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Molecular Motion of Poly(oxymethylene) in Solution

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ABSTRACT: The molecular motion of poly(oxymethylene) in dilute phenol solution has been studied by using the coupled spin relaxation of a methylene group ($^{13}CH_2$). Four unique spectral densities are measured. These are reexpressed in terms of second-rank correlation times. The ratio of τ_{zz} to τ_{yy} to τ_{xy} is 1.6:1:0.61. These anisotropies of motion are smaller than those measured for hydrocarbon chains in solution. Unlike the hydrocarbons, poly(oxymethylene) is most stable in the gauche conformer, which leads to helical chain configurations. The smaller anisotropy may reflect the lack of correlated motions of a few bonds in the polymer chain.

I. Introduction

The reorientational dynamics of polymer chains in solution have been of considerable interest in recent years. Technologically important properties such as phase-transition temperatures, elasticity, and solution and melt viscosities are thought to be correlated with molecular motion.[1,2] Thus, understanding the relation between chain structure and chain motion is an important factor in predicting polymer properties.

A wide variety of theoretical descriptions of the fundamental physics of chain motion has been offered,[3-7] but experimental tests of these models have been limited. Perhaps the most popular experimental method has been NMR spin relaxation. Typically in these studies the ^1H or ^{13}C T_1's of the polymer are studied as a function of temperature and/or field strength.[8,9] The results are then fit to expressions derived from the theoretical models, such as those by Jones and Stockmayer[10] or Weber and Helfand.[11]

Discrimination between models has been difficult, however. While experiments such as those described are very sensitive to the motional *times scales,* they lack descriptive details of the *geometry* of motion. This latter information is often needed to discriminate one model from another.

This paper describes NMR spin relaxation studies of poly(oxymethylene) (POM) in a dilute deuteriophenol solution. POM was synthesized with 10% of the monomers labeled with ^{13}C and the remaining 90% labeled with ^2H in the CH_2 groups in order to provide isolated $^{13}CH_2$ spin systems. The properties of this *coupled* three-spin system have been exploited to provide additional geometric information.

The relaxation of dipolar coupled spins is generally described in terms of autocorrelation spectral densities, which are the Fourier transforms of correlation functions relating the orientation of an internuclear dipole to itself at a later time.[12] For multiple-coupled spins, for example, $^{13}CH_2$, a complete description of the relaxation also includes cross-correlation terms between *pairs* of dipolar vectors. The traditional approach has been to regard these as unimportant and, using our example, to decouple the ^1H spins so as to enhance the ^{13}C sensitivity. Invariably, the proton-decoupled methylene ^{13}C spin will relax with an "effective" single-exponential recovery law as the multiple-exponential relaxation behavior of the coupled spins is obscured with the collapse of the proton-induced multiplet under decoupling.

Study of the fully coupled multiplets has been shown to provide significant additional information.[13,14] In the case of a methylene group, four independent spectral densities are required to describe the relaxation even in the extreme narrowing limit. These can be used to calculate four correlation times describing reorientation of the x, y, and z axes of a molecule fixed reference frame.[15] Such studies have been completed on small molecules,[16-19] *n*-alkanes,[20] lipids in bilayer membranes,[21,22] and poly(*cis*-1,4-butadiene) in solution.[23]

Poly(oxymethylene) exists in crystalline form in an all-gauche configuration, leading to a helical overall structure. This is in stark contrast to the all-trans form of linear polyethylene (PE). The dominant configurations are expected to be similar in solution. As such, the dynamics of POM, PE, and intermediate forms such as poly(oxyethylene) (POE) provide great insight into how intramolecular potentials affect molecular motion.

II. Experimental Section

[^{13}C]Paraformaldehyde, paraformaldehyde-d_2, and phenol-d_6 were obtained from MSD Isotopes. All other reagents were reagent grade. Solvents were freshly dried and distilled before use.

Isotopically labeled POM was synthesized by copolymerizing 10% [^{13}C]formaldehyde and 90% formaldehyde-d_2. The synthesis was as described elsewhere[24] with the following changes: labeled paraformaldehydes were pyrolyzed directly; the formaldehyde generated was swept into the reaction vessel by a gentle stream of dry-nitrogen gas; and the synthesis was done with 5.5 g of starting material. The yield was 0.44 g of POM. Stability of the polymer under the experimental conditions was enhanced by acetylation of the terminal hydroxyls.[25] The final yield was 0.39 g. The viscosity was measured for 0.5% w/v POM in phenol stabilized with 2% α-pinene at 80 °C by using an Ostwald viscometer. The reduced viscosity, η_{sp}/c was 4.1 dL g^{-1}, indicating a high molecular weight polymer.

Spectroscopic samples were 1% w/v POM in phenol-d_6 stabilized with 2% α-pinene. Samples were subjected to three freeze-pump-thaw cycles and then sealed in 10-mm NMR tubes under vacuum. No degradation of the sample during the course of the experiments was apparent from the ^{13}C NMR spectrum or from visual inspection.

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Table I
Spectral Densities from the Relaxation of Poly(oxymethylene)

	357 K	367 K	378 K	387 K
J_{CHCH}	0.099 ± 0.002	0.081 ± 0.002	0.066 ± 0.001	0.058 ± 0.001
$J_{\mathrm{HH'HH'}}$	0.091 ± 0.005	0.068 ± 0.006	0.058 ± 0.003	0.055 ± 0.005
$J_{\mathrm{CHCH'}}$	0.009 ± 0.006	0.001 ± 0.006	0.007 ± 0.003	0.004 ± 0.004
$J_{\mathrm{CHHH'}}$	0.059 ± 0.001	0.048 ± 0.002	0.040 ± 0.001	0.036 ± 0.001
j_{C}	0	0	0	0
j_{H}	−0.006 ± 0.004	0.003 ± 0.004	0.001 ± 0.002	0.003 ± 0.003

Table II
Cartesian Correlation Times for Poly(oxymethylene)[a]

	357 K	367 K	378 K	387 K
τ_{xx}	31 ± 8	13 ± 10	17 ± 5	15 ± 6
τ_{yy}	20.7 ± 1.1	15.5 ± 1.4	13.2 ± 0.7	12.5 ± 0.9
τ_{zz}	36 ± 6	22 ± 7	23 ± 3	18 ± 4
τ_{xy}	12.1 ± 0.8	10.7 ± 0.8	7.9 ± 0.4	7.2 ± 0.6

[a] In picoseconds.

All spectra were acquired on a Varian XL-400 spectrometer operating at a ^{13}C frequency of 100.6 MHz. For each spectrum 24 000 data points were acquired using a sweep width of 15 000 Hz. Typically 15 different delay times were used for each experiment, ordered randomly to reduce systematic errors. The number of scans per delay time was 256. Recycle delays were adjusted to be at least 10 times the nominal T_1 of the sample. Experiments were conducted at 84, 95, 105, and 114 °C. Temperatures are estimated to be accurate to ±1 °C. Outside this temperature range either the polymer begins to precipitate or else the sample boils.

Line intensities were obtained by integrating the peak amplitudes using Varian software. Multiparameter curve fitting was performed as reported previously.[18] Fitting parameters included pulse efficiencies, equilibrium intensities, scaling factors, and dipolar and random-field spectral densities.

III. Results

The relaxation of the methylene spin system may conveniently be expressed in terms of a number of magnetization modes.[26] These modes arise from the symmetry of the spin operators, but the observable ones can be thought of as linear combinations of transition intensities in the ^{1}H and ^{13}C spectra. As we look at only the ^{13}C spectrum, three modes can be observed: ${}^{a}\nu_1$, the total ^{13}C magnetization; ${}^{a}\nu_3$, the difference between the inner and outer line intensities of the ^{13}C triplet; ${}^{s}\nu_1$, the difference between the intensities of the outer two lines of the ^{13}C triplet.

Four different initial perturbations of the ^{13}CH$_2$ spin system were used: (1) a ^{13}C 180° pulse inverting the entire methylene triplet; (2) a ^{1}H 180° pulse inverting the proton doublet; (3) a low-power ^{1}H pulse inverting only the upfield line of the ^{1}H doublet (the intermediate soft pulse described by Bovee was used[27]); (4) a J pulse preparation on the ^{1}H magnetization (resembling a spin echo) resulting in the inversion of the outer lines of the ^{13}C triplet.[28] In each case the initial perturbation of the spin system was followed by a variable delay period and a ^{13}C sampling pulse as in a normal inversion–recovery experiment.

In the limit of extreme narrowing, the dipolar relaxation of a methylene group is completely described by four frequency-independent spectral densities. Two of these are autocorrelation terms related to the CH or HH′ internuclear vectors (J_{CHCH} and $J_{\mathrm{HH'HH'}}$). The others are cross-correlation terms relating one CH vector to the other ($J_{\mathrm{CHCH'}}$) or to the HH′ vector ($J_{\mathrm{CHHH'}}$). The spectral densities can be obtained from fitting the experimental data to the expressions for the relaxation generated from Redfield theory as described previously.[13]

In addition to the dipolar spectral densities and experimental parameters, we include random-field spectral densities in the fit to account for any other relaxation mechanisms operating in the sample. For the methylene spin system a complete set of random-field spectral densities would include an autocorrelation term at the carbon (j_{C}), an autocorrelation term at each hydrogen (j_{H}), and a cross-correlation term between the two hydrogens ($k_{\mathrm{HH'}}$). Previous work has always found that j_{H} and $k_{\mathrm{HH'}}$ are statistically indistinguishable and they have been locked to each other in the fit.[16,21,23] This practice is followed here as well.

Table III
Arrhenius Activation Energies

	E_a, kJ mol^{-1}		E_a, kJ mol^{-1}
τ_{xx}	23 ± 11	τ_{zz}	23 ± 5
τ_{yy}	19 ± 3	τ_{xy}	21 ± 6
average	21 ± 6		

The spectral densities obtained are listed in Table I as a function of temperature. Error limits listed are standard deviations. The spectral densities decrease as temperature increases, as would be expected for increasing rates of molecular motion. There is some fluctuation in $J_{\mathrm{CHCH'}}$, probably due to the extremely small magnitude of this term relative to the experimental precision. The fits reported have j_c locked to zero, as its value is always within 1 standard deviation of zero.

The four dipolar spectral densities that describe the relaxation of a methylene group are directly related to corresponding time correlation functions, but these (especially the cross-correlation functions) are not easily interpretable. It has been shown that the observed spectral densities can be reexpressed in terms of four second rank autocorrelation times (τ_{xx}, τ_{yy}, τ_{zz}, and τ_{xy}).[15] These model independent transformations are extremely useful in that the difficulty of interpreting cross-correlation functions is removed, and the results are presented relative to a molecule fixed Cartesian axis system as in most statistical mechanical treatments of chain dynamics. In the transformation to this basis no biases or assumptions are introduced about the dynamical behavior of the molecule as are encountered in using diffusional dynamical models.

The transformation to Cartesian correlation times requires that the geometry of the spin system be known. We shall adopt the HCH angle of 112° given by the best available X-ray diffraction study of the polymer.[29] For the CH distance we shall adopt the value of 1.11 Å given by the electron diffraction study of the small-molecule analogue dimethoxymethane.[30] We shall define the methylene group to lie in the xy plane of our Cartesian axis system, with the x axis bisecting the HCH angle. The Cartesian correlation times calculated by using these parameters are given in Table II.

Taking the inverse of the correlation time to be a motional *rate*, we can then find the Arrhenius activation energy by plotting ln $(1/\tau)$ versus $1/T$. The apparent activation energies for the second-rank correlation times are given in Table III, with the average being 21 ± 6 kJ mol^{-1}. Customarily the apparent activation energy of a polymer in solution is interpreted as the sum of contri-

Table IV
Motional Anisotropies

		τ_{zz}	τ_{yy}	τ_{xy}
poly(oxymethylene) (exptl)		1.6	1	0.61
5-nonane (exptl, 313 K)		2.2	1	0.38
11-heneicosane (exptl, 313 K)		2.3	1	0.45
poly(*cis*-1,4-butadiene) (exptl, 293 K)		2.4	1	0.48
polyethylene (calc, 330 K)	κ_0^{-1}	4.6	1	
	κ_1^{-1}	2.2	1	

butions from internal motion and solvent viscosity.[31] The activation energy measured for the viscosity of phenol at temperatures above 60 °C is 22.3 ± 0.2 kJ mol^{-1}.[32] Given the uncertainty in our value for E_a, all that can be suggested is that the activation energy for the internal motions is fairly small compared to the range most frequently observed of 13–20 kJ mol^{-1}.[31]

IV. Discussion

The configuration and dynamics of poly(oxymethylene) in solution have been the subject of considerable study. POM adopts an all-gauche structure in the crystalline state due to the "anomeric effect", the interaction of carbon–oxygen dipoles between monomers. This is in contrast to the all-trans structure of crystalline linear PE. These structures largely persist in solution.[1] Thus these polymers, and other intermediate polyethers, have been the systems used to explore the effect of intramolecular potentials on polymer properties. Earlier studies focussed primarily on being able to model the intramolecular potential sufficiently well to predict configurational properties.[1,33-36] More recently the dynamics of these chains have been of interest.[37,38]

The time scales of the motion reported here are comparable to those reported elswhere for linear polymers in solution, considering the elevated temperature. Of more interest is the anisotropy of the motion. The anisotropy is reported in Table IV as the ratio of correlation times, using τ_{yy} as a reference. τ_{xx} is omitted because of the large error limits associated with this value. The values given are the average of those at the individual temperatures, as the activation energies of each correlation time are statistically indistinguishable. The ideal comparisons for these anisotropies are those of PE and PEO. Data are not yet available for these molecules. Also reported in Table IV are the only other anisotropies available for other chain molecules.[11,20,23] Immediately noticeable is that the anisotropy of motion for POM is reduced compared to the hydrocarbon chains that have been studied.

Previous studies lend some insight into this observation. NMR studies of POM in the solid state show that the dominant motion there is an ultraslow twisting of 200° about the helix axis.[39] Such twisting is probably important in solution as well. Simulation of the dynamics of POM as Brownian motion on a tetrahedral lattice, properly weighted for the probabilities of various chain configurations, predicts the POM helix to be quite stiff in solution. The primary motions are conceived to be diffusion of trans defects between two helical sections and the "flip-flop" creation and destruction of trans defects in the helix. Both are three-bond motions.[37]

To give an example of a motion that leads to high anisotropies, in their simulation of the solution dynamics of PE Weber and Helfand find that the ratio of the correlation times τ_{zz} and τ_{yy} for uncorrelated rotations about single CC bonds (their κ_0 mode) is 4.6 to 1.[11] This motion efficiently reorients the y axis (which is parallel to the HH vector of the methylene) while only sweeping the z axis through a limited cone. Thus the correlation time for z is much longer. Correlated "crankshaft" motions (Weber and Helfand's κ_1) are also quite anisotropic but tend to reorient the three axes more equally. The similarity between the anisotropy calculated for this motion and that measured in the hydrocarbon chains cited led us to suggest this may be a dominant motion in the spin relaxation of these systems.[23]

In POM the helix axis is tilted at 55° with respect to the xy plane;[40] thus, the torsional motion described above does not preferentially reorient a particular axis. This should lead to low anisotropies. If the more correlated motions described above were important to the relaxation, we might expect higher anisotropies. In addition, it has been suggested that strongly hydrogen-bonding solvents such as phenol strengthen the anomeric effect.[41] This would tend to enhance the conformational rigidity of the POM helix in solution. We suggest, then, that the relaxation in POM is due to complex torsional jittering of the primarily helical chain (often called librational motion), rather than correlated jumps between rotational isomeric states. Supporting this point of view is the fact that the activation energies associated with each correlation time are indistinguishable and thus cannot be associated with differentiated motional processes. Also supporting this point of view is the failure of rotational isomeric state models to fit POM NMR relaxation data.[37]

Dejean de la Batie, Laupretre, and Monnerie have recently published a series of studies of local chain dynamics in polymer melts.[38,42] They measured ^{13}C T_1's at two field strengths and as a function of temperature for poly(vinyl methyl ether), poly(propylene oxide), poly(ethylene oxide), poly(*cis*-1,4-butadiene), poly(*cis*-1,4-isoprene), and polyisobutylene. They find they are unable to fit their data using conventional models based on conformational jumps of the chain coupled with some sort of damping mechanism.[10,11] They propose that rapid librational motions of the polymer are responsible and show that a model including this motion can fit their data. They model this libration as random fast anisotropic reorientation of the CH vector inside a cone whose semiangle they find varies from 23° to 40° depending on the polymer.

The interpretation of the results for POM presented here is consistent with the model proposed by Dejean de la Batie, Laupretre, and Monnerie. The complex torsional jittering suggested above will lead to a librational motion of the methylene group. It should be noted that our previously published work on chain dynamics also supports this position. In studies of acyl chain motion in lipids in bilayer membranes, we proposed a model including an identical fast libration, there finding a semiangle of 47°.[21,22] We have also studied one system examined by Dejean de la Batie, Laupretre, and Monnerie, poly(*cis*-1,4-butadiene) in solution.[23] As described above, we have suggested that specific conformational jumps amounting to a correlated crankshaft motion are important in the relaxation of this polymer. It must be noted, however, that this analysis does not preclude the existence of librational motion. Interestingly, Dejean de Batie, Laupretre, and Monnerie find that for poly(*cis*-1,4-butadiene) a similar model based on conformational jumps fits their data as well, although they prefer the librational model.

In this study we have measured the motional anisotropy of methylene groups in POM in dilute phenol solution. That anisotropy is smaller than that observed for hydrocarbon chain molecules. Whereas for the hydrocarbon chains, we suggested that correlated motions were an important relaxation mechanism, in POM we suggest that they are not and that rapid librational motions are dominant. Studies of polyethylene and poly(oxyethylene) in solution should further clarify the influence of chain structure on polymer motion.

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References and Notes

(1) Mark, J. E. *Acc. Chem. Res.* **1979**, *12*, 49.
(2) Bailey, R. T.; North, A. M.; Pethrick, R. A. *Molecular Motion in High Polymers*; Oxford University: New York, 1981.
(3) Weber, T. A. *J. Chem. Phys.* **1978**, *69*, 2347.
(4) Rebertus, D. W.; Berne, B. J.; Chandler, D. *J. Chem. Phys.* **1979**, *70*, 3395.
(5) Fixman, M. *J. Chem. Phys.* **1978**, *69*, 1527, 1538.
(6) Helfand, E. *J. Chem. Phys.* **1978**, *69*, 1010.
(7) Yamakawa, H.; Yoshizaki, T. *J. Chem. Phys.* **1981**, *75*, 1016. Yoshizaki, T.; Yamakawa, H. *J. Chem. Phys.* **1986**, *84*, 4684.
(8) Connolly, J. J.; Gordon, E.; Jones, A. A. *Macromolecules* **1984**, *17*, 722.
(9) Dais, P.; Nedea, M. E.; Morin, F. G.; Marchessault, R. H. *Macromolecules* **1989**, *22*, 4208.
(10) Jones, A. A.; Stockmayer, W. H. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 847.
(11) Weber, T. A.; Helfand, E. *J. Chem. Phys.* **1983**, *78*, 2881. Hall, C. K.; Helfand, E. *J. Chem. Phys.* **1982**, *77*, 3275.
(12) Abragam, A. *Principles of Nuclear Magnetism*; Oxford University: New York, 1961; Chapter VIII.
(13) Werbelow, L. G.; Grant, D. M. *Adv. Magn. Reson.* **1977**, *9*, 189.
(14) Vold, R. L.; Vold, R. R. *Prog. Nucl. Magn. Reson. Spectrosc.* **1978**, *12*, 79.
(15) Fuson, M. M.; Brown, M. S.; Grant, D. M.; Evans, G. T. *J. Am. Chem. Soc.* **1985**, *107*, 6695.
(16) Mayne, C. L.; Grant, D. M.; Alderman, D. M. *J. Chem. Phys.* **1976**, *65*, 1684.
(17) Fuson, M. M.; Prestegard, J. H. *J. Chem. Phys.* **1982**, *76*, 1539.
(18) Chenon, M. T.; Bernaussau, J. M.; Mayne, C. L.; Grant, D. M. *J. Phys. Chem.* **1982**, *86*, 2733.
(19) Brown, M. S.; Mayne, C. L.; Grant, D. M.; Chou, T. C.; Allred, E. L. *J. Phys. Chem.* **1984**, *88*, 2708.
(20) Brown, M. S.; Grant, D. M.; Horton, W. J.; Mayne, C. L.; Evans, G. T. *J. Am. Chem. Soc.* **1985**, *107*, 6698.
(21) Fuson, M. M.; Prestegard, J. H. *J. Am. Chem. Soc.* **1983**, *105*, 168.
(22) Fuson, M. M.; Presetegard, J. H. *Biochemistry* **1983**, *22*, 1311.
(23) Fuson, M. M.; Grant, D. M. *Macromolecules* **1988**, *21*, 944.
(24) MacDonald, R. A. *Macromol. Synth. Collect. Vol.* **1977**, *1*, 271.
(25) Jaacks, V.; Iwabuchi, S.; Kern, W. *Macromol. Synth. Collect. Vol.* **1977**, *1*, 279.
(26) Werbelow, L. G.; Grant, D. M.; Black, E. P.; Courtieu, J. M. *J. Chem. Phys.* **1978**, *69*, 2407.
(27) Bovee, W. M. M. J. *Mol. Phys.* **1975**, *29*, 1673.
(28) Liu, F.; Mayne, C. L.; Grant, D. M. *J. Magn. Reson.* **1989**, *84*, 344.
(29) Takahishi, Y.; Tadokoro, H. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 123.
(30) Alstrup, E. E. *Acta Chem. Scand.* **1971**, *25*, 1494. Alstrup, E. E. *Acta Chem. Scand.* **1973**, *27*, 3271.
(31) Batenev, G. M., Zelenev, Yu. V., Eds. *Relaxation Phenomena in Polymers*; John Wiley & Sons: New York, 1974.
(32) Bingham, E. C.; White, G. F. *J. Am. Chem. Soc.* **1911**, *33*, 1257.
(33) Uchida, T.; Kurita, Y.; Kubo, M. *J. Polym. Sci.* **1956**, *19*, 365.
(34) Flory, P. J.; Mark, J. E. *Makromol. Chem.* **1964**, *75*, 11.
(35) Abe, A.; Mark, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6468.
(36) Miyasaka, T.; Kinai, Y.; Imamura, Y. *Makromol. Chem.* **1981**, *182*, 3533.
(37) Geny, F.; Monnerie, L. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 131, 147.
(38) Dejean de la Batie, R.; Laupretre, F.; Monnerie, L. *Macromolecules* **1989**, *22*, 122.
(39) Kentgens, A. P. M.; de Boer, E.; Veeman, W. S. *J. Phys. Chem.* **1989**, *87*, 6859.
(40) Ushida, T.; Takadoro, H. *J. Polym. Sci., Part A* **1967**, *25*, 63.
(41) Praly, J.-P.; Lemieux, R. U. *Can. J. Chem.* **1987**, *65*, 213.
(42) Dejean de la Batie, R.; Laupretre, F.; Monnerie, L. *Macromolecules* **1988**, *21*, 2045, 2052. Dejean de la Batie, R.; Laupretre, F.; Monnerie, L. *Macromolecules* **1989**, *22*, 2617.

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