Table II
Summary of Coupling Constants

	^{1}H NMR			^{2}H NMR		^{13}C NMR
compound	$^3J_{AB}$	$^3J_{AX}$	$^3J_{BX}$	$^3J_{D-A}$	$^3J_{D-B}$	$^1J_{C-D}$
methyl acrylate[a]	1.51	17.3	10.2	2.61	1.57	25.9
butyl acrylate	1.68	17.3	10.3	2.57	1.61	25.0
acrylonitrile (D_2O)				2.68	1.77	27.4
acrylonitrile		17.6	11.7	2.64	1.84	26.8

[a] Deuterium donor was MeOD except for D_2O for entry three.

utes, although prolonged reaction led to Michael addition and aldol condensation products.[7]

The general procedure involves simply mixing together excess deuterium donor with the activated substrate, adding DABCO, and monitoring the reaction with ^{1}H or ^{2}H NMR. The first trial was performed with a MeOD to methyl acrylate ratio of 13:1, with subsequent trials using a ratio to give a theoretical percent deuteration of greater than 95%. Figure 2 gives representative spectra for methyl acrylate. The vinylic region of the ^{1}H spectrum displays a typical ABX pattern with coupling constants $^3J_{AB} = 1.5$, $^3J_{AX} = 17.3$, and $^3J_{BX} = 10.2$ Hz. The A and B represent the *E* and *Z* hydrogens, respectively. The deuterium spectrum displays splitting of the α-^{2}H by the trans and cis hydrogens with $^3J_{D-A} = 2.52$ and $^3J_{D-B} = 1.57$ Hz, respectively. Essentially complete ^{1}H–^{2}H equilibration was observed in most cases, e.g., for methyl acrylate, 94% found versus 92% theoretical.

The deuterium exchange using acrylonitrile was performed twice by using D_2O to give a final percent deuteriation of 93.7%. This reaction was run interfacially, and upon separation and drying, the deuteriated acrylonitrile was isolated. NMR and FTIR were used to confirm deuteriation at the α position. Coupling constants for acrylonitrile were determined to be $^3J_{AX} = 17.6$ and $^3J_{BX} = 11.7$ Hz. The deuterium splitting of the α-^{2}H was $^3J_{D-A} = 2.68$ and $^3J_{D-B} = 1.77$ Hz. Table II summarizes coupling constants, in hertz, for the ^{1}H, ^{2}H, and ^{13}C spectra. For identical coupling paths the ratio of hydrogen–hydrogen coupling constants to hydrogen–deuterium constants range from 6.4 to 6.7.

These labeled materials, in addition to their value in forming specifically labeled polymers, should be useful in probing mechanisms in organic and natural product syntheses involving a variety of Grignard, Michael, and Diels–Alder reactions.

Acknowledgment. We gratefully acknowledge an instrumental grant from the Department of Defense through the Office of Naval Research for purchase of our Bruker MSL-200 NMR. This work was supported in part by the Office of Naval Research.

Registry No. 1 (Z = Co_2Me), 96-33-3; 1 (Z = $CO_2(CH_2)_3Me$), 141-32-2; 1 (Z = CN), 107-13-1; 2 (Z = CO_2Me), 15020-05-0; 2 (Z = $CO_2(CH_2)_3Me$), 112741-03-4; 2 (Z = CN), 4635-82-9; DABCO, 280-57-9; MeOD, 4206-31-9; D_2O, 7789-20-0; methyl vinyl ketone, 78-94-4; methyl vinyl ketone (α-deuteriated), 112741-04-5.

References and Notes

(1) Spiess, H. W. *Colliod Polym. Sci.* **1983**, *261*, 193.
(2) Mathias, L. J.; Kusefoglu, S. H.; Kress, A. O. *Macromolecules* **1987**, *20*, 2326.
(3) Hoffman, H. M. R.; Rabe, J. *J. Org. Chem.* **1985**, *50*, 3849.
(4) Yokota, K.; Hirabayashi, T.; Takahashi, K. *Polym. J.* **1980**, *12*, 177.
(5) Yokota, K.; Hirabayashi, T. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 1609.
(6) Leitch, L. *Can. J. Chem.* **1957**, *35*, 345.
(7) Amri, H.; Villieras, J. *Tetrahedron Lett.* **1986**, *27*, 4307.

Lon J. Mathias* and Ronald F. Colletti

Department of Polymer Science
University of Southern Mississippi
Hattiesburg, Mississippi 39406-0076

Received November 3, 1987

Chain Diffusion of Polystyrene in CS_2

Since Wellinghoff et al.[1] found that atactic polystyrene can form a thermally reversible gel in various solvents, several further investigations[2-5] have ensued to understand the nature of the physical gelation. Tan et al.[2] and Boyer et al.[3] proposed that chain overlap is responsible for the gelation, whereas Gan et al.[5] suggested the formation of microcrystal in the gel state to explain their observation of the enhanced low-angle light scattering in the gel state. From calorimetry measurement, the concentration of the physical cross-links in the gel structure was estimated to be 5–10% by François et al.[6] Despite these efforts, the chain configuration in the gel state is not fully understood, and it demands further examination. In this experiment, the forced Rayleigh scattering (FRS) technique was used to study the translational diffusion of the individual polymer chains in the gel state. Our previous experiment on gelatin[7] showed that self-diffusion is quenched below the gel point. Whether chain diffusion is also quenched in polystyrene/CS_2 gel is a burning question. This paper is focused on the issue of self-diffusion of polystyrene chains in CS_2 above and below the gelation region. By examining the self-diffusion we hope to shed some light on the nature of this gelation phenomenon.

Experimental Section. Polystyrene was obtained from Pressure Chemical Co. ($M_w/M_n = 1.06$ and 1.04 for 35K and 90K samples, respectively). Dye-labeled polystyrene was prepared by reacting randomly and sparsely *p*-aminomethylated polystyrene with *p*-azobenzoyl chloride as described elsewhere.[8] The labeling content was about 1 dye moiety/400 monomer units.

Polystyrene containing less than 30% of the labeled chain was dissolved in carbon disulfide (HPLC grade, Aldrich Chemical), filtered through a 0.4-μm filter twice, and then placed in a 5-mm path length cuvette. After the sample was initially stabilized at 25 °C for 24 h, the temperature was lowered at a rate of less than 0.5 °C/min to −24 °C and then raised to a desired temperature, at which FRS measurements were performed. The sample was stabilized at each temperature for at least 12 h prior to the measurements. Afterwards, the temperature was varied again in the same manner, and the gelation was checked visually (sample cell tilting, as performed by Tan et al.[2]). Both gel *formation* upon lowering the temperature $T_{gel,f}$ and gel *melting* upon raising the temperature, $T_{gel,m}$, were reproduced within 1 °C, and they are indicated by arrows in Figures 2 and 3. We found invariably $T_{gel,f} < T_{gel,m}$. We also note that the concentrations chosen for the experiment, 25 wt % of 35K and 18 wt % of 90K molecular weight, are in the semidilute solution region while they are not yet in the entanglement concentration region, $C^* < C < C_e$, where $C_e = \rho M_c/M$ with ρ being the polystyrene bulk density and $M_c = 35\,000$.

The experimental details of the FRS measurement have been described elsewhere.[9,10] The data analysis here re-

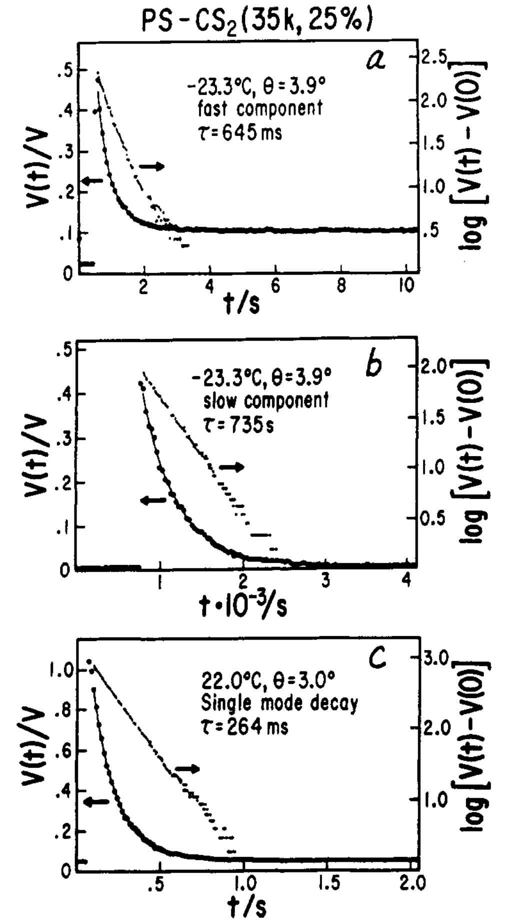


Figure 1. Examples of FRS signal decays for the sample of PS 35K in CS_2 at 25 wt %: (a) polystyrene self-diffusion in the gel state at −23.3 °C for a full time span of 10 s; (b) under the same conditions as in (a) except for a full time span of 4000 s; (c) polystyrene self-diffusion in solution at 22 °C.

quires some discussion. Normally, we use the model function

$$V(t) = [A \exp(-t/\tau) + B]^2 + C^2 \qquad (1)$$

where $V(t)$ is the PMT output, t is the characteristic decay constant, A is the intensity factor of the relaxation signal, B is the coherent background, and C^2 is the incoherent background including the stray light contribution. The four parameters were determined by a nonlinear regression routine. Having obtained the decay constants at several grating spacings at a particular temperature, we computed the diffusion coefficients from the slope of the least-squares fit through the data using the relation

$$1/\tau = Q^2D + 1/\tau_{\text{dye}} \qquad (Q^2 = 4\pi^2/d^2) \qquad (2)$$

where d is the spacing of the transient optical grating and τ_{dye} is the thermal lifetime of the photochromically shifted state of a given dye.

Results and Discussion. The self-diffusion in the gel state is presented in Figure 1a as a typical example, wherein we note two features. First of all, polymer chains diffuse with a diffusion coefficient of the order of 10^{-8} cm²/s, which is comparable to that of a moderately concentrated polystyrene solution at a comparable concentration.[8] Secondly, the decay curves have 10–20% of a "slow component" tail, which decreases in intensity as the temperature is increased and vanishes eventually above $T_{\text{gel,m}}$. Figure 1b shows the slow component examined on a much longer time scale, in fact by a factor of 400. A single-exponential decay behavior is found for this process as exemplified by the semilog plot. We infer from this that there are two components of the diffusion in the gel state, and they are separated by 3 orders of magnitude in time. Next, we examined the Q dependence of the slow component decay constant. It was found to have no discernible Q dependence; in fact the $1/\tau$ vs Q^2 plot at every temperature gave rise to a horizontal line within experimental error. Thus we are faced with the fact that the slow decay component of the FRS signal appears to be *not* of spatial (translational) origin. Alternatively, the lifetime of the photochromic dye is such that $1/\tau_{\text{dye}}$ term is predominant over the Q^2D term in eq 2 even though there still exists a translational diffusion process with a much smaller D. We cannot rule out this possibility with our results. Therefore, two possibilities can be suggested: (1) the slow component is spatially stationary, and therefore Figure 1b represents the relaxation signal of the excited dye moieties in the polymer chain; (2) there really exists a slow diffusion of the order of 10^{-11}–10^{-12} cm²/s.

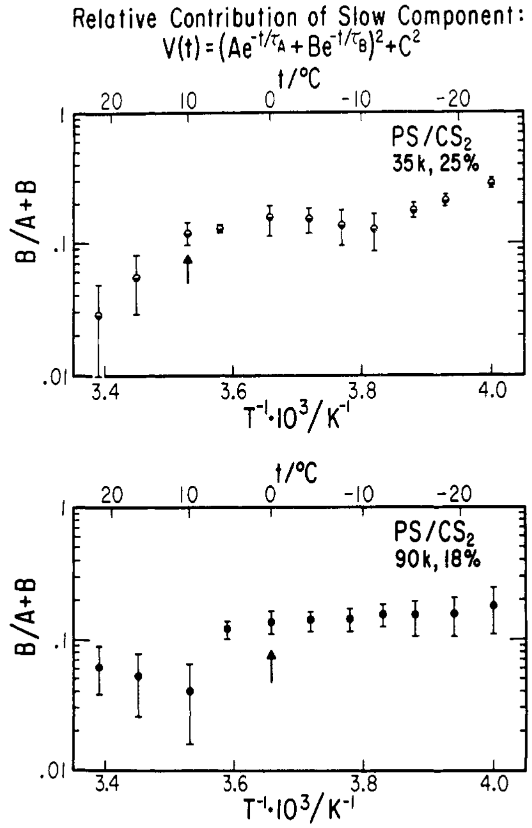


Figure 2. Contribution of the slow component to the total FRS signal intensity (A and B as defined in eq 1). Note that the error bars on points to the left side of the arrow ($T_{\text{gel,f}}$) in each become larger because the slow component becomes weaker in intensity at higher temperatures and eventually vanishes altogether.

Finally, when the temperature is raised above the gel melting point $T_{\text{gel,m}}$, the sample is in the solution state, and the diffusion has only one (fast) component as shown in Figure 1c.

The relative contribution of the slow component to the total relaxation signal, expressed as $B/(A + B)$, where A and B are the intensity factor and coherent background, respectively, is plotted against temperature in Figure 2. The temperature at which the slow component disappears coincides with the gel melting temperature $T_{\text{gel,m}}$ indicated by an arrow. To be exact, $A'\exp(-t/\tau_{\text{slow}})$ as an additional term should be introduced into the parentheses of eq 1, and $A'/(A + A)$ should be regarded as the slow component contribution. But $A'\exp(-t/\tau_{\text{slow}})$ is almost invariant in the time scale of the fast component and large compared

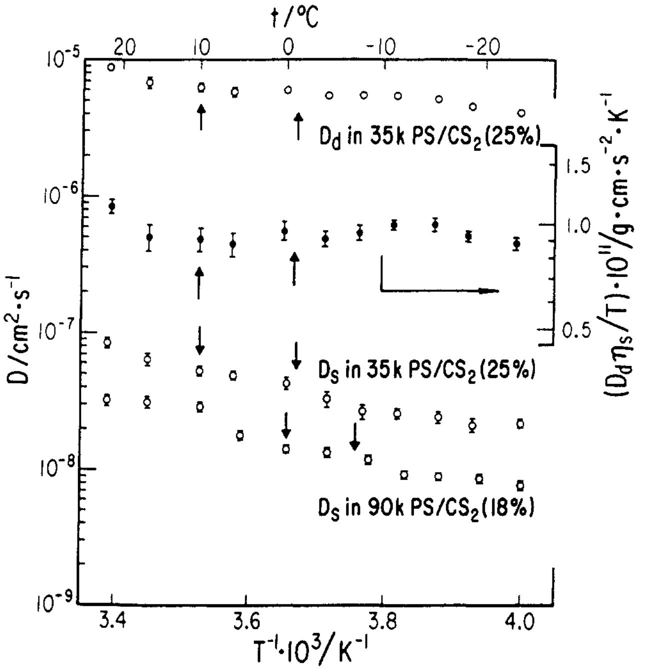


Figure 3. Temperature dependences of the diffusion coefficients are given by open circles. A pair of arrows on each sample run indicates $T_{gel,f}$ and $T_{gel,m}$, where $1/T_{gel,f} > 1/T_{gel,m}$: (top) probe dye (methyl yellow) diffusion coefficient D_d in 35K PS/CS$_2$ (25 wt %) matrix; (middle) the self-diffusion coefficient D_s of 35K PS/CS$_2$ (25 wt %); (bottom) the self-diffusion coefficient D_s of 90K PS/CS$_2$ (18 wt %). Solid circles of the second profile from the top represent the temperature-corrected and solvent viscosity corrected D_d, shown on the right-hand-side ordinate, indicating temperature invariance of the hydrodynamic radius of methyl yellow in the same matrix. Solvent viscosities at different temperatures η_s for evaluating $D_d\eta_s/T$ were obtained from ref 11.

to the coherent background; thus a constant B approximates the slow component. Therefore, $B/(A + B)$ reasonably represents the relative contribution of the slow component. An Arrhenius plot of the fast component together with the diffusion coefficient of a probe molecule, methyl yellow dye, is shown in Figure 3. The probe diffusion seems to have a monotonic temperature dependence and appears to be a simple hydrodynamic process (in Figure 3, solid circles) as exhibited by the constancy of solvent viscosity η_s and temperature-corrected diffusion coefficient (see the right ordinate scale). On the other hand, the self-diffusion has a minor indication of discontinuity at $T_{gel,f}$ and $T_{gel,m}$.

We conclude that most of the polymer chains still diffuse rather freely in the gel state and less than 20% of the chains is involved in "junctions" of the gel structure. Unfortunately, due to the limitation of the dye lifetime, we cannot be definite about whether the junctions are permanent or dynamic. If they are dynamic, then their time constant would be of the order of 10^{-11} cm^2/s or slower. If this were indeed the case, the rate of chain association and dissociation and the number of the junctions at a certain time scale should be considered as important factors in gelation.

Acknowledgment. This work is supported by the Polymers Program of the National Science Foundation.

Registry No. CS$_2$, 75-15-0; polystyrene, 9003-53-6.

References and Notes

(1) Wellinghoff, S.; Shaw, J.; Baer, E. *Macromolecules* **1979**, *12*, 932.
(2) Tan, H.-M.; Moet, A.; Hiltner, A.; Baer, E. *Macromolecules* **1983**, *16*, 28.
(3) Boyer, R. F.; Baer, E.; Hiltner, A. *Macromolecules* **1985**, *18*, 427.
(4) Koltisko, B.; Keller, A.; Litt, M.; Baer, E.; Hiltner, A. *Macromolecules* **1986**, *19*, 1207.
(5) Gan, J. Y. S.; François, J.; Guenet, J.-M. *Macromolecules* **1986**, *19*, 173.
(6) François, J.; Gan, J. Y. S.; Guenet, J.-M. *Macromolecules* **1986**, *19*, 2755.
(7) Chang, T.; Yu, H. *Macromolecules* **1984**, *17*, 115.
(8) Kim, H.; Chang, T.; Yohanan, J. M.; Wang, L.; Yu, H. *Macromolecules* **1986**, *19*, 2755.
(9) Wesson, J. A.; Takezoe, H.; Yu, H.; Chen, S. P. *J. Appl. Phys.* **1982**, *53*, 6513.
(10) Léger, L.; Hervet, H.; Rondelez, F. *Macromolecules* **1981**, *14*, 1732.
(11) *International Critical Table*; Washburn, E. W., West, C. J., Dorsey, N. E., Martha, D. R., Eds.; McGraw-Hill: New York, 1928; Vol. 7, p 213.

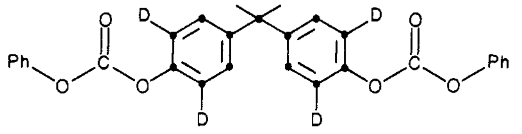
Jungsik Lee, Hongdoo Kim, and Hyuk Yu*

Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received July 20, 1987

Ring Dynamics in a Crystalline Analogue of Bisphenol A Polycarbonate

Intermolecular interactions may control the rate at which ring flips occur in bisphenol A polycarbonate.[3,4] Intermolecular structure is ill-defined in the amorphous polymer, but a crystal structure for 4,4′-isopropylidenediphenylbis(phenyl carbonate) (I), a model for bisphenol



I

A polycarbonate, has recently been reported.[5] We have prepared a deuteriated form of this material in the hope that ring flipping could be detected in a system related to polycarbonate for which the molecular conformation and the packing structure are well established. Characterization of motion in the model system may help to differentiate between alternate schemes for motion in the polymer.[5,6]

Unfortunately, the aromatic rings in the crystal structure of ref 5 are rigidly clamped. Even at 350 K, the deuterium spectrum is that of a rigid solid (Figure 1). The spectrum

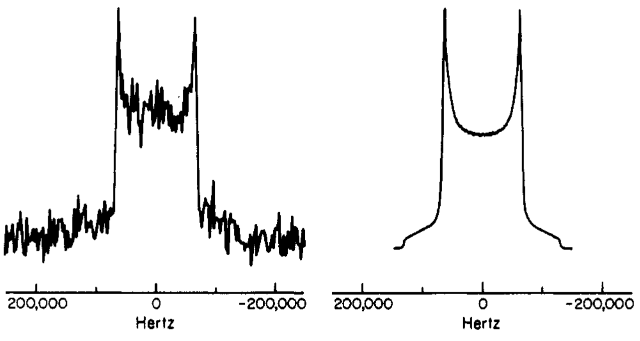


Figure 1. Experimental (left) and simulated (right) deuterium spectra at 41.445 MHz of rigid crystalline form of I at 350 K. A two-pulse sequence with 90° pulses of 3.2 μs, separated by 30 μs, and a relaxation delay of 40 s were used. The relatively low signal-to-noise ratio of the spectrum results from a very long deuterium spin-lattice relaxation time for this crystal form. The simulated spectrum was calculated with e^2qQ/h = 175 333 Hz and η = 0.034.

0024-9297/88/2221-0860$01.50/0