Because the reactivities are averaged over experiments carried out under different conditions, the reactivity found in an individual experiment may deviate from this order. Strong base-initiated copolymerizations are principally not useful to establish an order of reactivities, because the rates of incorporation not only depend on the reactivity of the reactants but also on the concentration of NCA anions, on the stability of the *N*-acyl-NCA chain ends, and on which mechanism is predominant. An exact comparison of two binary systems requires, of course, the reaction conditions and the conversion to be identical. Anyway, it is conspicious that a comparison of the bulkiness of the NCA side chains leads to a similar order of aminoacyl units: Gly < Ala < γ-MeGlu < *S*-BzlCys $\leq$ Leu < Val. Thus we conclude that the steric effect of the side chains and the positive inductive effect of aliphatic substituents which lowers the electrophilicity of the NCA carbonyl group C-5 are the main factors that govern the effective reactivities.

Finally, it should be noticed that above all the triethylamine-initiated copolymerizations are sensitive to various parameters, e.g., polarity of the solvent or addition of cocatalysts. Obviously, these parameters have a strong influence on the reaction mechanisms in agreement with our previous observations.[22,23] Furthermore, it is noteworthy that the pyridine-initiated copolymerizations behave differently from the triethylamine-initiated ones but resemble the primary amine-initiated experiments. An analogous observation has been made in the case of the copolymerization of enantiomeric NCA's.[22] Thus, one can conclude that the chain growth of the pyridine-initiated polymerizations proceeds predominantly via nucleophilic chain ends and not by the activated monomer mechanism; yet this conclusion is tentative and deserves further confirmation. In this connection it should be mentioned that these results also agree with those obtained in our investigation of the copolymerization of Gly-NCA and β-Ala-NCA.[2] Whatever is the correct mechanistic interpretation, the results of the present and of our previous study[2] clearly demonstrate that the copolymerization of amino acid NCA's is influenced by various factors. The sequences of copolypeptides obtained from NCA's are, therefore, not always random as assumed by several authors investigating the properties of copolypeptides without characterization of the primary structure.

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Field Dependent Proton Spin-Lattice Relaxation Times for Characterization of Correlation Times in Dissolved Macromolecules

Alan Anthony Jones,* Gary L. Robinson, Frederic E. Gerr, Michael Bisceglia, Shelley L. Shostak, and Ronald P. Lubianez

Jeppson Laboratory, Department of Chemistry, Clark University, Worcester, Massachusetts 01610. *Received June 28, 1979*

ABSTRACT: The observation of proton spin-lattice relaxation times (T_1's) as a function of static magnetic field strength or Larmor frequency is considered as an approach to extend the dynamic range sensed in nuclear spin relaxation studies. Direct experimental measurements over a wide frequency range are needed because of the complicated character of local motions in chain molecules, and the utility of the proposed procedure is tested by conducting high resolution pulse Fourier transform proton T_1 studies on three dissolved polymers as a function of Larmor frequency over the range 20-90 MHz. For polyethylene dissolved in decalin, T_1 is nearly independent of Larmor frequency, while for both polycarbonate and poly(phenylene oxide) in $CDCl_3$, T_1 displays an appreciable dependence. In all three cases the field or frequency dependence can be accounted for in terms of a dynamic description based on motions likely in the respective polymers. The interpretations are also consistent with carbon-13 relaxation observed under the same conditions. Since both carbon-13 and proton data are acquired with a single spectrometer and yet the spectral density is probed from 20 to 180 MHz, greater confidence in the significance of dynamic model parameters is achieved relatively easily.

Models used to interpret nuclear spin relaxation in terms of local chain motions frequently involve several parameters.[1,2] These parameters correspond to a number of exponential correlation times reflecting motion over a fairly wide range of time scales. In order to determine model parameters with some certainty, thereby testing an interpretational model, an extensive set of spin relaxation measurements is required.[2] The most common ap-

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proaches[3] are the measurement of carbon-13 spin–lattice relaxation times, T_1's, and carbon-13 nuclear Overhauser enhancements (NOE's). These two parameters test somewhat different components of the spectral density or somewhat different frequency ranges of dynamics. However, these data are restricted in frequency range and, to extend this, investigators[4,5] have conducted carbon-13 studies at two field strengths or combined carbon-13 with proton data. Both of these approaches extend the frequency range actually sampled by nuclear spin relaxation measurements.

However, carbon-13 relaxation studies at two field strengths require two spectrometers and considerable cost. Extension to a third strength requires addition of another spectrometer. An alternative method for expanding the data base is to conduct proton relaxation experiments as a function of field strength. Presently, a single modern spectrometer can be used for proton measurements over the range 5–100 MHz. Since the proton spin–lattice relaxation times depend upon both the Larmor frequency and twice the Larmor frequency, the dynamic range probed actually extends over 5–200 MHz.

There are drawbacks to utilizing proton data, namely interpretational difficulties stemming from cross-relaxation and intermolecular dipole–dipole relaxation.[6] There are, however, many systems suitable for study by ^{1}H NMR, and several examples will be presented to demonstrate that field dependent proton spin–lattice relaxation times are useful sources of dynamic information and are consistent with earlier interpretations[7,8] based on very extensive carbon-13 and proton data acquired at one field strength.

Some advantage may result from utilizing field dependent proton T_1's since the earlier interpretations[7,8] used for comparison often involved observation of the molecular weight dependence of T_1. Tedious fractionation procedures were required, and some uncertainty about the molecular weight distribution of each fraction always remained. Molecular weight dependent studies are useful because they provide a method for adjusting the correlation times for overall rotatory diffusion. At low molecular weights, when this correlation time is near the correlation time for local motion, the molecular weight dependence of T_1 and the NOE are quite informative. However, the results of the field dependent studies here indicate that they are suitable replacements for the experimentally difficult molecular weight studies.

A consistent interpretation of field dependent ^{13}C NMR relaxation has been difficult to obtain in some cases[4,5] but not in others.[9] However, thus, far, the field dependent proton data are adequately accounted for in terms of a specific motional model[2,10] based on motions likely in linear polymers.

To illustrate the approach in terms of data, interpretation, and general significance, three polymer systems, of rather different dynamics, have been chosen: polyethylene (PE), the polycarbonate of bisphenol A (BPA-PC), and poly(2,6-dimethyl-1,4-phenylene oxide) (M_2PPO).

Experimental Section

Sufficiently high molecular weights of the three polymers were used to avoid significant contributions to relaxation from overall rotatory diffusion. The molecular weight of the polyethylene is 2×10^3, and it was purchased from the Pressure Chemical Co. The molecular weights of the BPA-PC are 20×10^3 and 25×10^3, and these are the same samples as described elsewhere.[8] The molecular weight of the M_2PPO is 70×10^3, and it is also the same sample as described in an earlier investigation.[7]

The PE was studied as a 5 wt % solution in deuterated decalin, the BPA-PC as a 10 wt % solution in deuterated chloroform, and the M_2PPO as a 10 wt % solution in deuterated chloroform. All samples were degassed and sealed in NMR tubes.

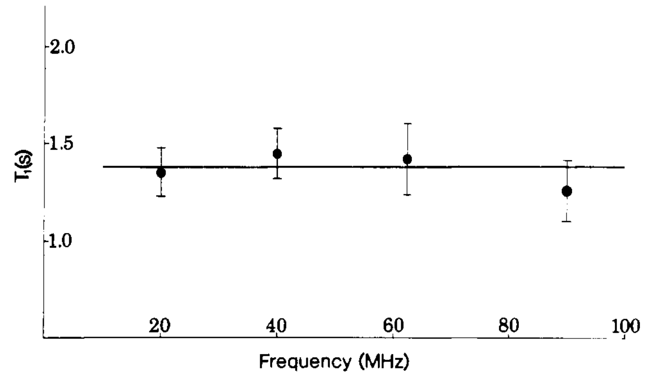

Figure 1. Proton spin–lattice relaxation time vs. Larmor frequency for a 5 wt % solution of polyethylene in deuterated decalin at 90 °C. The line represents an interpretation of the dependence on Larmor frequency based on eq 1 and the parameters from Table II.

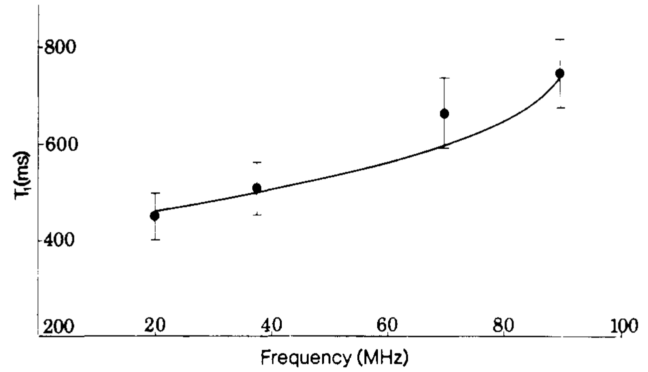

Figure 2. Phenyl proton spin–lattice relaxation time vs. Larmor frequency for a 10 wt % solution of polycarbonate in deuterated chloroform at 10 °C. The line represents an interpretation of the dependence on Larmor frequency based on eq 1 and the parameters from Table II.

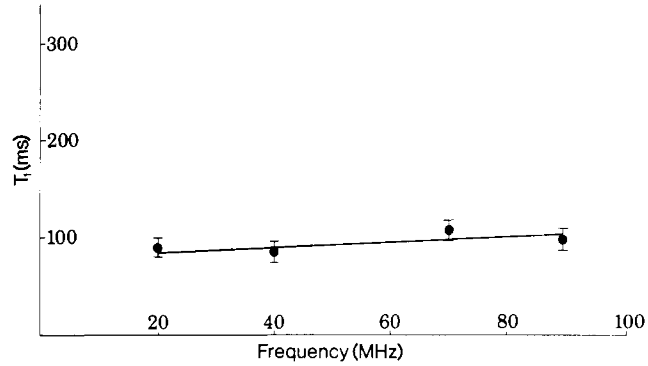

Figure 3. Methyl proton spin–lattice relaxation time vs. Larmor frequency for the same sample as Figure 2. The line represents an interpretation of the dependence on Larmor frequency based on eq 1 and the parameters from Table II.

Proton spin–lattice relaxation times were measured by a 180–τ–90 pulse sequence on a multinuclear, variable field, pulse Fourier transform Bruker SXP 20-100 at several Larmor frequencies between 20 and 90 MHz. Carbon-13 spin–lattice relaxation times were measured on the same spectrometer at 22.63 MHz.

Plots of the proton spin–lattice relaxation times vs. Larmor frequency are shown in Figure 1–4. Carbon-13 spin–lattice relaxations under the same conditions are given in Table I. All relaxation times have an uncertainty of about ±10%, and this uncertainty corresponds to the error bars on Figures 1–4.

Interpretational Model

The specific motional model of Jones and Stockmayer[2,10] serves here as the basis for the quantitative interpretation

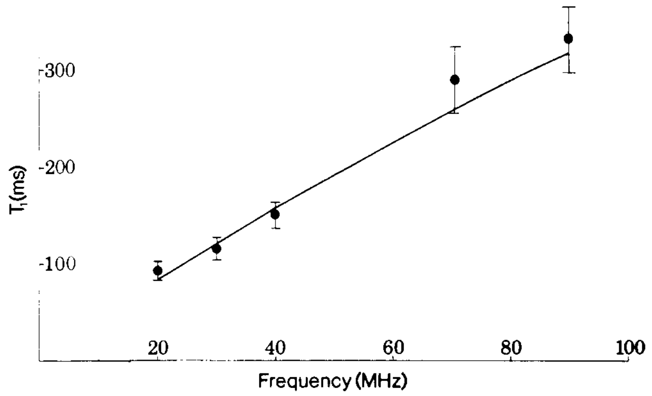

Figure 4. Methyl proton spin-lattice relaxation time vs. Larmor frequency for a 10 wt % solution of poly(phenylene oxide) in deuterated chloroform at 40 °C. The line represents an interpretation of the dependence of Larmor frequency based on eq 1 and the parameters from Table II.

Table I
Carbon-13 Spin-Lattice Relaxation Times

polymer	carbon-13 T_1 at 22.6 MHz, s
PE	1.36
BPA-PC	
protonated phenyl carbons	0.57
methyl carbons	0.109
M_2PPO	
protonated phenyl carbons	0.073

of nuclear spin relaxation in terms of chain motions. Three types of motions are considered in this model. The first is overall rotatory diffusion which can be estimated from the molecular weight, intrinsic viscosity, and Huggins' constant. As mentioned before, sufficiently high molecular weights were chosen so that the correlation time for the overall rotatory diffusion is much longer than the correlation times for local motions. In this case, there is no further need to consider this motion since it may either be included or dropped without consequence.

The second motion is segmental, or backbone rearrangement, which is described in terms of the occurrence of three bond jumps on a tetrahedral lattice. This description may be applied even when a chain is not approximated well by bonds placed on a tetrahedral lattice.[2,8] The principal parameter characterizing this motion is the rate of occurrence, w, of the three-bond jump, and this three-bond jump couples the motion of the backbone bonds, resulting in a distribution of exponential correlation times. A second parameter controls the extent of coupling along the backbone and can be expressed as the number of bonds in a segment of length $2m - 1$ within which motion of the central bond is coupled to the motion of m bonds (every other bond within the segment). The choice of segment length controls the distribution of exponential correlation times, with a long segment length corresponding to a broad distribution of correlation times.

The last type of motion included is anisotropic rotation of substituent groups, especially methyl and phenyl groups which are rigidly attached to the backbone. A Woessner[11,12] type formulation is employed with one parameter, τ_{ir}, for the time scale of internal rotation. For methyl group rotation the symbol τ_{irm} is used, and for phenyl group rotation τ_{irp} is used.

A composite spectral density is produced by considering each of the motions as independent sources modulating the dipole-dipole interaction, and it has the form[2]

$$J_i(\omega_i) = 2\sum_{k=1}^{s} G_k \frac{A\tau_{k0}}{1+\omega_i^2\tau_{k0}^2} + \frac{B\tau_{bk0}}{1+\omega_i^2\tau_{bk0}^2} + \frac{C\tau_{ck0}}{1+\omega_i^2\tau_{ck0}^2}$$

$$\tau_{k0}^{-1} = \tau_0^{-1} + \tau_k^{-1}$$

$$\tau_k^{-1} = w\lambda_k \qquad s = (m+1)/s$$

$$\lambda_k = 4\sin^2((2k-1)\pi/2(m+1)) \tag{1}$$

$$G_k = 1/s + (2/s)\sum_{q=1}^{s-1}\exp(-\gamma q)\cos((2k-1)\pi q/2r)$$

$$\gamma = \ln 9$$

$$A = (3\cos^2\Delta - 1)^2/4$$

$$B = 3(\sin^2 2\Delta)/4$$

$$C = 3(\sin^4\Delta)/4$$

for the twofold jump as the internal rotation,

$$\tau_{bk0}^{-1} = \tau_k^{-1} + \tau_{ir}^{-1} + \tau_0^{-1}$$

$$\tau_{ck0}^{-1} = \tau_{k0}^{-1} = \tau_0^{-1} + \tau_k^{-1}$$

for stochastic diffusion as the internal rotation,

$$\tau_{bk0}^{-1} = \tau_0^{-1} + \tau_k^{-1} + \tau_{ir}^{-1}$$

$$\tau_{ck0}^{-1} = \tau_0^{-1} + \tau_k^{-1} + (\tau_{ir}/4)^{-1}$$

for the threefold jump as the internal rotation,

$$\tau_{bk0}^{-1} = \tau_{ck0}^{-1} = \tau_0^{-1} + \tau_k^{-1} + \tau_{ir}^{-1}$$

The important model parameters have been mentioned with the remaining quantities being basic constants or constants determined from repeat unit geometry. The relationship between the spectral densities, J's, and either the proton or carbon spin-lattice relaxation times is familiar.[7,10]

The aforementioned complications often encountered with the interpretation of the relaxation of abundant spins like protons are minimal in the three systems chosen for study. Specifically, cross relaxation does not occur in PE since only one type of proton is present, but dipolar interactions between protons on several neighboring carbons must be considered. Cross relaxation in M_2PPO and BPA-PC is only a relatively small contribution in comparison to intragroup methyl relaxation in either polymer and to intragroup phenyl relaxation in BPA-PC. Cross relaxation dominates phenyl proton relaxation in M_2PPO so the associated magnetization is not considered here. Intermolecular dipole-dipole relaxation is only a minor contribution in all three cases since fairly dilute solutions of polymer are studied. Thus for the four proton magnetizations to be considered in these three polymers, the well-known relationships between spectral densities and spin-lattice relaxation times for intramolecular dipole-dipole interactions are applicable. Concentrated solutions or polymers with chemically distinct protons in close spatial proximity cannot be analyzed in this manner.

If attention is restricted to polymers with the dominant dipolar interactions among like protons on the same repeat unit, it should not matter whether the parameters of an interpretational model are set from proton or carbon-13 data. If either the dynamic model is inadequate or cross relaxation and intermolecular dipole-dipole relaxation are significant, then the proton and carbon-13 interpretations would likely be inconsistent. For the sake of a uniform approach in this paper, we shall arbitrarily consider all dynamic model parameters to be set from the proton data. Then these dynamic model parameters will be used to predict the carbon-13 relaxation times for comparison against the experimental data in Table I.

Discussion

The first case, PE, is relatively simple and quite uninformative. There is no dependence of the proton T_1's on Larmor frequency apparent in Figure 1. This is quite reasonable since a crude estimate of correlation times indicates PE is well into "the extreme narrowing limit" in the frequency or field range covered. In this case, no insight into the distribution of correlation times is available, since anything but an extremely broad distribution would be undetected by proton T_1's, carbon-13 T_1's, or carbon-13 nuclear Overhauser enhancements at these field strengths. In view of the lack of experimental input, the distribution of correlation times is arbitrarily set at the narrowest condition consistent with the model, namely $2m - 1 = 5$. Since only segmental motion is conceivable at high molecular weights, the only parameter left to fix is the rate of occurrence of the three-bond jump, which is conveniently reported as $\tau_h^{-1} = 2w$.

The proton T_1's may be used to set τ_h, if all the significant proton–proton interactions can be compiled. To do this, an effective proton–proton internuclear distance is calculated in the mode of Heatley[13] by including proton–proton interactions from the proton attached to the same carbon as the proton of interest and from protons attached to the next two carbons on either side of the reference methylene unit. Of course, the latter interactions depend on conformations, so an average over all conformations was made and weighted by the appropriate factors from the rotational isomeric state model.[14] The distance between the two protons on the same carbon is 1.78 Å, and the "effective distance" is 1.64 Å. With this value, the proton spin–lattice relaxation times in Figure 1 can be interpreted from the model. A value of $\tau_h = 7.7$ ps corresponds to the solid line in Figure 1 and also to the carbon-13 relaxation in Table I. The interpretation is consistent with both proton and carbon-13 experimental data but, as mentioned previously, it is uniformative since any aspect of the distribution of exponential correlation times is undetected.

Fortunately PE is atypical of most dissolved synthetic polymers. A more representative case is BPA-PC, which has two observable proton magnetizations: one from the phenyl protons and one from the methyl protons. The field dependence of the phenyl proton T_1, in Figure 2, is appreciable with almost a factor of 2 change between 20 and 90 MHz. The only motion modulating the major phenyl proton dipole–dipole interaction is segmental motion,[8] since this interaction is parallel to the axis of phenyl group rotation. The two model parameters characterizing segmental motion, τ_h and $2m - 1$, can both be fixed by simulating the 20 and 90 MHz T_1 values. There is essentially a unique choice of these two parameters, reported in Table II, indicating field dependent proton T_1 data can be used to determine the time scale and breadth of distribution of exponential correlation times associated with segmental motions. The solid line in Figure 2 is the prediction for T_1 values between 20 and 90 MHz which is in agreement with the experimental results.

In this case the protonated phenyl carbons cannot be used to directly set or check τ_h and $2m - 1$. First the ^{13}C NOE is full at this field strength so the distribution of correlation times is undetected. Second, another local motion besides segmental rearrangements affects the protonated phenyl carbon relaxation. Since the predominant dipole–dipole interaction for these carbons is at an angle of about 60° to the axis of phenyl group rotation,[8] the associated relaxation can be affected by both phenyl group rotation and segmental motion. Without the phenyl proton data, it would be considerably more difficult to unravel the dynamics. However, by first determining the segmental motion description from the phenyl proton data, the time scale of phenyl group rotation can then be set[8] from the carbon-13 T_1. A consistent interpretation is developed in this manner, but the carbon-13 T_1 of the protonated phenyl carbons does not provide a test of the segmental description.

Table II
Interpretational Parameters Including Correlation Times

polymer	τ_h	$2m - 1$	τ_{irp}	τ_{irm}
PE	7.7 ps	5		
BPA-PC	0.23 ns	5	0.16 ns	0.18 ns
M_2PPO	2.3 ns	5	0.25 ns	~1 ps

However, if we now turn to the methyl relaxation data in BPA-PC, a good check of the interpretation based on proton data against carbon-13 data is possible. The methyl proton T_1 values for BPA-PC shown in Figure 3 are very nearly independent of Larmor frequency or field strength. Here two motions are modulating the predominant proton dipole–dipole interaction within the methyl group. First, the same segmental motion as that characterized by the phenyl proton data contributes since the methyl groups are rigidly attached to the backbone. Second, the methyl groups can rotate about the threefold symmetry axis. If the segmental parameters determined from the phenyl proton data are employed, the rate of methyl group rotation can be fixed by adjusting τ_{irm} to account for the methyl proton data. With all dynamic parameters associated with methyl group motions fixed, the carbon-13 T_1 value can then be predicted. The correlation times given for BPA-PC in Table II correspond to the solid line in Figure 3 and predict the methyl carbon-13 T_1 in Table I. Again it does not matter whether one considers the methyl correlation time to be set from the carbon-13 data or from the proton data.

It can be seen in Figure 3 that the lack of dependence of the methyl proton relaxation on Larmor frequency is well interpreted but contrasts with the strong field dependence of phenyl proton relaxation. The methyl field dependence is reduced because the segmental motion and methyl group rotation have about the same correlation time,[8] and the combination of the two motions shifts the average time scale closer to the extreme narrowing limit. This can be seen in the context of the model (eq 1) since the reciprocals of the correlation times for segmental motion and methyl group rotation are added, yielding a shorter net correlation time. Also, only a single correlation time is used to characterize methyl group rotation. If a distribution of exponential correlation times were used to describe this motion[1] similar to the distribution of correlation times for segmental motion, a greater field dependence would be expected since some of the components of the distribution would lie toward the slow side of the extreme narrowing limit. Since little field dependence is observed, it would seem the single correlation time model is best for methyl group rotation in BPA-PC. On the other hand, the stronger field dependence of the phenyl protons reflects the unshifted influence of the distribution of correlation times from segmental motion.

The last polymer chosen to exemplify the utility of field dependent T_1 measurements is M_2PPO. Only the methyl proton data are presented in Figure 4, since the phenyl proton relaxation is dominated by intergroup dipolar interactions between methyl and phenyl protons which are difficult to interpret.[15] The methyl proton spin–lattice relaxation is complicated by cross correlation effects,[7,15] but these are minimized by identifying T_1 with only the initial part of the decay curve. A very strong field dependence is observed for the methyl proton, with about a factor of 4 change between 20 and 90 MHz. Dipolar interactions within the methyl group are subject to three motions, and these have been characterized earlier[7] based on the observation of the methyl proton T_1's as a function of molecular weight at 30 MHz. The motions are: segmental motion, phenyl group rotation, and methyl group rotation. According to the earlier analysis, relaxation is dominated by rapid phenyl group rotation. Segmental motion also contributes significantly, but methyl group rotation is so rapid that it serves only to partially average the dipolar interaction within the methyl group. Employing the correlation times, shown in Table II, which were fixed in an earlier study,[7] the solid line in Figure 4 can be calculated for the field dependence of T_1. The agreement between the calculated field dependence and the observed values is again quite good, falling within the 10% experimental uncertainties. A slightly better fit could be obtained by small adjustments in the model parameters, but this is of marginal significance, especially since here again the correlation times developed from the proton data also account[7] for the carbon-13 T_1 in Table I.

The large field dependence arises in M_2PPO because the segmental motion is far slower than the time scale of the extreme narrowing limit. Phenyl group rotation is somewhat faster, but since this is an anisotropic motion, some components of dipolar interaction are only modulated by slow segmental motion. The methyl proton T_1's are essentially independent of the correlation time for methyl group rotation, which is of the order of picoseconds.

Conclusions

For a number of synthetic polymers, proton T_1's are field dependent and provide information on the spectrum of correlation times associated with local motions. This tool should be combined with other spectroscopic probes, notably carbon-13 T_1's, which were observed in each of the systems discussed with the interpretation accounting for both proton and carbon-13 results. However, in some cases such as the BPA-PC, the proton data provide information not readily extracted from the carbon-13 data. The field-dependent studies can also reduce the need for difficult experimental procedures, including the molecular weight dependent method used in the M_2PPO case.[7] Although all work presented here employed only one spectrometer, if high field spectrometers are also available, motion could be probed over a decade of frequency or more. The value of such an approach can be appreciated by considering the analogy to dielectric experiments, where the need for a broad frequency range is well known. With respect to dynamic range, ^1H NMR is superior to the currently more popular carbon-13 NMR, both because high sensitivity allows low field experiments and the large gyromagnetic ratio extends the high frequency range at high fields. For example, in the case of BPA-PC presented here, the phenyl proton T_1's are field dependent from 5 to 22 kG because of the large gyromagnetic ratio, but the carbon-13 NOE at 22 kG is still experimentally indistinguishable from the maximum value of 3 indicative of the extreme narrowing limit. Not all synthetic polymers have suitably simple proton spectra, but field dependent proton relaxation should be able to contribute to the elucidation of dynamics in a number of cases.

Acknowledgment. The authors thank Mr. Francis Shea for his assistance in the operation of the NMR spectrometer. The research was carried out with financial support of the National Science Foundation, Grant DMR 7716088, Polymers Program. This research was also supported in part by a National Science Foundation Equipment Grant No. CHE 77-09059 and in part by a Hercules Incorporated Research Grant of the Research Corporation.

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