Distributions of Correlation Times and the Carbon-13 Nuclear Magnetic Resonance Spectra of Polymers

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ABSTRACT: Carbon-13 spin-lattice relaxation times, line widths, and nuclear Overhauser enhancement factors have been measured at 22.6 MHz and 35° for a solution of isotactic polystyrene, solid *cis*-polyisoprene, and solid *cis*-polybutadiene. The data are interpreted in terms of a broad asymmetric distribution of correlation times. A log-χ^2 density function is used to describe the distribution, and a rationale is presented for its use. The width of the distribution can be related to the number of degrees of freedom involved in the main-chain segmental motion, and hence is suggested to be a relative measure of the extent of cooperative segmental motion. Of the three polymer systems considered, cooperative motions, at 35°, are the most pronounced in *cis*-polybutadiene.

The ^{13}C spin-lattice relaxation times (T_1) of the methine and methylene main-chain carbons of an *o*-dichlorobenzene solution of isotactic polystyrene at 35° differ by a factor of 2, within experimental error.[1] This means a reasonable description of those segmental motions of the chain responsible for T_1 can be made in terms of an isotropic model of motion involving a single rotational correlation time.[2] Similar simple models involving only one, or perhaps a few, correlation times appear to be adequate for describing the ^{13}C spin-lattice relaxation times of a variety of other polymer solutions,[1] as well as of gels and some solid elastomers above their glass transition temperatures.[3] However, the values for the correlation times obtained from such analyses are generally far too small to describe the experimental line widths. This observation can be explained qualitatively by assuming that in viscous systems there is a net slow motion of chains which results in dipolar interactions occurring mostly at low frequencies. These dipolar interactions are not averaged to zero in a time associated with the time scale of the line width, T_2, and therefore contribute to line broadening.

For some viscous solutions and for solid elastomers such as polybutadiene another complication arises. The correlation times associated with the high-frequency motions which normally determine T_1 are inadequate to describe the substantial but less than maximum observed nuclear Overhauser enhancements.[1,3] For *cis*-polybutadiene, for example, spin-lattice relaxation times for the methine and methylene main-chain carbons are on the order of 0.5 sec, comparable to what is observed for dipolar dominated relaxation in solutions of modest sized molecules.[2] Even allowing for the effect on T_1 of some internal motion, spin-lattice relaxation times this long suggest a considerable amount of overall segmental mobility for *cis*-polybutadiene, which is reasonable since the polymer is on the order of 100° above T_g at room temperature. However, unlike the full Overhauser enhancement of 3.0 expected for such mobile molecular systems,[2,4] the enhancement for polybutadiene is 2.4. This deviation from the theoretical maximum cannot be accounted for by nondipolar relaxation mechanisms since these are known to be absent,[3] or by the presence of some very long correlation times (which may determine T_2), since the Overhauser enhancement depends primarily on T_1-like processes. The deviation appears to require the presence of some motions associated with correlation times which are long compared to those determining T_1, but short compared to those determining T_2.

These results suggest that a description of the ^{13}C nmr relaxation phenomena of polymers in highly viscous systems should be in terms of a broad distribution of correlation times. This is not an unreasonable approach. As pointed out by Connor,[5,6] many studies of polymers and glass-forming materials by dielectric and mechanical loss methods, as well as by nmr techniques, have been interpreted by assuming that the molecular motions involved are best described (at least in some sort of an approximate way) by a distribution of correlation times. In this paper we will present the results of some transient nuclear Overhauser experiments on viscous solutions of polymers and solid elastomers which, together with T_1 and line-width measurements, establish the presence of unusual combinations of ^{13}C relaxation times and Overhauser enhancements. These parameters cannot all be interpreted in terms of the usual theories of nmr relaxation and one or two correlation times. Instead we interpret the data in terms of a broad asymmetric distribution of correlation times. The density function describing the distribution is introduced on an empirical basis, and a rationale or justification is suggested for its use.

Experimental Section

Natural abundance ^{13}C nmr spectra were obtained at 22.6 MHz by Fourier transform techniques using a Bruker spectrometer, some details of which have been described before.[1,3] Measurements were performed on three materials, an isotactic polystyrene (Monsanto Co., Springfield, Mass.), *cis*-polyisoprene (Grade A natural rubber), and *cis*-polybutadiene (Ameripol CB 220, B. F. Goodrich Chemical Co., Cleveland, Ohio). All of these materials are high polymers. Spin-lattice relaxation times were measured from partially relaxed Fourier transform spectra obtained from 180-*t*-90 sequences. Nuclear Overhauser enhancements were measured both by comparisons of coupled and decoupled spectra and by a transient technique.[7] In the transient technique the ^{1}H decoupling frequency was gated, and a 90° pulse sampled the ^{13}C magnetization as a function of a variable delay from the time at which the decoupler was turned either on or off. The ^{13}C magnetization was then manipulated in one of two ways. First, the entire free induction decay was accumulated, Fourier transformed, and integrated in the usual way. Second, that part of the free induction decay arising from all but one kind of carbon was removed by an appropriately tight low-pass filter. The resulting analog signal controlled a gated voltage variable oscillator whose square-wave output was accumulated by the time-averaging computer operating in the pulse-count mode. Each address in

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(1) J. Schaefer and D. F. S. Natusch, *Macromolecules*, **5**, 416 (1972).

(2) A. Allerhand, D. Doddrell, and R. Komoroski, *J. Chem. Phys.*, **55**, 189 (1971).

(3) J. Schaefer, *Macromolecules*, **5**, 427 (1972).

(4) D. Doddrell, V. Glushko, and A. Allerhand, *J. Chem. Phys.*, **56**, 3683 (1972).

(5) T. M. Connor, *Trans. Faraday Soc.*, **60**, 1574 (1964).

(6) T. M. Connor in "NMR, Basic Principles and Processes," P. Diehl, E. Fluck, and R. Kosfeld, Ed., Vol. 4, Springer-Verlag, New York, N. Y., 1971.

(7) K. F. Kuhlman, D. M. Grant, and R. K. Harris, *J. Chem. Phys.*, **52**, 3439 (1970).

Table I
Proton-Decoupled, ($\gamma H_2/2\pi$ = 2 kHz) ^{13}C T_1, T_2 and NOEF Values for Three Polymers at 22.6 MHz and 35°

Polymer	State	Carbon	$T_1{}^a$ (msec)	$T_2{}^b$ (msec)	NOEF^c
Isotactic polystyrene	*o*-Dichlorobenzene solution	Methine	65	26	0.8
		Methylene	35	13	0.8
cis-Polyisoprene	Solid	Methine	95	29	1.2
		Methylene	52	18	1.2
cis-Polybutadiene	Solid	Methine	600	48	1.4
		Methylene	400	33	1.4

^{a} Accuracy is ±10%. ^{b} Accuracy is ±10%; $T_2 = (\pi \times \text{line width})^{-1}$. ^{c} Accuracy is ±0.1.

the computer was associated with a different time delay in the transient Overhauser experiment so that a visual display of the approach to equilibrium of the ^{13}C magnetization of a single carbon was obtained. The Fourier transform and integration steps were thereby avoided. The spin–spin relaxation time, T_2, was measured directly from the line width. Relatively small deviations of line shape from Lorentzian behavior were ignored.

Theoretical Description of the Transient Nuclear Overhauser Experiments[8,9]

Denoting the ^{13}C spin by I and the ^{1}H spin by S, we have for an isolated two-spin system

$$\frac{d\langle I_z\rangle}{dt} = -\frac{1}{T_1{}^{II}}(\langle I_z\rangle - I_0) - \frac{1}{T_1{}^{IS}}(\langle S_z\rangle - S_0) \quad (1a)$$

$$\frac{d\langle S_z\rangle}{dt} = -\frac{1}{T_1{}^{SI}}(\langle I_z\rangle - I_0) - \frac{1}{T_1{}^{SS}}(\langle S_z\rangle - S_0) \quad (1b)$$

where the z subscript indicates the magnetization in the longitudinal or z direction; $T_1{}^{II}$ is the ^{13}C spin–lattice relaxation time, $T_1{}^{SS}$ the ^{1}H spin–lattice relaxation time, and $T_1{}^{IS}$ (which equals $T_1{}^{SI}$) the ^{13}C—^{1}H cross-relaxation time; I_0 and S_0 are the respective ^{13}C and ^{1}H magnetizations in the absence of any coupling. The solution to the above coupled equations for the ^{13}C spin immediately after *removal* of a saturating decoupling field from the ^{1}H spin is

$$\langle I_z(t)\rangle = I_0 + c_1e^{-\lambda_1 t} + c_2e^{-\lambda_2 t} \quad (2)$$

where

$$\lambda_{1,2} = \frac{1}{2}\{(R_1{}^{II} + R_1{}^{SS}) \pm [(R_1{}^{II} - R_1{}^{SS})^2 + 4R_1{}^{IS}R_1{}^{IS}]^{1/2}\} \quad (3)$$

$$R_1{}^{ij} = (T_1{}^{ij})^{-1} \quad (4)$$

and

$$c_1 = \frac{R_1{}^{IS}}{R_1{}^{II}}\frac{\lambda_2}{(\lambda_2 - \lambda_1)}S_0 \quad (5a)$$

$$c_2 = \frac{R^{IS}}{R^{II}}\frac{\lambda_1}{(\lambda_1 - \lambda_2)}S_0 \quad (5b)$$

The initial conditions are described by

$$S_z(0) = 0 \quad (6)$$

$$I_z(0) = I_0 + R_1{}^{IS}S_0/R_1{}^{II} \quad (7a)$$

$$= I_0 + \gamma_S\rho I_0/\gamma_I \quad (7b)$$

$$= (1 + 3.976\rho)I_0 \quad (7c)$$

The term in parentheses in eq 7c is called the nuclear Overhauser enhancement. The parameter ρ describes the nature and effectiveness of the dynamic coupling between the ^{13}C and ^{1}H spins.[1] For the polymer systems to be considered here, this coupling is exclusively dipolar; ρ varies from almost zero to a maximum of 0.5. (The variation of ρ from one kind of polymer to another is discussed in detail elsewhere.[1]) Since the ^{13}C magnetization $\langle I_z(t)\rangle$ depends on a sum of exponentials, the experimental data (as a semilog plot of $[\langle I_z(t)\rangle - I_0]/I_0$ *vs.* time) behave as a two-exponential decay curve and depend on $T_1{}^{II}$, $T_1{}^{SS}$, and $T_1{}^{IS}$. The intercept at $t = 0$ is 3.976ρ, the nuclear Overhauser enhancement factor (NOEF).

The solution to the coupled eq 1 describing the ^{13}C magnetization in the *presence* of a decoupling field at the ^{1}H spins is

$$\langle I_z(t)\rangle = I_0 + 3.976\rho I_0(1 - e^{-t/T_1{}^{II}}) \quad (8)$$

with the initial conditions

$$\langle I_z(0)\rangle = I_0 \quad (9)$$

$$\langle S_z(t)\rangle = S_z(0) = 0 \quad (10)$$

Thus, a semilog plot of $[\langle I_z(\infty)\rangle - \langle I_z(t)\rangle]/I_0$ *vs.* time is a straight line whose slope is the ^{13}C spin–lattice relaxation time and whose intercept is the NOEF.

Experimental Results

The line widths, ($\pi T_2{}^{-1}$), and spin–lattice relaxation times for the main-chain carbons of a 5% *o*-dichlorobenzene solution of isotactic polystyrene, and of solid *cis*-polyisoprene and *cis*-polybutadiene are presented in Table I. These values were obtained from normal and partially relaxed Fourier transform spectra at 35°. The T_1/T_2 ratio is as large as 15 even though all three polymer systems are well to the high-temperature side of the T_1 minimum.[10] Nuclear Overhauser enhancements for these polymers are also reported in Table I. Overhauser enhancements measured by comparisons of integrated intensities of coupled and decoupled spectra, and by transient techniques were in agreement, within experimental error. To demonstrate this agreement, the results of the normal transient NOE experiments are illustrated for the methine and methylene main-chain carbons of *cis*-polybutadiene in Figures 1 and 2, respectively. The solid circles show the experimental data. The solid lines are not fitted to those data points, but were independently calculated using eq 2 and 8, the ^{13}C spin–lattice relaxation times of Table I, observed NOEF's from the steady-state experiments, and the literature estimate for the ^{1}H spin–lattice relaxation time at 90 MHz and 35°, 300 msec.[10] The agreement between the observed and calculated values is well within experimental error. The observed NOEF is 1.4 ± 0.1, for both methine and methylene carbons. Using the untransformed transient Overhauser magnetization data alone, the enhancement factor for both carbons is 1.50, with an error of 0.10. The Overhauser enhancements for the main-chain

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(8) A. Abragam, "Principles of Nuclear Magnetism," Oxford University Press, London, 1961, p 295.

(9) J. H. Noggle and R. E. Schirmer, "The Nuclear Overhauser Effect," Academic Press, New York, N. Y., 1971, pp 113-118.

(10) W. P. Slichter and D. D. Davis, *J. Appl. Phys.*, **35**, 3103 (1964).

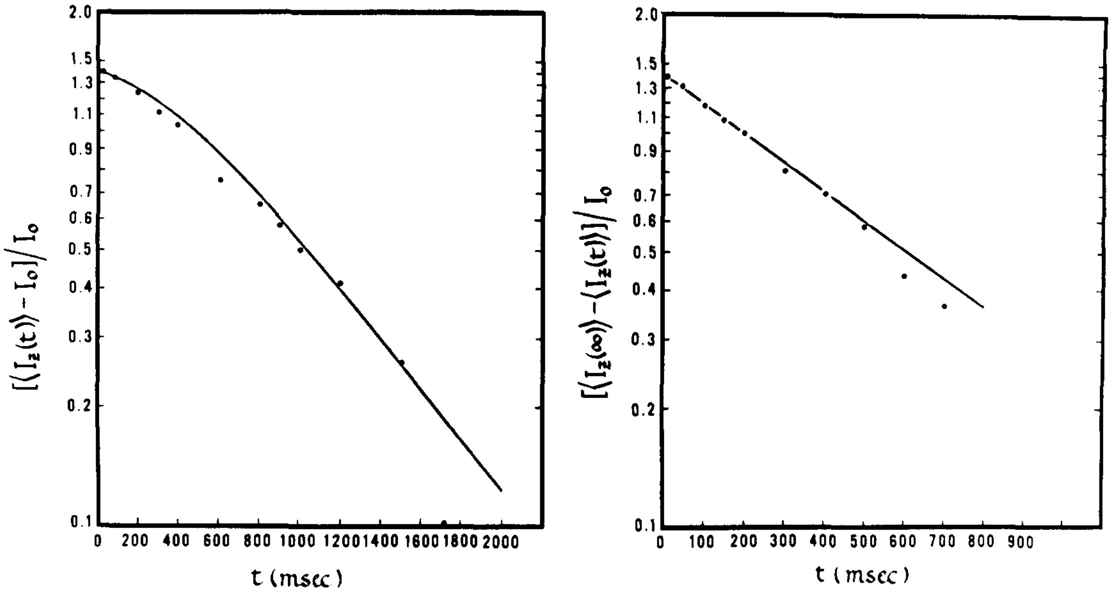

Figure 1. Results of transient nuclear Overhauser enhancement experiments for the methine carbon of solid *cis*-polybutadiene at 22.6 MHz and 35°. The plot on the left is for intensity measurements made in the absence of decoupling, and that on the right in the presence of decoupling. Circles show experimental points, and solid curves the theoretical dependence.

carbons of *cis*-polybutadiene are therefore less than the theoretical maximum at 35°, even though the spin-lattice relaxation times are on the order of 0.5 sec. At 0°, the methylene carbon T_1 is reduced from 400 to 130 msec, and the NOEF is reduced from 1.4 to 1.1.

Carbon-13 Relaxation Parameters in Terms of a Distribution of Correlation Times

Assuming only dipolar interactions between a methine carbon and its directly bonded, completely spin-spin-decoupled proton, the ^{13}C spin-lattice relaxation time (for simplicity denoted hereafter as T_1 without the C-13 superscripts), spin-spin relaxation time (T_2), and nuclear Overhauser enhancement factor (NOEF) are given by[1,2]

$$\frac{1}{T_1} = 2.190 \times 10^9\{f(\omega_1) + 3f(\omega_2) + 6f(\omega_3)\}\text{sec}^{-1} \quad (11)$$

$$\frac{1}{T_2} = 1.095 \times 10^9\{4g + f(\omega_1) + 3f(\omega_2) + 6f(\omega_3) + 6f(\omega_4)\}\text{sec}^{-1} \quad (12)$$

$$\text{NOEF} = 3.976\left\{\frac{-f(\omega_1) + 6f(\omega_3)}{f(\omega_1) + 3f(\omega_2) + 6f(\omega_3)}\right\} \quad (13)$$

where for ^{13}C measurements at 22.6 MHz, $\omega_1 = 4.232 \times 10^8$ rad sec^{-1}, $\omega_2 = 1.422 \times 10^8$ rad sec^{-1}, $\omega_3 = 7.077 \times 10^8$ rad sec^{-1}, $\omega_4 = 5.655 \times 10^8$ rad sec^{-1}. The quantity in braces in eq 13 is ρ of eq 7c. Nuclear Overhauser enhancements are sometimes quoted as the NOE, which is 1 + NOEF. Assuming the applicability of a model involving a single correlation time, τ, to describe isotropic rotation, and of the Bloembergen, Purcell, and Pound theory of nuclear magnetic relaxation[11]

$$f(\omega_i) = \tau/(1 + \omega_i^2\tau^2) \quad (14)$$

$$g = \tau \quad (15)$$

Molecular motions in viscous polymer solutions or in solid elastomers are probably anisotropic, and hence not well described by eq 14-15. For example, one kind of likely segmental motion is oscillatory, involving changes within a conformation, rather than genuine rotational changes from one conformation to another.[12] Using this kind of a motional model results in an expression for $f(\omega_i)$ which is altered by a scaling factor (less than one) related to the geometrical assumptions of the oscillatory motion,[13] and an expression for g which now has a contribution from a static (or low-frequency) dipolar interaction. If the relaxation behavior of viscous polymers were to be described by only a single correlation time, this kind of a model, while inadequate to explain the data of Table I,[14] is still clearly to be preferred to a simple isotropic rotor.

However, it may be unrealistic to try to describe the segmental motion of long chains in terms of just one or two correlation times. While we may view the motion of any given monomer unit in the chain as inherently simple,[15] complications arise because of the many possible cooperative interactions between units. Furthermore, because of variations in the through-space distances involved, the correlation times associated with these cooperative interactions may occur on different time scales.

This situation seems to suggest that a description of the ^{13}C nmr relaxation phenomena in viscous polymeric systems should be in terms of a broad distribution of correlation times. In terms of a distribution of correlation times for isotropic reorientations, the f function of eq 14 becomes

$$f(\omega_i) = \int_0^\infty \frac{G(\tau_l)\tau_l \mathrm{d}\tau_l}{1 + \omega_i^2\tau_l^2} \quad (16)$$

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(11) N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, 73, 679 (1948).

(12) Y. K. Levine, P. Partington, G. C. K. Roberts, N. J. M. Birdsall, A. G. Lee, and J. C. Metcalfe, *FEBS (Fed. Eur. Biochem. Soc.) Lett.*, 23, 203 (1972).

(13) K. van Putte, *J. Magn. Resonance*, 2, 23 (1970).

(14) Since the NOEF is a ratio of $f(\omega_i)$'s the geometrical scaling factor drops out. Thus the NOEF determines the single correlation time. Since the NOEF's of polyisoprene and polybutadiene are just about the same, they must have about the same segmental oscillatory correlation time. However, the geometrical factor must be smaller for polybutadiene to explain its much larger T_1. This would predict a much smaller T_2 because of the increased static dipolar interaction. This is not observed.

(15) The actual motion of a unit segment of the polymer is, in fact, not simple, in the sense that the autocorrelation function of the motion involves a nonexponential time dependence. As discussed by Connor,[6] it is not normally possible to distinguish mathematically between the results of an assumption of simple motion but the presence of a distribution of correlation times, and a mechanism for molecular motion which is described by a nonexponential autocorrelation function.

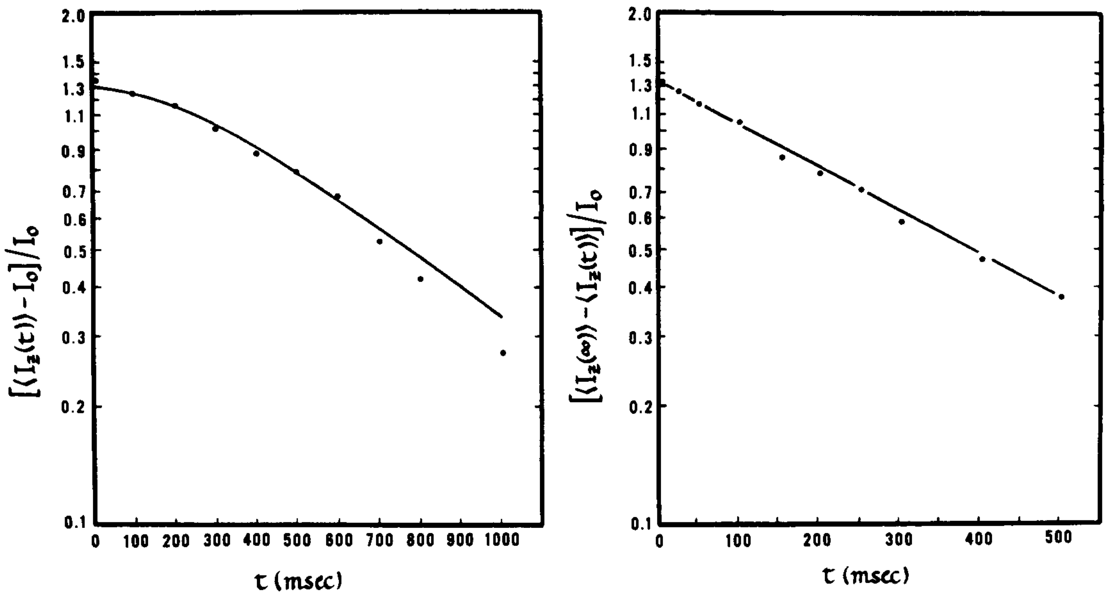

Figure 2. Results similar to those of Figure 1, but for the methylene carbon of solid *cis*-polybutadiene.

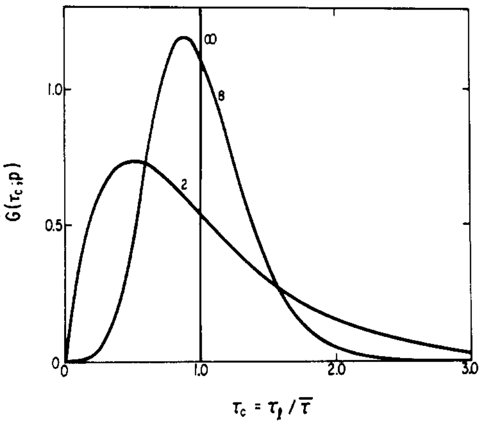

Figure 3. A chi-square distribution of correlation times for three values of the width parameter, *p*.

or, in terms of a reduced correlation time

$$f(\omega_i) = \int_0^{\infty} \frac{G(\tau_c)(\bar{\tau}\tau_c)\mathrm{d}\tau_c}{1 + \omega_i^2(\bar{\tau}\tau_c)^2} \tag{17}$$

where

$$\tau_c = \tau_l/\bar{\tau} \tag{18}$$

and

$$\int_0^{\infty} G(\tau_c)\mathrm{d}\tau_c = 1 \tag{19}$$

The choice of the density function, $G(\tau_c)$, remains. Physical variables in complicated systems are frequently assumed to be normally distributed. In fact, normal distributions have been used to describe multiple correlation times in viscous media of various kinds.[5] For polymers, however, it seems reasonable to suppose that, seemingly unlikely, long-range, cooperative motions do occur. Thus, a density function based on a normal distribution, in effect, discriminates against these kinds of cooperative motions, many of which necessarily have long correlation times. Thus, we suspect that $G(\tau_c)$ must be a distribution which, while not altogether dissimilar from a normal distribution, is asymmetric, having greater density for very large correlation times than for very small ones. A versatile distribution which fits this description is the chi-square distribution given by

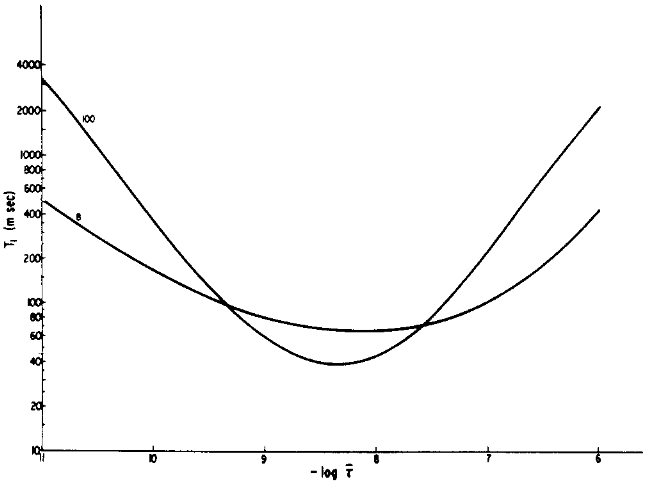

Figure 4. Plots of the calculated spin-decoupled methine carbon spin-lattice relaxation time (at 22.6 MHz) for two values of the width parameter, *p*, of a log–χ^2 distribution of correlation times (b = 1000).

$$\tilde{G}(\tau_c;\, p)\mathrm{d}\tau_c = \frac{1}{\Gamma(p)}(p\tau_c)^{p-1}e^{-p\tau_c}p\mathrm{d}\tau_c \tag{20}$$

where the tilde indicates that this is a trial density function, and not necessarily the function to be used in eq 17. The Γ function, $\Gamma(p)$, normalizes $\tilde{G}(\tau_c;p)$ to unity. The distribution is defined by its width and mean. The width of the distribution is characterized by p. The larger p becomes, the narrower the distribution, eventually approaching a δ function for very large p (Figure 3). The literature on statistics refers to p as a measure of the number of degrees of freedom, and this terminology is also used in physical discussions.[16]

The origin of this terminology arises from the fact that the sum of two or more chi-square distributions is also a chi-square distribution, but of higher order; that is, having a larger p. As applied to a polymer chain, if half of the motions of a *unit* of the chain are independent of the other

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(16) C. E. Porter and R. G. Thomas, *Phys. Rev.*, 104, 483 (1956).

Table II
Calculated ^{13}C Nmr Parameters (at 22.6 MHz) for Some Main-Chain Methine Carbons^{a-c}

Polymer	State	b	p	r	$-\mathrm{Log}\,\bar{\tau}$	T_1 (msec)	T_2 (msec)	NOEF
Isotactic polystyrene	*o*-Dichlorobenzene solution	1000	18	1.0	9.0	68	27	1.0
		400	14	1.0	9.0	68	26	1.0
		100	9	1.0	9.0	68	26	1.0
		10	4	1.0	8.9	62	33	1.0
cis-Polyisoprene	Solid	1000	14	1.3	9.4	98	32	1.2
		400	11	1.3	9.4	99	31	1.2
		100	7	1.3	9.4	101	30	1.2
		10	3	1.3	9.3	95	37	1.3
cis-Polybutadiene	Solid	1000	9	2.0	11.0	550	42	1.4
		400	7	2.0	11.0	480	34	1.4
		100^d						
		10^d						

[a] Experimental values for comparison are presented in Table I. [b] $\bar{\tau}$, p, b, and r are defined in eq 18, 21, 22, and 27, respectively. Isotactic polystyrene is chosen as the reference polymer for the values of r shown in the table. [c] Calculated methylene carbon T_1 and T_2 values are ½ of the methine carbon values. Calculated NOEF values are the same for both kinds of carbons. [d] A reasonable fit of data was not possible with this choice of base.

half, and if the distribution of correlation times associated with the motions of each half is described by the same chi-square distribution of order p, then a chi-square distribution of order $2p$ describes the overall distribution. Eventually, as all the motions of any unit in the chain become totally independent, a chi-square distribution of extremely high order is required to describe the distribution of correlation times. This description is then indistinguishable from one using a single average correlation time.

Correlation times for motions in polymers can differ by many orders of magnitude. In order that our density function be sufficiently wide to account for this variation (which the trial function of eq 20 *cannot* do), we adopt a logarithmic time scale (of log base b), and assume the functional form of the χ^2 distribution remains applicable on this log scale. Thus

$$F^{(p)}(s)\mathrm{d}s = \frac{1}{\Gamma(p)}(ps)^{p-1}e^{-ps}p\mathrm{d}s \tag{21}$$

$$s = \log_b\,[1 + (b - 1)\tau_l/\bar{\tau}] \tag{22}$$

so that

$$F^{(p)}(s) = [(b - 1)^{-1} + \tau_c]G(\tau_c;p) \tag{23}$$

and

$$\int_0^\infty F^{(p)}(s)\mathrm{d}s = 1 \tag{24}$$

Equation 23 defines the $G(\tau_c;p)$ to be used in eq 17. The effect on $G(\tau_c;p)$ of the choice of a log-χ^2 distribution for $F^{(p)}(s)$ is to produce a highly asymmetric distribution with a pronounced tail in the long-correlation time region. We emphasize that this distribution allows us, at best, to describe the effects of cooperative motions in polymers on nmr relaxation times only in an approximate way. Strictly speaking, distributions of Debye oscillators [such as eq 16] can never *exactly* represent cooperative motion.

Now we can write for eq 17

$$f(\omega_i) = \int_0^\infty \frac{\bar{\tau}F^{(p)}(s)\{\exp_b\ s - 1\}\mathrm{d}s}{\{b - 1\}\{1 + \omega_i^2\bar{\tau}^2[\{\exp_b s - 1\}/(b - 1)]^2\}} \tag{25}$$

and for the g function

$$g = \int_0^\infty \bar{\tau}F^{(p)}(s)\{\exp_b\ s - 1\}\mathrm{d}s \tag{26}$$

With these last two expressions we can numerically calculate T_1, T_2, and the NOEF as a function of p, $\bar{\tau}$, and b.

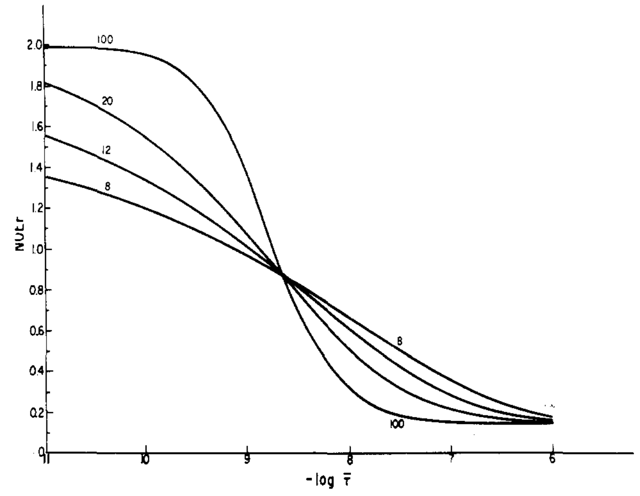

Figure 5. Plots of the calculated nuclear Overhauser enhancement factor (at 22.6 MHz) for four values of the width parameter, p, of a log-χ^2 distribution of correlation times (b = 1000).

Two examples of the T_1 calculation are shown in Figure 4. For a narrow distribution (p = 100, b = 1000) the calculation is essentially identical with the prediction of the Bloembergen-Purcell-Pound theory[11] using a correlation time, $\bar{\tau}$. For a wider distribution (p = 8, b = 1000), the T_1 *vs.* log $\bar{\tau}$ plot is shallower, flatter, and asymmetric. The asymmetry results in a shift of the T_1 minimum of about 0.3 log unit. Examples of the NOEF calculation are shown in Figure 5. For p less than 20 and $\bar{\tau}$ less than 10^{-9} sec, the NOEF is not a strong function of $\bar{\tau}$ and can be substantially less than the 2.0 theoretical maximum. For the most part, these results are due to the width and pronounced asymmetry of the χ^2 distribution.

Actually, only the first two of the three distribution parameters, p, $\bar{\tau}$, and b, need be specified in order to generate distributions to fit the experimental data for several polymers and thereby permit relative comparisons. This is illustrated in Table II where calculated values for the methine carbon T_1, T_2, and NOEF for three polymers are presented. Comparison of these values with the observed values (Table I) indicate a reasonably good fit. In addition, for sufficiently large b, an integral value of p can always be found which produces fits essentially identical with the observed values, even using the same $\bar{\tau}$. Furthermore, and most importantly, the comparison of fitted values of p from one polymer to the next is independent of the choice of base. That is, we can define a ratio

$$r = p(b;\ \text{polymer 1})/p(b;\ \text{polymer 2}) \qquad (27)$$

which is independent of b (Table II). This is not surprising. The choice of a variable log base simply allows the width, and so the shape of $G(\tau_c;\ p)$ to be conveniently adjusted. A commonly used function to describe distributions of correlation times is a log-normal distribution of variable width.[5] A base 10 log scale is adopted, but only by convention. If some other base were adopted, equivalent results could be obtained by choosing a different width parameter. Our purpose in introducing b in the first place and then showing its relative unimportance is to maintain the simplicity of the chi-square distribution with integral values of p, while at the same time having a wide-range control over the width of the total distribution.

Discussion

As shown in Tables I and II, the qualitative (and most of the quantitative) features of the ^{13}C T_1, T_2, and NOEF experimental data for a variety of polymer systems can be fit using a log-χ^2 distribution of correlation times. Furthermore, for each polymer, the fit of three independent data points (at a single temperature) is in terms of only two essential parameters, the average correlation time, $\bar{\tau}$, and the width of the distribution, which is related to p. In the spirit of the analysis of the previous section, the parameter p can be related to the number of degrees of freedom in the distribution of correlation times. Thus, a relative comparison of p values for two polymers can be considered a comparison of the relative extent of cooperative motion in the system. For a polymer whose distribution of motions is characterized by many degrees of freedom, long-range cooperativity is unlikely and p is large. The opposite is true in systems characterized by few degrees of freedom.

By this interpretation, the ratios of p values shown in Table II suggest that long-range cooperative motions are most likely for the flexible polybutadiene relative to either polyisoprene or solutions of polystyrene. This conclusion is a little surprising. It can be argued that since polybutadiene is the most flexible (as measured by $\bar{\tau}$) of the three polymers of Table II, it should be the one whose behavior most closely approaches that of a liquid, in which long-range cooperativity is unlikely. Apparently what must be added to this picture is the competition of another effect. As a rigid chain is made more flexible (for example, by removal of side groups), long-range cooperative motions which would otherwise have been hampered now become possible. Only after considerably more freedom is achieved (for example, by the presence of a solvent) can these long-range cooperative motions finally be eliminated by the incoherent averaging resulting from more complete liquid-like behavior. The apparent cooperativity in the segmental motion of solid *cis*-polybutadiene at 35° is therefore attributed to its flexible main chain, uncluttered by side groups. Naturally, cooperative motions in more rigid chains can also occur, but necessarily at much lower frequency. However, in systems such as solid polyisoprene, these cooperative motions, while most likely present, are apparently not highly probable since the observed absolute value of T_2 and the T_1/T_2 ratio are well described with a relatively narrow distribution containing few long correlation times.

The comparisons of the observed and calculated relaxation parameters for polybutadiene are not quantitatively very satisfying. Actually, the pronounced deviation from 2 of the ratio of the experimental methine and methylene carbon T_1's (Table I) indicates that any kind of quantitative description of segmental motion in polybutadiene very likely must take the pronounced anisotropy of the main-chain motion[17] into account. This was not done in arriving at the calculated values of Table II. Undoubtedly we could get a better fit using distributed anisotropic rotors as a model, and this would probably mean a more realistic value for the average main-chain segmental reorientation correlation time, as well. However, we feel that the present calculations are not qualitatively misleading. Even if the true $\bar{\tau}$ for polybutadiene were an order of magnitude greater than the value indicated in Table II, the polybutadiene main chain is still determined to be the most flexible of those considered. In addition, since its main-chain carbon T_1's are observed to be *comparable* in size to those in small molecules, despite the fact that the Overhauser enhancement is less than the theoretical maximum, a broad distribution of correlation times is justified. Regardless of the details of any reasonable calculation of nmr parameters (even if an anisotropic motional model were employed to account for the difference between methine and methylene carbons), the width of this distribution must be greater for polybutadiene than for the other polymer systems considered, in order to account for its substantially larger T_1/T_2 ratio.

It seems reasonable to suppose that increased freedom can be introduced into these polymer systems by increasing the temperature. This not only will have the effect of increasing $\bar{\tau}$, but also of changing the shape of the distribution by increasing p. We therefore expect that measurements performed on polymer solutions at elevated temperatures would produce qualitatively different behavior from that of Table I. That is, not only should T_1 increase, but the T_1/T_2 ratio should approach unity and the full theoretical NOEF should be observed. In terms of our distribution of correlation times, this occurs since $\bar{\tau}$ becomes small and p becomes large at elevated temperatures.

The shape of the distribution of correlation times describing polymer segmental motion might also be expected to change as a result of chemical cross-linking, or by the physical introduction into solid systems of filler particles, such as carbon blacks. In both cases entanglements prohibit complete motional averaging, thereby resulting in residual dipolar interactions which are associated with long-correlation times.[3] To a first approximation at least, the various slow motions resulting from entanglements can be treated as superpositions of simple isotropic motions with long correlation times. Thus, in terms of our distribution of correlation times for the homogeneous unfilled systems, the filled system can be qualitatively described by the same or similar $\bar{\tau}$, but by a smaller p. This corresponds to increasing the tail in the distribution to represent the increased numbers of reorientational motions associated with long correlation times. Since only the long correlation time or low-frequency end of the distribution is affected, we expect T_2 to be more affected than T_1 or the NOEF. This is observed.[3] Addition of crosslinks and filler to solid polyisoprene above the glass transition temperature has little effect on T_1 or the NOEF, but shortens the methine carbon T_2 by a factor of about 5-10. Thus, typical observed values[3] for T_1, T_2, and the NOEF of methine carbons in carbon-black-filled polyisoprene are 100, 5, and 1.2 msec, respectively. Calculated values using the same $\bar{\tau}$ as for the unfilled polyisoprene (Table II, $b = 1000$), but with a value of p lowered from 14 to 10, are 102, 4, and 1.1 msec, respectively, in reasonable agreement. Of course, this calculation assumes that the methine carbon relaxa-

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(17) For example, see J. E. Mark, *J. Amer. Chem. Soc.*, 88, 3454 (1966).

tion is due exclusively to its directly bonded proton, which is not strictly correct. Nevertheless, the qualitative features of the calculation, and the resulting conclusions are still, we feel, correct.

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Structure–Property Relations of Thermoreversible Macromolecular Hydrogels

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ABSTRACT: Thermoreversible hydrogels of agarose and gelatin have been studied as models for more complex polysaccharide and protein biogels. In addition a study is made of the gelation of poly(vinyl alcohol) (PVA) in ethylene glycol–water mixtures. The structures are characterized by means of optical rotation and low-angle light scattering. The time-dependent and equilibrium mechanical behavior is measured in unilateral compression. Gelatin gels are found to be randomly cross-linked by the formation of "collage-fold like" junction zones. The viscoelastic relaxation and equilibrium stress are both rubberlike, provided junction breakdown and bacterial degradation is eliminated by a suitable extrapolation procedure. Agarose gels are not rubberlike in their mechanical behavior. Their structure consists of a regular array of micron-sized spherical polymer-rich regions probably formed by a nucleation free- (spinodal) phase separation. Hysteresis in the optical rotation indicates the existence of a wide spectrum of junction zones, present in agarose but absent in gelatin gels. The PVA gels are formed *via* an initial liquid–liquid, nucleated phase separation, followed by syneresis caused by the formation of small crystallites in the polymer-rich regions. The findings show that the structural makeup of hydrogels is strongly reflected in their time-dependent and equilibrium mechanical behavior, and that a structural model based on randomly cross-linked Gaussian chains is often times inadequate.

Macromolecular gels that occur in nature are frequently reversible, *i.e.*, the chains are not chemically cross-linked but exhibit certain junction zones, depending on pH, temperature, and electrolyte concentration. It is the purpose of the present article to investigate the relation between the structure and mechanical properties of such hydrogels, by considering three model systems, *viz.*, gelatin, agarose, and poly(vinyl alcohol). In all three systems an aqueous polymer solution is brought to gelation by lowering the temperature. We will show that the resulting gels vary widely in structure and properties.

Gelatin is prepared by partial hydrolytic degradation and disorganization of collagen.[2a] In the native state collagen occurs in organized fibrils of triple helices of collagen molecules, each molecule being about 100,000 in molecular weight.[2b] The molecules are rich in glycine, proline, and hydroxyproline sequences and are twisted together in the triple-helical "collagen fold" in which the individual molecules occur in the poly(L-proline II) (trans) helical conformation, stabilized by interchain hydrogen bonding provided by the glycine, which occurs at every third residue along the chain.

In gelatin solutions (3–20 wt %) above the gelling temperature the single-strand molecules occur in the random-coil conformation and upon cooling, some re-formation of the collagen fold is thought to occur either as double or as triple helices,[2a] giving rise to junction zones. Only at high concentrations (>30 wt %) does X-ray diffraction reveal some crystallinity.

Agarose is a naturally occurring, alternating copolymer of (1→4)-linked 3,6-anhydro-α-L-galactose and (1→3)-linked β-D-galactose. According to Rees[3] the energetically favored conformational agreement is an extended 3_1 double helix. Upon cooling, agarose solutions above about 0.3 wt % in concentration will set into a gel in which chain segments are thought to form double-helical regions in which stabilization is enhanced by interchain hydrogen bonding. Simultaneously aggregation of these double-helical regions takes place into larger domains.[3]

Poly(vinyl alcohol) (PVA) is a water-soluble synthetic macromolecule which forms a thermoreversible gel in mixed solvents, as, for example, water–ethylene glycol. After gelation, the gel exhibits a pronounced exudation of diluent (syneresis) and develops crystallinity.[4–6] Because of the smallness of the hydroxyl group the extended chains fit into a crystal lattice similar to that of polyethylene even when the macromolecules are atactic.[7]

Conformational changes occurring during gelation can be conveniently monitored by measuring the optical rotatory power during the sol ⇄ gel transition, provided, of course, that the macromolecules contain asymmetric carbon atoms. This is the case for gelatin and agarose, but not for PVA. Conformational restraints (whether intra- or intermolecular) caused by the cooling and gelation enhance the intrinsic rotatory power of a molecule. This method thus provides structural information about the

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(1) Based upon part of a thesis submitted by E. P. in partial fulfillment of the requirements for the Ph.D. in Biophysics at Syracuse University, 1972.

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