between the T_g and the conformational entropy. Rather than dealing with the actual polymer segment as in the present calculations, these authors calculated the conformational entropy of fragments of molecules and used the group additivity concept to predict the T_g. In addition, they used the mass moments of the side group atoms in a multiple regression analysis, although the contribution from this factor was found to be small. This is neglected in the present calculations.

Conclusions

The correlation derived here is based on the calculations for a homologous series of polycarbonates, with different substituents at the C_α atom. While the group additivity method of Hopfinger et al.[7,8] can be used generally for any polymer for which the appropriate contribution factors are known, the method of calculating the conformational entropy for the actual polymer segment, as adopted here, is useful for comparing a homologous series. Since all that is required is the energies of all the possible states of the segment, this method can be conveniently coupled with the usual conformational analysis of a related series of polymers. The different set of relationships between S/n and T_g for the symmetric and asymmetric substituents indicated in the present calculations is also worthy of further investigation.

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References and Notes

(1) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969.
(2) Hopfinger, A. J. *Conformational Properties of Macromolecules*; Academic Press: New York, 1973.
(3) Sundararajan, P. R. *Macromolecules* **1988**, *21*, 1256.
(4) Sundararajan, P. R. *Macromolecules* **1989**, *22*, 2149.
(5) Gibbs, J. H.; DiMarzio, E. A. *J. Chem. Phys.* **1958**, *28*, 373.
(6) Tonelli, A. E. *Macromolecules* **1973**, *6*, 503; **1974**, *7*, 632; **1975**, *8*, 544; **1977**, *10*, 633; **1977**, *10*, 716.
(7) Hopfinger, A. J.; Koehler, M. G.; Pearlstein, R. A.; Tripathy, S. K. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 2007 and references therein.
(8) Koehler, M. G.; Hopfinger, A. J. *Polymer* **1989**, *30*, 116.
(9) Sundararajan, P. R. *Bull. Am. Phys. Soc.* **1988**, *33* (3), 251.
(10) Sundararajan, P. R. *Macromolecules* **1987**, *20*, 1534.
(11) Garrido, L.; Riande, E.; Guzman, J. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 725.
(12) Yee, A. F.; Smith, S. A. *Macromolecules* **1981**, *14*, 54.
(13) Schnell, H. *Chemistry and Physics of Polycarbonates*; Interscience: New York, 1964.
(14) Takegawa, I.; Yamamoto, K. Personal communication.
(15) Van Krevelen, D. W. *Properties of Polymers*, 2nd ed.; Elsevier: New York, 1976.
(16) Bruno, G.; Montaudo, G.; Hien, N. V.; Marchessault, R. H.; Sundararajan, P. R.; Lenz, R. W. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *13*, 559.

Study of the Relative Molecular Mobilities of Bisphenol A and Cyclohexyl Polycarbonates by CP/MAS NMR Spectroscopy

M. G. TAYLOR[†] AND P. R. SUNDARARAJAN*

Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, Ontario L5K 2L1, Canada.

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Introduction

A comparison of the conformational features of polycarbonates with different types of substituents at the C_α atom was published recently.[1] In terms of the molecular motion of the phenyl group, the conformational analysis showed that the nature of the substituent dictates whether the phenyl groups execute π-flips or large scale local oscillations. In addition, the steric map of the Bisphenol A polycarbonate (BPAPC) could account for the model derived from NMR studies[2] that involves both π-flip and small-amplitude motions of the phenyl groups and supported the concept of synchronous rotation of contiguous phenyl groups. The calculations[1] for cyclohexyl polycarbonate showed that the steric freedom in this case is less than that of BPAPC.

Polycarbonate is perhaps the most extensively studied polymer with regard to molecular motion,[3] using NMR and dynamical mechanical spectroscopy (DMS). In addition to BPAPC, Jones et al.[4] analyzed the molecular motion in chloral polycarbonate and concluded that the molecular motion in this case is restricted compared to that in BPAPC. Yee and Smith[5] compared polycarbonates with different types of substituents, using DMS.

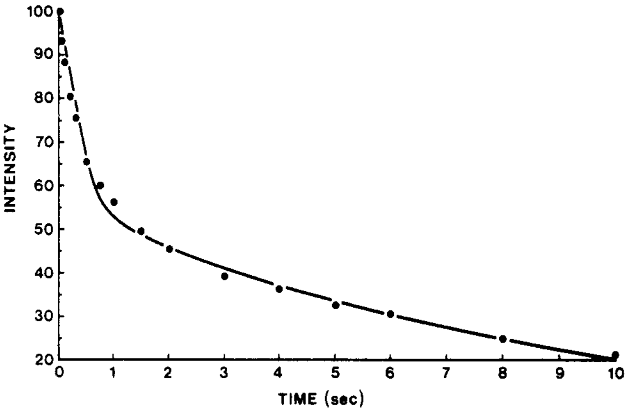

Figure 1. Intensity of the ortho carbon resonance as a function of time during ^{13}C relaxation of BPAPC at 0 °C.

In this paper, a comparison of the results of the ^{13}C spin-lattice relaxation measurements performed on BPAPC and the cyclohexyl polycarbonate is presented. The use of ^{13}C spin-lattice relaxation measurements to probe molecular dynamics is attractive since the NMR measurements can be carried out without specific isotopic enrichment, allowing application to any polycarbonate.

Experimental Section

A sample of BPAPC with M_w = 100 000 and two samples of cyclohexyl polycarbonate with M_w = 16 000 and 77 000 were

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[†] Present address: Esso Petroleum Canada Research, P.O. Box 3022, 453 Christina Street South, Sarnia, Ontario N7T 7M1, Canada.

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used. The *p*-dichlorobenzene was obtained from Aldrich. Film samples were prepared by casting from methylene chloride solution. The films were allowed to air-dry overnight, followed by drying at 80 °C for 30 min. Disk samples were prepared by punching the films with a paper punch. Stacks of disks were loaded into cylindrical 7-mm (o.d.) sapphire rotors. The NMR spectra were acquired using a Bruker CXP-200 spectrometer, with a variable-temperature, cross-polarization, magic angle spinning (CP/MAS) probe from Doty Scientific. Temperature variation was carried out by regulating the temperature of the N_2 gas used for spinning with a Bruker BVT-1000 controller. The ^{13}C spin-lattice (T_1) relaxation measurements were made using the CP sequence described by Torchia.[6] The T_1 values were calculated from the intensity decays in the relaxation sequence using RS/1 software running under VMS on a VAX-11/750 computer.

Results and Discussion

The ^{13}C CP/MAS spectrum of BPAPC showed several overlapping lines, but the lines associated with the protonated phenyl carbons were well resolved. The measurements described below focus on the behavior of the resonance due to carbons ortho to the carbonate function. Since the phenyl ring is "rigid", the behavior of this carbon describes the dynamic behavior of the entire phenyl moiety.

The peak intensity measurements of a representative relaxation decay for the ortho carbon resonance in BPAPC at 0 °C are shown in Figure 1. In a homogeneous system with a single T_1 value, this decay would be in the form of a simple exponential. On the basis of previous NMR studies,[2,3] we expect heterogeneous dynamic behavior for the phenyl groups. A fraction of the phenyl rings execute rapid π-flips about the C_1–C_4 axis while this motional mode is restricted in the remaining groups. For such a heterogeneous case, we expect the ^{13}C T_1 relaxation behavior to reflect the presence of two types of motion.

The intensity data in Figure 1 were fit by nonlinear regression using a sum of two exponential decays. The solid curve in the figure represents the calculated fit for this two-component model. From this analysis, one can extract the individual T_1 values along with their relative contributions to the total decay. The more rapidly relaxing component is assigned to the mobile fraction of the phenyl groups undergoing π-flips. This high-frequency motion is responsible for a more efficient T_1 relaxation. The other component is assigned to the remaining phenyl groups, which undergo slower relaxation due to main-chain motions and low-amplitude torsional motions about the C_1–C_4 axis. The possibility of one of the phenyls executing a π-flip while the contiguous one rotates only about 60° has been discussed previously in terms of the conformational map.[1]

Two types of "calibration" experiments were carried out to confirm the assignment of the two relaxation components to flipping and nonflipping fractions of the BPAPC phenyl moieties. First, the T_1 measurements were made for BPAPC over a range of temperatures. Second, the effect of an additive known to alter the proportion of the flipping phenyl groups was studied.

The variable-temperature measurements were made over the range −27 to +25 °C. The relaxation decays were analyzed as described above to extract the two T_1 values and the relative contribution to each. The calculated T_1 values are shown in Figure 2. The "fast" component, assigned to the π-flipping groups, shows little variation over this temperature range. In contrast, the T_1 value of the "slow" component exhibits a continuous decrease as the sample temperature is increased. The percent contribution of the fast component at each temperature is also shown in Figure 2. A dramatic increase in this contribution with temperature is observed.

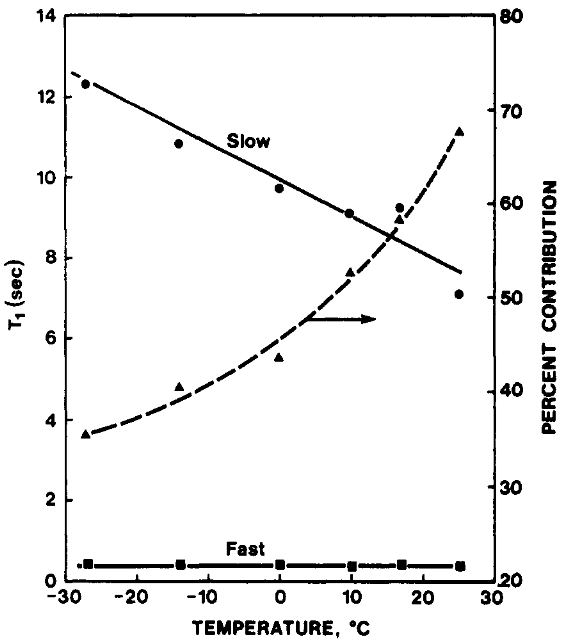

Figure 2. Variation of the fast (■) and slow (●) components of the ^{13}C T_1 values of the ortho carbon of BPAPC with temperature. The percent contribution of the fast component (▲) is shown by the dashed curve (right ordinate).

These observations are consistent with the assignment made above for the two relaxing components. Increasing temperature should increase the proportion of phenyl groups that are able to undergo π-flips. This leads to the observed increase in the contribution of the rapidly relaxing component to the total relaxation behavior. The temperature variation of the individual T_1 values monitors changes in the rates of the two types of motion. The decrease in the T_1 values for the slow component with increasing temperature reflects an increase in motional freedom associated with the main-chain polymer motions. The insensitivity of the measured fast-component T_1 values of temperature variation implies that the actual rate of π-flipping is not thermally activated although the probability of executing this motion increases as the temperature is raised.

In the second series of experiments, the effect of adding an "antiplasticizer", *p*-dichlorobenzene, on the phenyl group relaxation was studied. Previous ^2H NMR measurements have shown that this small-molecule additive restricts phenyl group motion, leading to a decreased proportion of π-flipping groups.[7] Relaxation measurements were carried out for samples containing up to 30 mol % of *p*-dichlorobenzene relative to the BPAPC unit. The ^{13}C T_1 decays were analyzed as described above for each mixture.

Figure 3 shows the variation in the individual T_1 values. As observed for the variable-temperature measurements, the T_1 value for the rapidly relaxing component shows little variation. The slow T_1 component increases as *p*-dichlorobenzene is added, reflecting a decrease in motional freedom with the addition of this small molecule. The variation in the relative contribution of the fast T_1 component with *p*-dichlorobenzene content is also shown in Figure 3. As expected, addition of *p*-dichlorobenzene to BPAPC leads to a decrease in the contribution of this component, reflecting the decrease in the proportion of phenyl groups executing π-flip motion. It is recognized that the π-flip motion is best described as

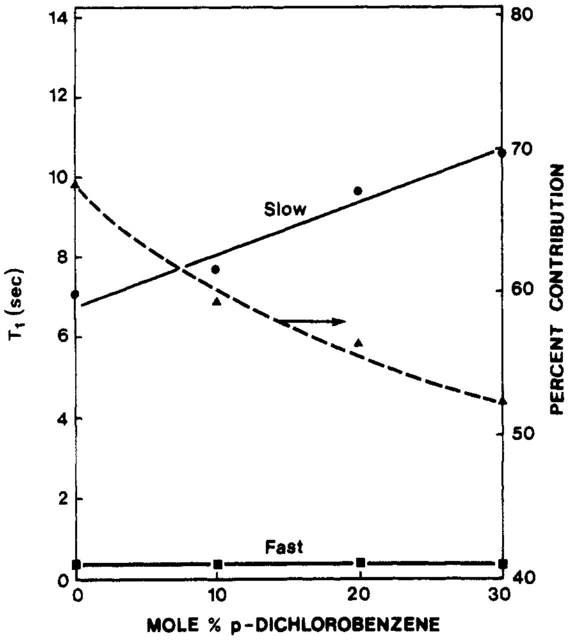

Figure 3. Variation of the fast (■) and slow (●) components of the ^{13}C T_1 values of the ortho carbon of BPAPC as a function of the concentration of *p*-dichlorobenzene. The percent contribution of the fast component (▲) is shown by the dashed curve (right ordinate).

having a broad distribution of rates. However, these calibration experiments indicate that the T_1 measurements, which do not require isotopic enrichment or complex line-shape simulations, correctly reflect the changes in the phenyl ring motion.

This methodology was also applied to probe the phenyl dynamics in cyclohexyl polycarbonate where the isopropylidene moiety of the BPAPC is replaced by a cyclohexyl group. The ^{13}C T_1 measurements were carried out at 25 °C for comparison with the BPAPC data. The observed relaxation behavior was qualitatively similar to that of BPAPC described above, with two distinct T_1 components. The results are summarized in Table I, along with the data collected for BPAPC at 25 °C, for comparison. This comparison points out a significant difference in the degree of motional freedom for the phenyl groups in the two polycarbonates.

The longer T_1 values observed for the slow component of the relaxation of cyclohexyl polycarbonate relative to BPAPC suggest restriction of the low-amplitude chain motions in the former. In addition, the contribution from the fast component is much smaller for cyclohexyl polycarbonate, indicating that the proportion of π-flipping phenyl rings is smaller in this polycarbonate. Conformational analysis[1] of the two polycarbonates showed that the extent of steric freedom is less in the case of cyclohexyl polycarbonate, as compared with BPAPC. The reader is referred to the conformational maps in Figures 2 and 8 of ref 1. The conformational partition function for BPAPC was calculated to be 179.3, whereas for cyclohexyl polycarbonate it was only 40.1. The conformational map for BPAPC showed that a wide range of accessible conformations are possible for this case, with synchronized variations in the rotations[8] Φ and Ψ. However, the conformational map for the cyclohexyl polycarbonate showed that only for discrete values of the torsion angle $\Phi \approx \pm 90°$, the value of Ψ can vary from −180 to +180°, within a barrier of ~3.5 kcal·mol^{-1}. Similarly, only with $\Psi \approx \pm 90°$, the value of Φ can vary over the entire range of −180 to +180°. Thus, in the case of cyclohexyl polycarbonate, only for select dispositions of one of the phenyl groups, the contiguous moiety can enjoy a wide range of accessible conformations. Thus, the conformational heterogeneity is more pronounced in the case of cyclohexyl polycarbonate. This is reflected in the smaller contribution of the fast component in this case as compared to the case of BPAPC.

Table I
Relaxation Data for the BPAPC and Cyclohexyl Polycarbonates

		cyclohexyl polycarbonate	
component	BPAPC	M_w = 16 000	M_w = 77 000
slow component T_1, s	7.1	11.9	11.8
fast component T_1, s	0.37	0.39	0.32
fast-component contribution, %	68	42	41

Acknowledgment. It is a pleasure to thank Dr. G. K. Hamer of this laboratory for his suggestions.

References and Notes

(1) Sundararajan, P. R. *Macromolecules* **1989**, *22*, 2149.
(2) Spiess, H. W. *Colloid Polym. Sci.* **1983**, *261*, 193.
(3) Jones, A. A. In *High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk*; Komoroski, R. A., Ed.; VCH Publishers: Deerfield Beach, FL, 1986; Chapter 7 and references therein.
(4) Jones, A. A.; O'Gara, J. F.; Inglefield, P. T.; Bendler, J. T.; Yee, A. F.; Ngai, K. L. *Macromolecules* **1983**, *16*, 658.
(5) Yee, A. F.; Smith, S. A. *Macromolecules* **1981**, *14*, 54.
(6) Torchia, D. A. *J. Magn. Reson.* **1978**, *30*, 613.
(7) Spiess, H. W. *Pure Appl. Chem.* **1985**, *57*, 1617.
(8) The relative rotations of contiguous phenyls about the C_1–C_α and C_α–C_4' bonds are denoted by Φ and Ψ, respectively, and these are defined in ref 1.