Effect of high hydrostatic pressure on the phenylene motion in polycarbonate as revealed by ^{2}H spin-lattice relaxation

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The temperature dependence of the deuteron n.m.r. spin-lattice relaxation time of polycarbonate was measured as a function of hydrostatic pressure, which causes a denser packing of the polymer. Observed activation volumes and activation energies illustrate the marked density dependence of the amplitude of phenylene motions.

(Keywords: polycarbonate; molecular motions; ^{2}H n.m.r.; high pressure)

Introduction

The molecular dynamics in glassy bisphenol-A polycarbonate (PC) is of key interest for understanding the favourable mechanical properties of this material[1]. Deuteron as well as ^{13}C n.m.r. experiments[2–5] have demonstrated that rapid 180° flips of the phenylene rings around their 1,4-axis, augmented by small-angle fluctuations, occur in the glassy state on the time scale of microseconds to seconds. In addition, Schaefer *et al.*[5] and Henrichs *et al.*[6] proposed a 'ring wiggling' motion. Employing two-dimensional (2D) exchange n.m.r. on PC under tensile stress we recently showed[7] that the flip angle of a given phenylene unit can deviate substantially, namely ~30° from the mean value of 180°. Moreover, this uncertainty increases with tensile stress by a factor of two. These findings show that the phenylene ring motion is a sensitive detector of the local free volume around it.

Another possibility to probe the effect of free volume on molecular motions is to apply hydrostatic pressure. In this communication we report the influence of high pressure on the spin-lattice relaxation of the phenylene deuterons. The aim of applying high pressure is to distinguish between the effects of changes in temperature from changes in density.

Experimental

The average molecular weight of the phenylene-deuterated[7], amorphous PC-d_4 was 40 000 as determined by g.p.c. A cylindrical rod (diameter 6.5 mm) was prepared by injection-moulding and a sample (9 mm long) was cut from the rod.

The n.m.r. experiments, in the temperature range between 233 K and 298 K, were performed using a home-built spectrometer operating at a frequency of 41.43 MHz for deuterons. The equipment for generating pressure, the high-pressure n.m.r. probe, the cryostat and the temperature control used in these experiments are described elsewhere[8]. The sample was pressurized up to 2500 bar‡ with nitrogen gas. The pressure was measured using a manometer calibrated within 5 bar against a pressure balance having an absolute accuracy better than 1:10 000. The temperature was controlled to within 0.01 K. For measuring the spin-lattice relaxation time, a standard sequence consisting of saturation pulses followed by a variable delay up to 20 s and a quadrupolar echo ($\tau_1 = 25\ \mu$s) was used[9].

Results and discussion

The ^{2}H spin-lattice relaxation in polycarbonate was found to be non-exponential in the temperature range of our experiment. This effect is caused by the fact that the motions of the C–^{2}H bonds mentioned in the Introduction are restricted and heterogeneous in the glassy state. It remains visible due to the slow spin diffusion process (on a time-scale on the order of seconds) in the ^{2}H system.

In order to give a quantitative description of the relaxation curve the data were fitted to a Kohlrausch–Williams–Watts (KWW) function[10]:

$$\frac{M_\infty - M(t)}{M_\infty} = \exp[(-t/T_1)^\beta] \qquad (1)$$

where T_1 is a measure of the time constants involved in the decay. β changes from 0.6 at 233 K to 0.3 at 298 K. This marked temperature dependence is a first hint that the contributions of the above-mentioned different motions change with temperature (see below). In reality we are dealing with a distribution of relaxation times, $\rho(T_1)$, thus

$$\frac{M_\infty - M(t)}{M_\infty} = \int_0^\infty \rho(T_1)\exp(-t/T_1)\mathrm{d}T_1 \qquad (2)$$

Based on the KWW distribution one can obtain an average relaxation time[11]:

$$\langle T_1 \rangle = (T_1/\beta)\Gamma(\beta^{-1}) \qquad (3)$$

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‡1 bar = 1 × 10^5 Pa

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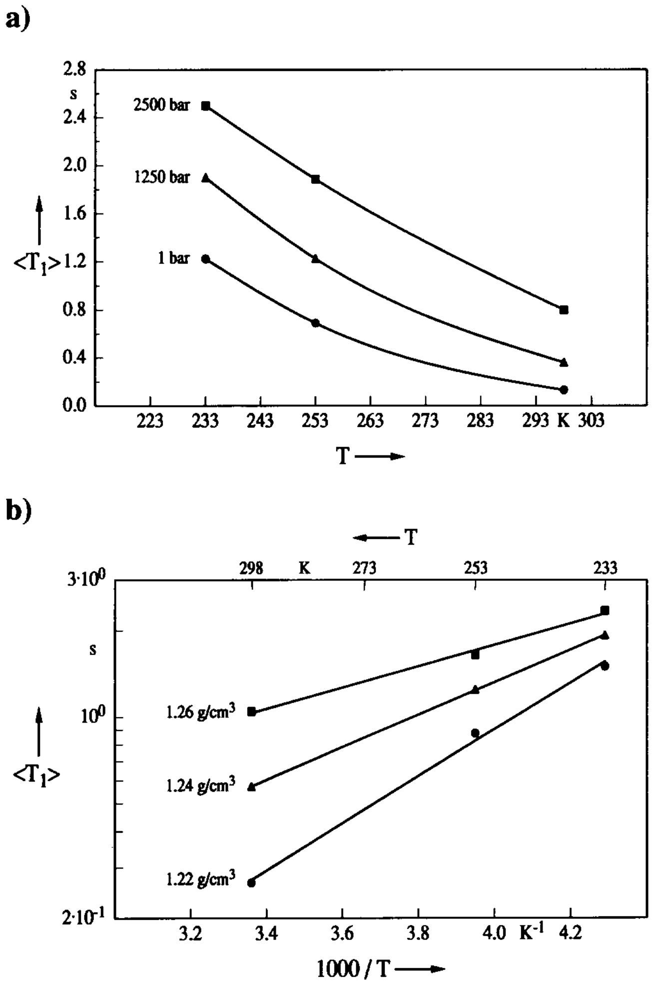

Figure 1 $^2H\langle T_1\rangle$ as a function of temperature at (a) different hydrostatic pressures and (b) constant densities

where Γ is the gamma function. Average spin-lattice relaxation times as a function of temperature at different pressure values are shown in *Figure 1a*. Note that the measurements were carried out on the low-temperature side of the T_1 minimum, which has a calculated value of 3 ms for isotropic motion of the C–^{2}H bonds. The T_1 isobars in *Figure 1a* show a shift of roughly 16 K at a pressure change of 1 kbar. That shift agrees with the ^{1}H T_2 results of Walton *et al.*[12]. The effect of pressure was reversible at all temperatures.

Wehrle *et al.*[3] analysed ^{2}H quadrupolar echo spectra assuming 180° flips of the phenylene group having a distribution of correlation times, superimposed by small-angle fluctuations along the flip axes. The mean correlation times obtained from the average T_1 values do not coincide with the results found in lineshape analyses, although they are located inside the distribution. Presumably, the slow dynamics observed in the ^{2}H quadrupolar echo spectra is not responsible for the spin-lattice relaxation. Note that spin-lattice relaxation probes[13] the spectral density of the molecular dynamics in the vicinity of the Larmor frequency ω_L. In this case $\omega_L = 41.43(2\pi)$ MHz is considerably larger than the average rate of phenylene flips[3]. Apparently, motions other than 180° flips contribute to the relaxation mechanism. Small-angle fluctuations play a minor role in the change of the quadrupolar lineshape because their effect is already averaged out on the time-scale of the quadrupolar echo experiment. Also, ring wiggling must be fast at the applied temperatures, otherwise the change in the geometry of the flip should be visible in 2D exchange spectra, contrary to our findings[14]. A distribution of correlation times should generally be considered for all existing types of motion. In summary, ^{2}H spin-lattice relaxation is attributed to three processes: 180° phenylene flips, small-angle fluctuations about the flip axes and wiggling about axes perpendicular to the rings.

Since equation-of-state data are not available for the investigated temperature interval, extrapolated data have to be used. Hence, the density and compressibility at each temperature were calculated[15] from the higher temperature data[16]. From this analysis one can transform the $\langle T_1\rangle$ isobars of *Figure 1a* to the $\langle T_1\rangle$ isochors of *Figure 1b*. It appears that the relative change of $\langle T_1\rangle$ is correlated to the compressibility of the sample. An increase in temperature leads to higher compressibilities as well as larger relative variations of $\langle T_1\rangle$. As can be seen in *Figure 1a*, on applying 2500 bar at $T = 298$ K, $\langle T_1\rangle$ increases by a factor of six while only by a factor of two at $T = 233$ K. This effect can be understood assuming that lowering the temperature reduces the free volume available for the phenylene motion. A change in pressure at 233 K has a smaller effect on the relaxation time because the phenylene flip motion is already highly restricted.

Assuming that the motion is an activated process[17,18], the correlation time τ_c is given by

$$\tau_c = \tau_0 \exp(-\Delta G/RT) \qquad (4)$$

where ΔG is the Gibbs free energy of activation. The distribution of ΔG causes the large variations of τ_c. Taking into account that in the slow motion limit T_1 is proportional to τ_c, we have calculated activation volumes ΔV and activation energies ΔE according to

$$\Delta V = RT\left(\frac{\partial \ln T_1}{\partial p}\right)_T \qquad \Delta E = R\left(\frac{\partial \ln T_1}{\partial 1/T}\right)_\rho \qquad (5)$$

where ρ is the density of the sample (*Figure 1b*).

The results are shown in *Table 1*. While the total volume at ambient pressure changes only by 1.5% in the temperature range studied, ΔV changes by a factor of four. However, even at $T = 298$ K ΔV is only 10% of the volume of the repeat unit, estimated at 200 cm³ mol⁻¹ from X-ray diffraction data[19]. Thus, large volume fluctuations can be excluded as a mechanism of the phenylene motion. Instead, the motion is highly restricted as is typical for the glassy state where large-scale conformational motions are frozen. The substantial increase of ΔV with temperature indicates that phenylene motions become somewhat less restricted at elevated temperatures. Therefore, the relative contributions from small-angle fluctuations and large-angle flips apparently change. A similar effect was observed in ^{2}H 2D exchange experiments in the slow motion region of 180° flips.

Table 1 Activation volumes ΔV and activation energies ΔE of PC-d_4

T (K)	ΔV (cm³ mol⁻¹)	ρ (g cm⁻³)	ΔE (kJ mol⁻¹)
233	5.02 ± 0.24	1.26	7.00 ± 0.57
253	8.45 ± 0.83	1.24	10.79 ± 0.86
298	20.72 ± 1.64	1.22	15.59 ± 1.25

Application of a 50 MPa tensile stress, which enlarges the sample volume by ~1%, broadens the flip angle distribution around 180° by a factor of two, thereby also demonstrating the reduction of motional restrictions[7]. The same conclusion is supported by the behaviour of ΔE as a function of density (*Table 1*). All values are substantially smaller than $\Delta E \sim 30$–$45\ \mathrm{kJ\ mol^{-1}}$ reported for the flip motion[3]. The marked increase in ΔE with decreasing density hints to an enlarged contribution of flips indicating the important role of density in allowing the phenylene groups to reorient.

This study of ^{2}H spin-lattice relaxation of the phenylene rings in PC under hydrostatic pressure shows that the phenylene dynamics is a sensitive probe of the distribution of free volume. Both large-scale flips and small-angle fluctuations contribute to spin-lattice relaxation while, on the other hand, the former dominates the ^{2}H n.m.r. lineshape. Since these processes have markedly different activation volumes and activation energies, they can be unravelled by applying hydrostatic pressure. Similar studies in other glassy polymers are in progress[20].

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