Influence of Tensile Stress on the Phenylene Flips in Polycarbonate Studied by Two-Dimensional Solid-State NMR

M. T. Hansen, B. Blümich, C. Boeffel, and H. W. Spiess*

Max-Planck-Institut für Polymerforschung, Postfach 3148, D-6500 Mainz, Germany

L. Morbitzer and A. Zembrod

Bayer AG, Abteilung ZF-TPP, D-5090 Leverkusen, Germany

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Introduction. One of the most prominent features of polycarbonate (PC) is its ductility, leading to a yield point at approximately 60 MPa stress accompanied by a strain of 7%.[1] Dynamic mechanical measurements were performed to obtain knowledge about the molecular motions involved. From these studies it was already concluded that the low-temperature γ relaxation has to be connected with the phenylene motions, since the substitution of the ring protons changes the temperature of this maximum significantly while variations of the other groups cause only slight shifts, if at all.[2] Only a few alterations of the isopropylidene group exhibit larger effects, which are supposed to be generated by steric hindrance or reduced cooperativity of the phenylene ring motions. Loss modulus spectra of *strained* PC exhibit intensification and broadening of the γ peak with increasing strain, but no significant temperature shift is observed.[3] Thus, the relaxation strength is enhanced, which means that the phenylene motions should be enlarged without alteration of the correlation times. Deuteron as well as ^{13}C NMR experiments 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.[4-8] The mixing of PC with additives like *p*-dichlorobenzene or polychlorinated biphenyls causes the material to become brittle and slows down the ring motion significantly by broadening the distribution of correlation times and shifting its mean value to lower frequencies.[5] Simultaneously, the γ relaxation peak is suppressed,[9] indicating that these properties are correlated.

Further, infrared dichroism measurements of PC at small strains (up to 2%) suggest that the transition from linear (below 1% strain) to nonlinear behavior is accompanied by the onset of rotations around backbone bonds.[10] All these methods lack direct information about the geometry of the involved motions. Therefore, in this investigation the deuteron two-dimensional (2D) exchange NMR experiment was applied to study ultraslow reorientations of the phenylene groups in PC under tensile stress up to 50 MPa (3% strain). By this means, the geometrical information can be obtained directly and model-free by inspecting the off-diagonal intensities in the 2D plane,[11] a method that has been successfully applied already to study chain motions in crystalline polymers[12] as well as amorphous polymers[13] at their glass transition.

In this paper only the main results of this study are presented, namely, those concerning the 2D ^2H NMR experiment and the spin alignment echo[14] measurements for the determination of slow motions on the time scale of milliseconds to hundreds of milliseconds and their dependence on applied tensile stress. Further details as well as solid-echo spectra and the results of T_1 relaxation measurements under hydrostatic pressure (NMR techniques sensitive to faster motions) are published elsewhere.[15,16]

Sample Preparation and Instrumentation. Phenylene-deuterated, amorphous Bisphenol A polycarbonates PC-d_4 and PC-d_8 were used to detect the ring motions exclusively. The material had a weight-average molecular weight of 40 000 as determined by GPC. Rodlike specimens were prepared by injection-molding using 543 K as the melting temperature and a mold temperature of 403 K. The stretchable region had a cylindrical shape (diameter, 5 mm; length, 33 mm). By threads on each end the rods were bolted into claws for application of tensile stress. The design and building of the stretching device,[17] which is able to produce forces up to 1500 N, will be described elsewhere.[15] Every sample was equipped with its own radio-frequency coil, tightly wrapped around the rod, yielding best S/N and minimal duration of 90° pulses (2.5 μs). This parameter is extremely important, since beyond approximately 3.5 μs, the desired information is lost as a result of reduced excitation bandwidth. A Bruker MSL 300 NMR spectrometer was used operating at 46.07 MHz for ^2H NMR. The stretching apparatus was driven pneumatically and could be triggered by the spectrometer software. Thus, a synchronization of the radio-frequency pulses and the applied stress was made possible.[17]

Results and Discussion. The measurements were carried out in the temperature range between 293 and 233 K. In this interval the phenylene flips slow down significantly.[5] Below 273 K the detected 2D spectra exhibit distinct off-diagonal intensities at mixing times t_m on the order of 100 ms, forming elliptical ridge patterns. Their intensity increases with decreasing temperature and can be observed best at 233 K with t_m = 500 ms (see Figure 1). From the contour lines of this spectrum (Figure 1), the mean reorientation angle, that is, the angle θ between the initial and final position of the C–^2H bonds (cf. Figure 2), is deduced to be 120°, which corresponds to a 180° flip of the phenylene rings around the 1,4-axis. The elliptical intensity is reduced, however, in the vicinity of the diagonal spectrum. This indicates significant deviations of the flip angle of a given phenylene unit undergoing a single flip from the mean angle of 180°. Thus, the simulation of such 2D spectra has to take into account distributions of flip angles $P(\Phi)$ (cf. Figure 2). For simplicity, Gaussians were assumed centered around 0° and 180°. The spectra, shown in Figure 1a, could be fit by an asymmetric flip angle distribution, meaning that for large angles it is significantly broader than for small angles. Note that the mixing time is such that most of the phenylene groups have flipped only once, if at all. Thus, the distribution around 0° mainly reflects the small-angle rotation of rings prior to a flip, whereas the broad distribution at large angles (around 180°) gives the uncertainty of the phenylene ring orientation after a flip. This shows that after rotation, a phenylene group finds itself in a slightly different environment fluctuating around a mean packing geometry. This explains the above-mentioned observation that the phenylene flip is directly linked to the dynamic process that provides the mechanism for mechanical relaxation. Therefore, the *width* of the flip angle distribution around 180° is an indicator of the relaxation strength. The distribution around 0° is not to be confused with small-angle fluctuations of the phenylene groups at high rates (10^7 Hz).[18,19] Note that the asymmetry of the total flip angle distributions is not apparent in the corresponding reorientational angle distributions (RAD) $P(\theta)$, which were previously considered[20] and found to consist of approx-

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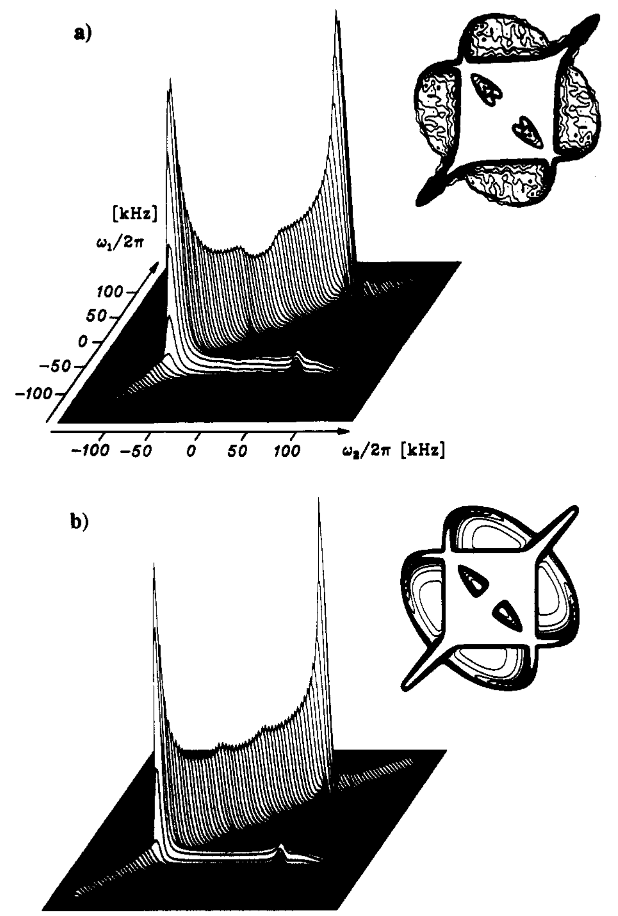

Figure 1. (a) Experimental 2D exchange spectrum of PC-d_8, T = 233 K, t_m = 500 ms. (b) Simulation.

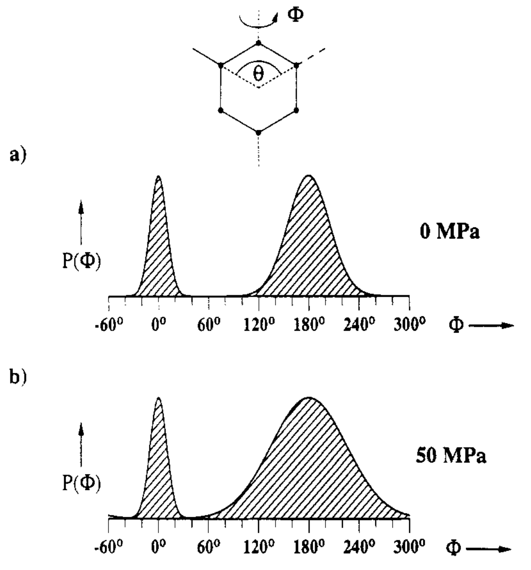

Figure 2. Distributions of flip angles Φ. Width of Gaussians: (a) 20°/50° (unstretched); (b) 20°/90° (stretched). The amplitudes are not drawn to scale.

imate Gaussians having nearly the same width. Furthermore, the analysis demonstrated the impossibility to fit the spectra assuming symmetrical flip angle distributions.

Application of stress in the nonlinear region (50 MPa) at temperatures between 273 and 253 K causes additional reduction of the elliptical ridges near the major apices. This indicates an enlarged distribution around 180°, which is about twice as broad as that in the unstretched state (cf. Figure 2). Hence, tensile stress loosens the angular restriction of the slow phenylene flip motion in polycarbonate even further. This is attributed to increased free volume generated by the mechanical load. These results are consistent with strain-induced gain of relaxation strength,[3] infrared dichroism,[10] stress relaxation,[21] and permeability of noble gases,[22] which reflect enhanced molecular motions and increased free volume respectively.

In addition, the sample volume is raised by about 1% at 3% strain, which corresponds to the calculated expansion[23] assuming a Poisson ratio of 0.37.[24] Notice that the volume increase at the yield point is comparable to the thermal expansion when the sample is heated to the glass transition temperature (423 K).

While the *geometry* of the flip motion changes, the distribution of existing correlation times, which spreads over a few decades,[5] does not: Solid-echo spectra are not affected by applied stress. Only spin–lattice relaxation is slightly accelerated in agreement with a small shift (less than 5 K) of the γ peak toward higher temperatures.[3]

In order to check whether stress induces phenylene flips, spin alignment echoes were recorded, with mechanical strain synchronized with the NMR pulse sequence. The sample was stretched up to 1% during the mixing period at 263 K using t_m = 150 ms and a stress rate of 0.1 MPa/ms as optimum parameters. No significant reduction of the echo amplitude was detected. Note that phenylene flips reduce the spin alignment amplitude by a factor of 2. This experiment thus shows that significant strain-induced flipping does not occur. Therefore, we conclude that the spatial arrangement in the neighborhood of each phenylene group remains essentially unchanged by an applied stress. This means that external stress in the linear region cannot cause large-scale rearrangements of PC chains but rather small slippage of adjacent chains that do not induce phenylene flips. Recent calculations show that the local volumes undergoing plastic relaxation must be quite large,[25] namely, with side lengths on the order of 40–60 Å, which agrees with our experimental findings.

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References and Notes

(1) Schnell, H. *Chemistry and Physics of Polycarbonates*; Interscience: New York, 1964.
(2) Yee, A. F.; Smith, S. A. *Macromolecules* **1981**, *14*, 54.
(3) Litt, M. H.; Torp, S. *J. Appl. Phys.* **1973**, *44*, 4282.
(4) Spiess, H. W. *Colloid Polym. Sci.* **1983**, *261*, 193.
(5) Wehrle, M.; Hellmann, G. P.; Spiess, H. W. *Colloid Polym. Sci.* **1987**, *265*, 815.
(6) Inglefield, P. T.; Amici, R. M.; O'Gara, J. F.; Hung, C.-C.; Jones, A. A. *Macromolecules* **1983**, *16*, 1552.
(7) Schaefer, J.; Stejskal, E. O.; McKay, R. A.; Dixon, W. T. *Macromolecules* **1984**, *17*, 1479.
(8) Jones, A. A. In Polymer Motion in the Solid State. *High-Resolution NMR Spectroscopy of Synthetic Polymers in Bulk*; Komoroski, R. A., Ed.; VCH: Weinheim, Germany, 1986; pp 247–281.
(9) Fischer, E. W.; Hellmann, G. P.; Spiess, H. W.; Hörth, F. J.; Ecarius, U.; Wehrle, M. *Macromol. Chem., Suppl.* **1985**, *12*, 189.
(10) Jansson, J.-F.; Yannas, I. V. *J. Polym. Sci.* **1977**, *15*, 2103.
(11) Schmidt, C.; Wefing, S.; Blümich, B.; Spiess, H. W. *Chem. Phys. Lett.* **1986**, *130*, 84.
(12) Hirschinger, J.; Schaefer, D.; Spiess, H. W.; Lovinger, A. J. *Macromolecules* **1991**, *24*, 2428.
(13) Schaefer, D.; Spiess, H. W.; Suter, U. W.; Fleming, W. W. *Macromolecules* **1990**, *23*, 3431.
(14) Spiess, H. W. *J. Chem. Phys.* **1980**, *72*, 6755.
(15) Hansen, M. T.; Boeffel, C.; Spiess, H. W. *Colloid Polym. Sci*, in press.
(16) Hansen, M. T.; Kulik, A.; Prins, K. O.; Spiess, H. W. *Polymer* **1992**, *33*, 2231.
(17) Hensen, M. T. Ph.D. Thesis, University of Mainz, 1991. See also: Spiess, H. W. *Annu. Rev. Mater. Sci.* **1991**, *21*, 131.
(18) English, A. D. *Macromolecules* **1984**, *17*, 2182.

(19) Hirschinger, J.; Miura, H.; Gardner, K. H.; English, A. D. *Macromolecules* **1990**, *23*, 2153.
(20) Schaefer, D.; Hansen, M.; Blümich, B.; Spiess, H. W. *J. Non-Cryst. Solids* **1991**, *131–133*, 777.
(21) Yee, A. F. *J. Polym. Sci.* **1988**, *26*, 2463.
(22) Smith, T. L.; Oppermann, W.; Chan, A. H.; Levita, G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1983**, *24* (1), 83.
(23) Koenen, J. A.; Heise, B.; Kilian, H.-G. *J. Polym. Sci.* **1989**, *27*, 1235.
(24) Krimm, H.; Peilstöcker, G. In Die Polycarbonate. *Kunststoff-Handbuch*; Vieweg, R., Goerden, L., Eds.; Hanser: München, Germany, 1973; Vol. VIII, pp 1–245.
(25) Hutnik, M.; Argon, A. S.; Suter, U. W. *Macromolecules* **1991**, *24*, 5970.

Registry No. Bisphenol A PC (copolymer), 25037-45-0; Bisphenol A PC (SRU), 24936-68-3.