Macromolecules **1983,** *16,* 1552–1554

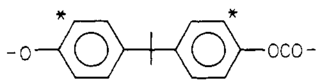
Communications to the Editor

Solid-State Carbon and Proton Line Shapes for the Characterization of Phenylene Group Motion in Polycarbonates

The line shapes obtained from proton, carbon, and deuterium magnetic resonance have been used to characterize the geometry of motions in solid polymers, including polycarbonates.[1-5] In polycarbonates, much attention has focused on the motion of the phenylene group; the first report of proton line shape data relevant to phenylene group motion[1] pointed to some form of rotation or restricted rotation about the C_1C_4 axis as the largest amplitude, highest frequency phenylene group motion. However, the proton data are completely insensitive to the amplitude of the rotation and whether it proceeds by small steps or large-amplitude flips.

Variable-temperature carbon-13 magic angle sample spinning spectra on a related polymer[3,5] are also unable to define the latter aspects of the pheylene group motion though Garroway et al. modeled the motion as π flips about the C_1C_4 axis. Deuterium line shapes are considerably more sensitive to the nature of the motion, and Spiess[4] concluded that the rotation took place primarily as π flips about the C_1C_4 axis. Carbon–proton dipolar rotational spin-echo line shape experiments by Schaefer[2] could also be explained by π flips or alternatively by rotational diffusion restricted to an angular range of about 50°. Schaefer[6] noted that theoretical simulations in the high-temperature limit of deterium or dipolar line shapes for π flips are rather similar to certain choices of restricted angular diffusion and therefore difficult to distinguish. On the other hand, a significant difference is predicted in the chemical shift anisotropy tensor for the two motions, and this allowed Schaefer[7] to substantiate the presence of π flips for some phenyl groups in polystyrene as originally reported by Spiess[4] based on deuterium data.

In this communication, we report the chemical shift anisotropy (CSA) line shape for a phenyl carbon in polycarbonate in the low-temperature limit at −160 °C and in the high-temperature limit which persists over a range of about 100 °C below T_g. These spectra, shown in Figure 1, were obtained on a carbon-13 labeled polycarbonate of bisphenol A where 90% of one of the two carbons in the phenylene group ortho to the carbonate are isotopically enriched. Either a simple $\pi/2$ pulse or cross polarization followed by proton dipolar decoupling was found to yield adequate CSA spectra below T_g. At low temperatures, the CSA spectrum is distinctly asymmetric, which allows for a more definitive characterization of dynamics than either deuterium or dipolar line shapes, which are essentially axially symmetric. Indeed as shown in Figure 1, the attempts to simulate the high-temperature limit,[8,9] which is nearly axially symmetric, clearly distinguishes between fairly large-amplitude restricted rotational diffusion and π flips. The simulations utilize the principal values of the shielding tensor observed at low temperatures ($\sigma_{11} = -17$, $\sigma_{22} = 52$, $\sigma_{33} = 175$ ppm on the CS_2 scale) and assumes the orientation of the principal axes reported for benzene.[10] The chemical shift tensor in the principal axis system σ_{123} can be transformed with the appropriate matrix, $\mathbf{R}$, to a desired molecular axis system (σ_{xyz}), where the x axis is selected as the axis of rotation: $\sigma_{xyz} = \mathbf{R}\sigma_{123}\mathbf{R}^{-1}$. Rotation about the x axis by an angle α gives $\sigma_{xyz}(\alpha) = R_\alpha\sigma_{123}$. R_α and the CSA line shape corresponding to either flips or restricted rotation about this axis are then generated. Besides π flips having a significantly different shape from restricted rotation, neither replicates the observed high-temperature limit, though π flips are close to the general shape. If π flips are combined with fairly large-amplitude restricted rotation (60°), the observed high-temperature limit is quite well simulated.



Certain other processes also simulate the high-temperature limit. For instance, both flips between 0 and 140° about the C_1C_4 axis and restricted rotation about an axis inclined at 70° produce reasonable replications of the observed spectrum. The maximum of the CSA line shape in the 70° axis rotation spectrum is slightly displaced from the observed peak, but this shape can be definitively ruled out by considering the proton dipolar line shape.

As mentioned, proton dipolar line shapes for the phenylene protons in the polycarbonate of 1,1,-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (chloral) have been reported.[1] Since this polymer contains only phenylene protons with one major intramolecular dipole–dipole interaction parallel to the chain backbone, the persistence of this interaction at high temperature implies motions that do not significantly reorient the C_1C_4 axis.[1] The simplest motion meeting this requirement is some form of rotation about that axis though rotations about a parallel axis are also possible candidates.[11]

To perform the analogous proton dipolar experiment on BPA as just discussed for the chloral polycarbonate, it was necessary to deuterate the methyl groups to produce BPA-d_6. A level of 98% deuteration of the methyl groups was achieved while retaining 93% of the protons in the phenylene group.

To obtain the best possible spectrum of the Pake splitting, BPA-d_6 was dissolved in perdeuterio-BPA to obtain the spectra shown in Figure 2. Here, the Pake line shape is apparent because of reduced intermolecular dipole–dipole interactions. The center spike in this spectrum arises from residual protons of the perdeuterio-BPA, which constitutes 85% of the sample by weight and has 2% residual protons. The residual protons in BPA-d_6 and perdeuterio-BPA were determined from proton and deuterium spectra of the dissolved polymers, and the simulations in Figure 2, specifically the intensity of the center spike, are consistent with the known level of residual protons.

The Pake splitting can be determined from simulations of the spectra in Figure 2 by folding a Pake pattern with either Gaussian or Lorentzian broadening. A decrease of 10% in the Pake splitting from the low-temperature limit to the high-temperature limit is indicated by the simulation, but this small decrease is comparable to the uncertainty in the simulation. A 10% decrease could reflect the presence of some wobble of the C_1C_4 axis, and such a wobble has been reported by Schaefer[2] based upon carbon–proton dipolar rotational spin-echo line shapes of the methyl carbons in BPA. The persistence of the Pake splitting does allow for the rejection of one of the CSA line shape simulations, namely, rotation about an axis inclined

0024-9297/83/2216-1552$01.50/0
© 1983 American Chemical Society

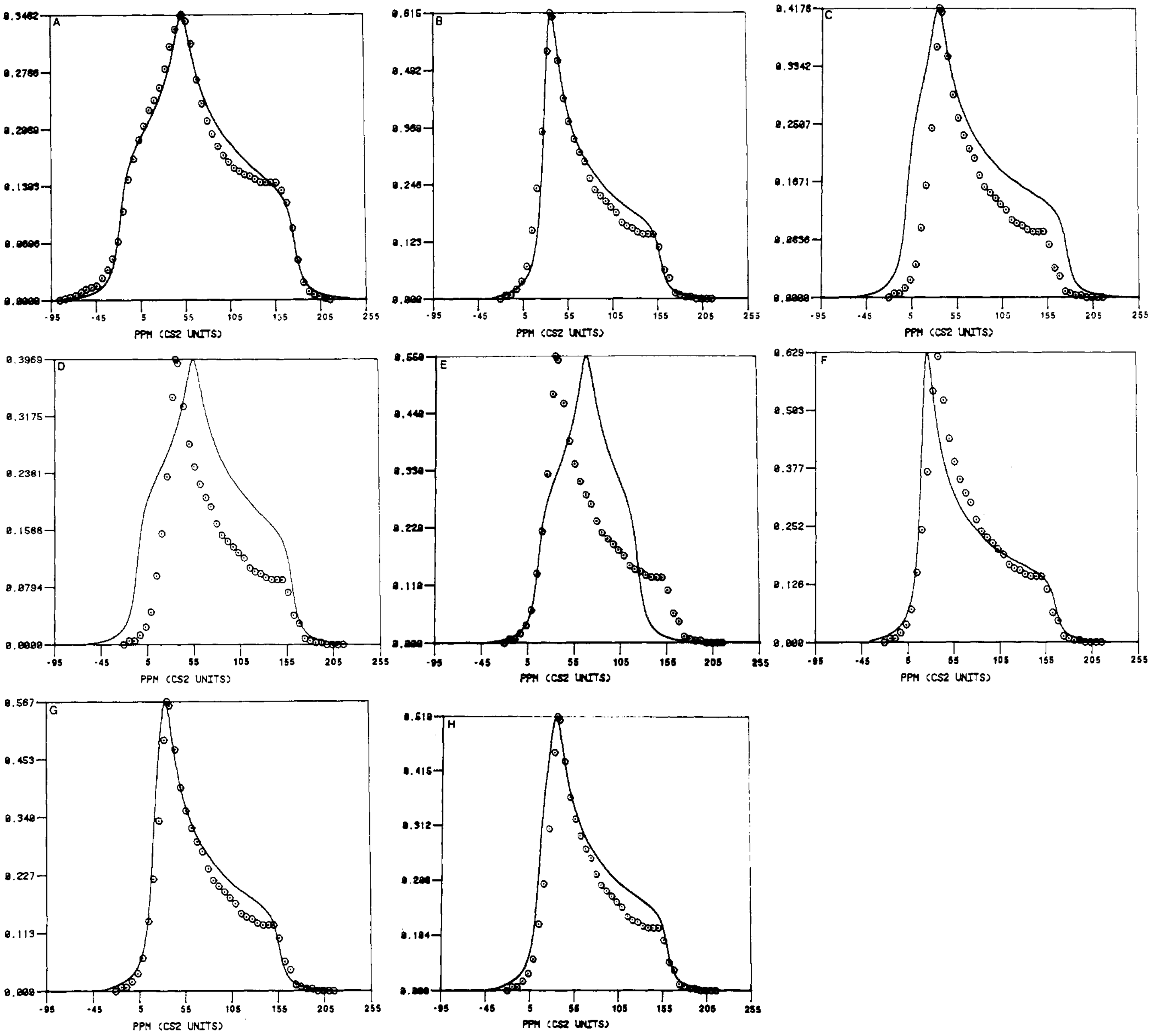


Figure 1. ^{13}C chemical shift anisotropy (CSA) line shapes: (A) low-temperature data and simulation based on powder pattern function;[10] (B) high-temperature data and simulation based on powder pattern function;[10] (C) high-temperature data and simulation based on π flips about the C_1C_4 axis; (D) high-temperature data and simulation based on restricted rotation about the C_1C_4 axis over a 60° range; (E) high-temperature data and simulation based on restricted rotation about the C_1C_4 axis over a 120° range; (F) high-temperature data and simulation based on restricted rotation over a 180° range about an axis inclined at 70° to C_1C_4 (parallel to the O–CO bond axis); (G) high-temperature data and simulation based on flips between 0 and 140° about the C_1C_4 axis; (H) high-temperature data and simultaion based on C_1C_4 axis π flips plus restricted rotation over a 60° range. The points represent experimental data and the line the theoretical simulations.

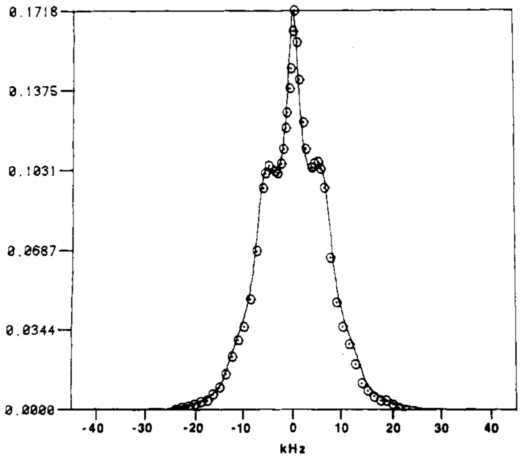


Figure 2. ^1H dipolar line shapes of BPA-d_6 in perdeuterio-BPA. The points represent experimental data and the line the theoretical simulations in the high-temperature limit simulation.

by 70° from the C_1C_4 axis. This motion would collapse the Pake splitting in the proton spectrum by 50% rather than the 10% or less observed.

The CSA line shape itself ruled out restricted rotation about the C_1C_4 axis, but two remaining possibilities consistent with both the carbon and proton data are π flips plus restricted rotation and flips between 0 and 140°. The first motion seems physically plausible; while the second is unexpected, it is not inconceivable. In any case, these line shapes are consistent with the presence of π flips if considerable restricted rotation is also present. This interpretation is in excellent agreement with the model presented by Spiess[4] based on deuterium line shape measurements. It should be noted that this author suggested that the amplitudes of the restricted rotations are not identical for different phenyl groups, and this could be responsible for the minor discrepancies present in the simulations.

Acknowledgment. We are grateful to Drs. P. D.

McMaster, E. W. Byrnes, and J. Campbell for synthesis of the carbon-13 labeled monomer and polymer. The research was carried out with financial support of the U.S. Army Research Office (Grant DAAG 29-82-G-0001) and the National Science Foundation (Grants DMR-790677, CHE 77-09059, and DMR-8108679).

Registry No. Bisphenol A polycarbonate, 24936-68-3; carbonic acid/bisphenol A copolymer, 25037-45-0.

References and Notes

(1) Inglefield, P. T.; Jones, A. A.; Lubianez, R. P.; O'Gara, J. F. *Macromolecules* **1981**, *14*, 288.
(2) Schaefer, J.; Sefcik, M. D.; Stejskal, E. O.; McKay, R. A.; Dixon, W. T. "28th Macromolecular Symposium Proceedings"; International Union of Pure and Applied Chemistry, 1982, p 25.
(3) Garroway, A. N.; Ritchey, W. M.; Moniz, W. B. "28th Macromolecular Symposium Proceedings"; International Union of Pure and Applied Chemistry, 1982, p1.
(4) Spiess, H. W. "28th Macromolecular Symposium Proceedings"; International Union of Pure and Applied Chemistry, 1982, p 35. *Colloid Polym. Sci.* **1983**, *261*, 193.
(5) Garroway, A. N.; Ritchey, W. M.; Moniz, W. B. *Macromolecules* **1982**, *15*, 1051.
(6) Schaefer, J.; private communication.
(7) Schaefer, J.; Sefcik, M. D.; Stejskal, E. O.; McDay, R. A.; Dixon, W. T.; Cais, R. E. *Prepr., Div. Org. Coat. Plast. Chem.* **1983**, *48*, 87.
(8) Slotfeldt-Ellingsen, D.; Resing, H. A. *J. Phys. Chem.* **1980**, *84*, 2204.
(9) Nye, J. F. "The Physical Properties of Crystals"; Oxford Press: London, 1957.
(10) Mehring, M. *NMR Basic Princ. Prog.* **1976**, *11*.
(11) Jones, A. A.; O'Gara, J. F.; Inglefield, P. T.; Bendler, J. T.; Yee, A. F.; Ngai, K. L. *Macromolecules* **1983**, *16*, 658.

Paul T. Inglefield* and Robert M. Amici

Department of Chemistry
College of the Holy Cross
Worcester, Massachusetts 01610

John F. O'Gara, Chi-Cheng Hung, and Alan Anthony Jones

Jeppson Laboratory, Department of Chemistry
Clark University, Worcester, Massachusetts 01610

Received May 17, 1983

CORRECTIONS

Frank S. Bates* and Gregory L. Baker*: Soluble Polyacetylene Graft Copolymers. Volume 16, Number 4, April 1983, page 704.

It has come to our attention that the NMR results presented in *Macromolecules* 1983, *16*, 704 and attributed to *trans*-polyacetylene in fact derive from toluene. The actual NMR behavior of polyacetylene graft copolymers is presently being investigated and will be reported in the future.