sup>. The conclusion indicated is that the more restricted (axial) phenylene ring is the one whose motion correlates with the high temperature side of the mechanical loss and it is the phenylene ring dynamics which correlates with the unusual shift in the low temperature loss characteristic of the

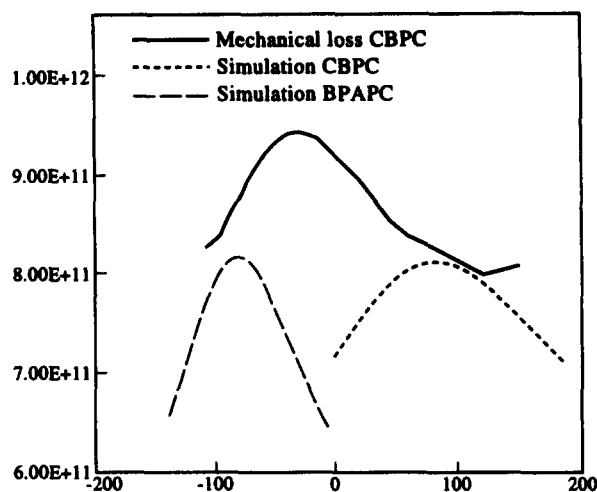


Figure 8 Experimental mechanical loss compared with simulation from n.m.r. data

cyclohexyl substitution and the increased breadth of the relaxation relative to BPAPC.

## ACKNOWLEDGEMENTS

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