Study of the Stereochemical Configuration and Chain Conformation of Three Olefin–Sulfur Dioxide Copolymers by 1D and 2D ^{1}H and ^{13}C NMR Spectroscopy

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ABSTRACT: As a contribution toward better understanding of the dynamic behavior of 1:1 olefin–SO_2 copolymers in solution, we present a ^{1}H and ^{13}C NMR study of the polysulfones of butene-1, hexene-1, and decene-1. We show (a) by ^{1}H and ^{13}C NMR that all three polymers are of random tacticity; (b) we show by 2D *J*-resolved proton spectroscopy at 500 MHz that the main-chain vicinal and geminal ^{1}H–^{1}H *J* couplings are independent of side-chain length but exhibit temperature and solvent dependence. The main-chain vicinal proton couplings have not to our knowledge been reported previously. If interpreted in terms of the usual staggered trans and gauche conformers about the carbon–carbon bond, the reported values lead to the conclusion that this bond is preferentially trans, being more so in DMSO than in dioxane. These findings are discussed in relation to dielectric relaxation studies reported by others, which clearly show both high-frequency (10–50 MHz) and low-frequency (10^3–5×10^3) motional modes. The former are in agreement with NMR line widths and T_1 evidence, but the slow motions are not detected in present NMR studies. The substantial magnitude of the low-frequency loss is not clearly understood.

Introduction

Comparison of the behavior of olefin–sulfur dioxide copolymers as observed in solution by dielectric relaxation and by NMR has long presented a challenge. In 1967, Bates, Ivin, and Williams[1] observed a strong low-frequency dielectric dispersion for solutions of 1:1 hexene-1–SO_2 and pentene-1–SO_2 copolymers in benzene, toluene, and dioxane. The dipole correlation time, as judged from the dispersion maximum, moved toward longer values with increasing molecular weight *M*, obeying the relationship $\tau \simeq M[\eta]\eta_0/RT$, where $[\eta]$ is the intrinsic viscosity of the polymer and η_0 is the viscosity of the solvent. This finding implied either that a very large longitudinal dipole exists within each repeat unit or that the overall tumbling of the copolymer molecule as a whole accounts for the dielectric relaxation. The former possibility appearing unlikely, it was therefore concluded that the chains must be dynamically stiff, segmental motion making no appreciable contribution since high-frequency relaxation, which would be expected for such motion, could not be detected. The supposed barriers to internal motion could be attributed to strong interactions of sulfone groups, which have a dipole moment of 4.5 D.

This seemingly consistent picture was rudely shaken by the observation by three independent groups[2-4] that in fact polysulfone chains are not stiff but, as judged from ^{13}C spin-lattice relaxation measurements, enjoy segmental motion corresponding to C–H bond correlation times of at most a few nanoseconds, at least 10^4 times faster than the dielectric relaxation. This motion somehow escaped detection in the dielectric loss spectrum, and at the time it therefore seemed appropriate to propose motional models which permitted rapid C–H bond reorientation without attendant sulfone dipole relaxation.[2,3] Some of these proposals required the C–C bond to remain trans.

Later measurements by Mashimo et al.[5] by resonance circuit and transmission line methods and (particularly) by time-domain reflectometry showed that in fact there is a marked high-frequency loss for poly(olefin sulfones). It is in the 10–20-MHz region, moving toward the lower frequency with increasing side-chain length and decreasing temperature but essentially independent of molecular weight. These observations remove the inconsistency between the dielectric and NMR data so far as high-frequency behavior is concerned, obviating the need for the special motional models, but they leave us with a need to explain the low-frequency dielectric loss. This loss appears to require a substantial dipole component to be projected parallel to the contour of the polymer chain. A similar circumstance exists in poly(propylene oxide),[6,7] but in this case the low-frequency loss peak is very weak compared to that at high frequency—i.e. the reverse of the behavior of the polysulfones—and is sufficiently accounted for by a parallel dipole moment component of 0.18 D, compared to 1.0 D for the perpendicular component. (It may be noted that poly(propylene oxide) chains are exceptionally flexible, as judged by ^{13}C T_1 observations,[8] clearly precluding any arguments based on chain stiffness.) For the polysulfones a very much larger parallel dipole component would have to be postulated, greater than seems reasonable on ordinary grounds. For this reason, special conformational hypotheses have been put forward[5,9-12] (vide infra) to account for the observed loss.

It is important to note that the low-frequency dielectric loss peak does not appear if (a) the hydrocarbon unit is symmetrical, e.g. in copolymers of butene-2 or cyclohexene[13] (here indeed one could hardly argue for a parallel dipole component), or if (b) the sulfone dipoles are on average more widely spaced than in the olefin copolymers. Thus, a 2.3:1 sytrene–SO_2 copolymer[2] exhibits no low-frequency loss peak.[14] It appears that a certain minimum degree of coupling of the sulfone dipoles is necessary to develop an observable parallel component; it is not at present clear why this should be so.

Two groups have independently proposed that the large effective parallel dipole component arises from the existence of helical conformations. Stockmayer, Mansfield, and co-workers[5,11,12] have reached this conclusion from observations on olefin–SO_2 copolymers with side chains having up to 18 carbon atoms, while Fawcett et al.[9,10] have based their hypothesis on the dielectric response of a series of terpolymers of hexene-1 and cyclohexene. These proposals seem to face a difficulty in that such stiff components of the chains are not consistent with the observed ^{13}C T_1 measurements on these polymers.[2-5] Stockmayer et al. attribute the low-frequency loss to helical conformations, which (so it would seem) must last at least a few tenths of a millisecond. In their picture, random coil portions of

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the chain—admittedly in fast conformational exchange—provide the high-frequency loss. Fawcett et al. regard the entire chain as stiff and must therefore look to overall rotation about the axes of the assumed helices as the source of the high-frequency loss. (In connection with this proposal, it is an awkward fact that for poly(hexene-1 sulfone) the high-frequency loss peak is at higher frequency in dioxane than in benzene although dioxane has twice the viscosity of benzene.)

We will not scrutinize these hypotheses further here but instead present relevant new NMR data with regard to the 1:1 polysulfones of butene-1, hexene-1, and decene-1. We show (a) by ^{13}C and ^{1}H NMR that all three polymers are of random tacticity; (b) we show by 2D J-resolved ^{1}H spectroscopy at 500 MHz that the main-chain vicinal and geminal $^{1}H-^{1}H$ J couplings are independent of side-chain length but the former exhibit some dependence on solvent. The main-chain vicinal proton couplings, though very germane to the question of main-chain conformation, have not to our knowledge been reported previously. If interpreted in terms of the usual staggered trans and gauche conformers about the carbon–carbon bond, their observed values lead to the conclusion that this bond is preferentially but not exclusively trans; for poly(butene-1 sulfone) it is more trans in DMSO (high dipole moment) than in dioxane (zero dipole moment).

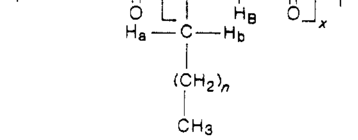
Experimental Section

Materials. The poly(butene-1 sulfone) was kindly provided by Dr. M. J. Bowden. The polymer was prepared at 40 °C by AIBN initiation from a monomer feed mixture containing about 6 mol % butene-1 and $CBrCl_3$ as a chain-transfer agent. The $\bar{M}_w$, $\bar{M}_n$, and polydispersity of the sample were 272 500, 131 200, and 2.1, respectively.[2] The poly(hexene-1 sulfone) was generously supplied by Dr. R. E. Cais. It was prepared by AIBN initiation at 35 °C from a monomer mixture containing 30.8% hexene-1. The molecular weight data for this polymer are as follows: $\bar{M}_w = 1\,719\,000$, $\bar{M}_n = 973\,500$, polydispersity 1.77. The poly(decene-1 sulfone) was kindly furnished by Professor W. H. Stockmayer. This sample has a $\bar{M}_w$ of 4×10^6.

Methods. The NMR data were recorded on a JEOL GX-500 NMR spectrometer. The proton spectra were recorded on samples prepared at a concentration of 2% by weight using TMS as an internal reference. The 2D J-resolved spectra were gathered using f_1 and f_2 frequency ranges of 70 and 2600 Hz, respectively. The original 64×4096 data matrix was zero filled to a 256×4096 matrix. The 2D COSY spectra were recorded using a 256×1024 data matrix, which was zero filled along the t_1 dimension to yield a 1K × 1K matrix. All manipulations of the two-dimensional data were carried out on a Micro Vax-II computer using software designed by D. Hare (Infinity Systems). For measurement of the carbon data samples were prepared at a concentration of 5–15% by weight and HMDS was employed as the internal reference. Between 5000 and 25 000 scans were recorded for each sample.

Results and Discussion

Stereochemical Configuration. In Figure 1 are shown 125-MHz ^{13}C spectra of (a) poly(butene-1 sulfone) in DMSO-d_6 at 60 °C, (b) poly(hexene-1 sulfone) in DMSO-d_6–$CDCl_3$ (2:1) at 60 °C, and (c) poly(decene-1 sulfone) in DMSO-d_6–$CDCl_3$ (2:1) at 60 °C. Carbons and protons are designated as follows:



For these polymers, $n = 0$, 2, and 6. The α-carbon appears at lowest field (ca. 57 ppm), the β-carbon at ca. 48–49 ppm, and the side-chain carbons at higher field. Only the backbone carbons and the first carbon of the side chain are sensitive to the stereochemical configuration of the chain. The narrowest lines and best resolution are observed in DMSO-d_6 and dioxane-d_8, and the broadest lines and poorest resolution, in benzene-d_6 and chloroform-d. We will comment on this observation a little later. For the present we note (as shown in Figure 2) that the β-carbon resonances of all three polymers exhibit four resonances, as expected for the four triad sequences shown in Figure 3. The first side-chain carbon shows only dyad sensitivity although both neighboring asymmetric carbons are four bonds away.

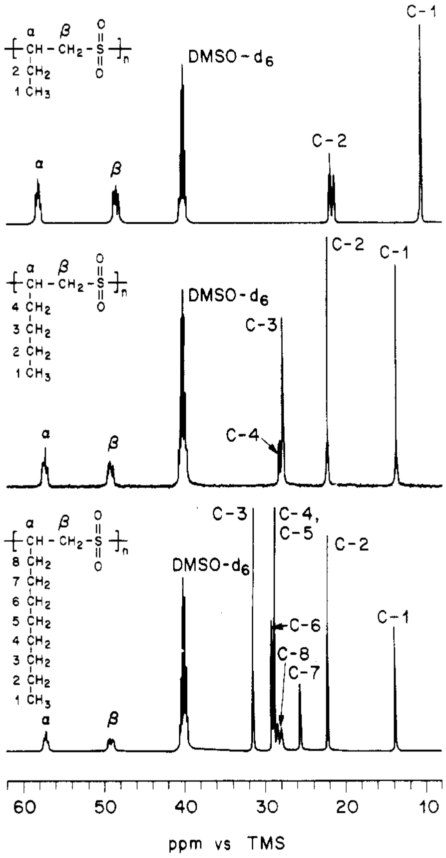


Figure 1. 125-MHz ^{13}C NMR spectra at 60 °C for (a) poly(butene-1 sulfone) in DMSO-d_6; (b) poly(hexene-1 sulfone) in DMSO-d_6–$CDCl_3$ (2:1 by volume); and (c) poly(decene-1 sulfone) in DMSO-d_6–$CDCl_3$ (2:1 by volume).

In Figure 4 is shown the 500-MHz proton spectrum of poly(butene-1 sulfone) in dioxane-d_8 at 60 °C. The assignments are not self-evident, in part because backbone proton chemical shifts are sensitive to solvent so that published data in other solvents are not applicable. To establish assignments with certainty, a 2D COSY spectrum was run at 500 MHz in the phase-sensitive mode employing the same conditions (dioxane-d_8 at 60 °C) as in Figure 4. This is shown in Figure 5. The tie lines between diagonal and off-diagonal resonances show those protons that are correlated through geminal and vicinal couplings. The β-methylene protons are thus found to partially straddle the α-proton resonance, exhibiting a geminal chemical shift differentiation of ca. 0.5 ppm; H_A, the less shielded, appears to reflect dyad sensitivity, half of the H_A resonance apparently being under the H_C resonance. H_B is highly sensitive to stereochemical configuration. The side-chain methylene protons show a geminal differentiation of ca. 0.2 ppm; the more shielded proton, designated H_a, reflects tacticity more markedly than H_b.

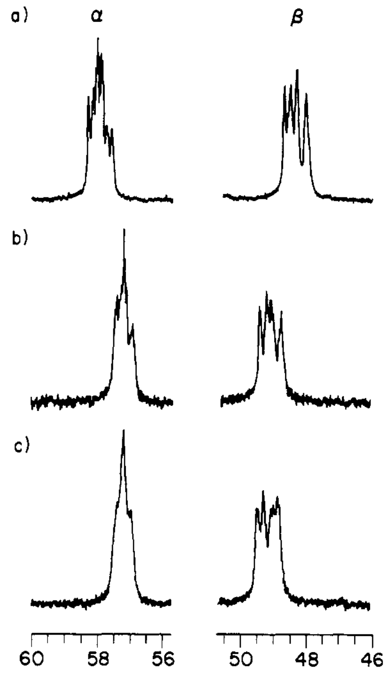
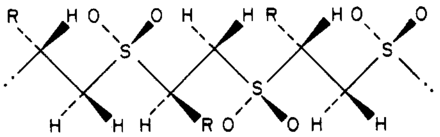
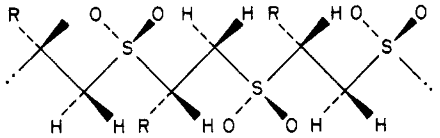


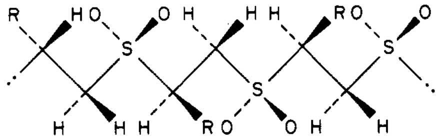
Figure 2. Expansion of backbone carbon resonances of polysulfones from Figure 1.



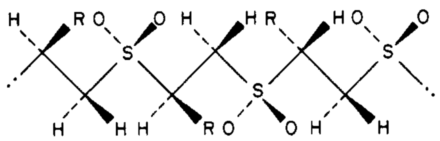
isotactic, RRR or SSS



syndiotactic, RSR or SRS



heterotactic-1 RRS or SSR



heterotactic-2 SRR or RSS

Figure 3. Triad sequences in olefin–SO_2 copolymers.

The results of Ivin and Navrátil[15] employing SO_2 copolymers of *cis*-propene-*1,2*-d_2 prepared at low temperature (−90 °C) clearly show that in the main chain the more shielded methylene proton H_B projects on the same side of the planar zigzag as the R group (here $-CH_2CH_3$) when the chain is all-trans. We assume the same holds for the present polymers.

In order to extract proton *J* couplings and details of chemical shifts, it is necessary to employ 2D *J*-resolved spectroscopy,[16] which permits the separation of these parameters on different axes and achieves a degree of resolution of both far beyond what is attainable in the 1D spectrum. In Figure 6 the downfield portion of the 500-MHz *J*-resolved spectrum of poly(butene-1 sulfone), obtained under the same conditions (dioxane-d_8 solution at 60 °C) as in Figures 4 and 5, is shown; chemical shifts are displayed on the horizontal axis while *J* couplings are plotted on the vertical axis.[17]

As already indicated, the β-proton H_A exhibits tacticity at the dyad level. The H_B resonance is resolved into four triad peaks, each of which is split again into two tetrad resonances, although it is not clear in which direction along

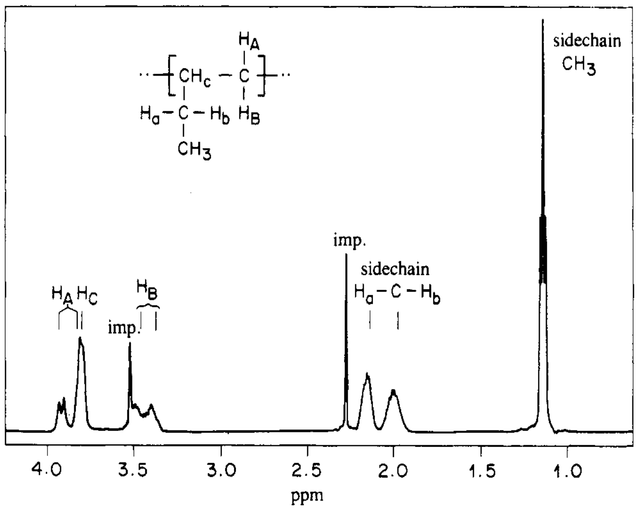


Figure 4. 500-MHz ^1H NMR spectrum of poly(butene-1 sulfone) in dioxane-d_8 at 60 °C.

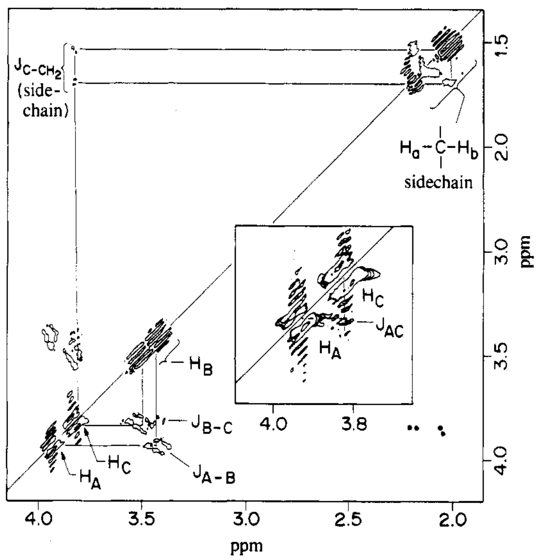


Figure 5. 500-MHz ^1H 2D COSY spectrum of poly(butene-1 sulfone) in dioxane-d_8 at 60 °C. (See text.)

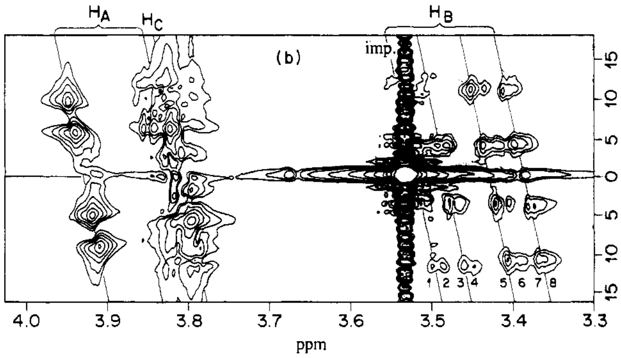


Figure 6. 500-MHz ^1H 2D *J*-resolved spectrum of poly(butene-1 sulfone) in dioxane-d_8 at 60 °C. Only the low-field portion of the spectrum is shown.

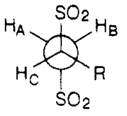
Table I
Main-Chain Proton Couplings in Poly(alkene-1 sulfones)

polymer	solvent	temp, °C	J,[a] Hz gem A–B	A–C	B–C	[t]	[t]/[g]
butene-1 sulfone	dioxane	60	−14.7	4.2	7.4	0.72	2.57
	DMSO	60	−14.8	3.6	8.7	0.84	5.25
	DMSO	80	−14.5	3.7	8.0	0.79	3.76
hexene-1 sulfone	dioxane	60	−14.7	4.5	7.0	0.67	2.03
	$CDCl_3$-DMSO (1:5)	60	−14.7	3.9	7.6	0.75	3.00
decene-1 sulfone	dioxane	60	−15.0	4.7	7.7	0.70	2.33

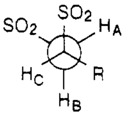
[a] Probable uncertainty ±0.1 Hz.

the chain this further discrimination occurs.[18] It is clear that all sequences have equal probability within experimental error and therefore that the addition of olefin units to the $-CH_2CHR-SO_2^{\bullet}$ radical occurs without steric or tactic bias.[19] The propagation reaction is thus not only Bernoullian but strictly random, a circumstance which generally does *not* prevail in vinyl polymerization. Similar proton study of the hexene-1 and decene-1 copolymers shows that they too are of random stereochemistry, confirming the indications of the ^{13}C spectra.

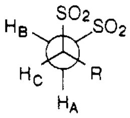
The geminal and vicinal main-chain proton couplings are shown in Table I. The interpretation of the vicinal J values requires some assumptions concerning the nature of the possible conformers present at the C_α–C_β bond. (The NMR data provide no information concerning the torsional states at the carbon–sulfur bonds.) We make the usual assumption that the C_α–C_β bond conformers are staggered (or nearly so) and may be represented as trans, gauche$^+$, and gauche$^-$:



t



g^+



g^-

With two vicinal couplings available, it would appear that we might solve for the proportions of both gauche conformers without any assumption that one of them must be excluded, presumably g$^-$ because of its crowded nature. In fact we cannot do this because we do not have direct knowledge of J_{trans} or J_{gauche}. The coefficients of the Karplus equations vary with structure and are not accurately known for this case. We assume the relationships

$$J_{0-90^\circ} = 8.5 \cos^2 \phi \qquad J_{90-180^\circ} = 9.5 \cos^2 \phi \tag{1}$$

ϕ being the dihedral angle.[20] We also assume that [g$^-$] is in fact ca. zero, justifying these assumptions by the self-consistency of the results. It follows that J_{trans} = 9.5 Hz and J_{gauche} = 2.1 Hz, and it is readily shown that

$$[\mathrm{t}] = \frac{\Delta J + \delta J}{2\Delta J} \tag{2}$$

where $\Delta J = J_{\mathrm{trans}} - J_{\mathrm{gauche}}$ = 7.4 Hz and $\delta J = J_{\mathrm{BC}} - J_{\mathrm{AC}}$. It further follows that if these assumptions are correct, then

$$J_{\mathrm{AC}} + J_{\mathrm{BC}} = J_{\mathrm{trans}} + J_{\mathrm{gauche}} = 11.6 \text{ Hz} \tag{3}$$

which is in fact the case within experimental error. Table I contains the conclusions concerning the C_α – C_β bond, which follow from (2). This bond is strongly trans but is not exclusively so, contrary to the suggestion of Cais and Bovey.[2] This finding seems reasonable on the basis of a simple dipole model of the sulfone group, since such dipoles will perfer to adopt an antiparallel state. (However, Fawcett et al.,[9,10] adopting a more complex tripolar or quadrupolar picture of the sulfone group, suggested that the conformation of minimum energy is gauche, presumably g$^+$. This cannot be consistent with our findings unless we have reversed the identification of H_A and H_B, which does not appear probable in view of the observations of Ivin and Navrâtil.[15]) We further find that the trans preference is independent of the length of the side-chain R, decreases with temperature (to be expected), and is greater in DMSO than in dioxane.

Conclusions

These findings are not in themselves necessarily inconsistent with the general notion of helical conformations in polysulfone chains as proposed by Stockmayer, Mansfield, et al.[11,12] They do appear to contradict the proposals of Fawcett et al.[9,10] so far as these require predominantly gauche conformations at the C_α–C_β bonds. The most serious difficulties that NMR poses for the helical hypothesis still concern the ^{13}C T_1 observations. The NMR line-widths, both for ^1H and ^{13}C, observed in chloroform and benzene, suggest stiffening of the chains in these solvents compared to dioxane and DMSO. However, plots of the temperature dependence of T_1 in these solvents, as reported by Stockmayer et al.,[5] show that chain segmental motion is well on the "fast" side; i.e., $\omega_0\tau_c < 1$ in all of them. There is no consistent differentiation.

The results of dielectric relaxation measurements indicate both kilohertz and megahertz motional modes in polysulfone chains in solution. The high-frequency mode is consistent with NMR relaxation observations; NMR does not probe the low-frequency mode. Thus, there is no inconsistency in the results obtained by these two methods. The problem is, how can helical or other proposed "stiff" structures be composed of segments with conformational lifetimes 10 000 times shorter?

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Registry No. (1-Butene)(SO_2) (copolymer), 25104-10-3; (1-hexene)(SO_2) (copolymer), 34903-07-6; (1-decene)(SO_2) (copolymer), 33990-98-6.

References and Notes

(1) Bates, T. W.; Ivin, K. J.; Williams, G. *Trans. Faraday Soc.* **1967**, *63*, 1964, 1976.
(2) Cais, R. E.; Bovey, F. A. *Macromolecules* **1977**, *10*, 757.
(3) Fawcett, A. H.; Heatley, F.; Ivin, K. J.; Stewart, C. D.; Watt, P. *Macromolecules* **1977**, *10*, 765.
(4) Stockmayer, W. H.; Jones, A. A.; Treadwell, T. L. *Macromolecules* **1977**, *10*, 762.
(5) Mashimo, S.; Winsor, P., IV; Cole, R. H.; Matsuo, K.; Stockmayer, W. H. *Macromolecules* **1986**, *19*, 682.
(6) Baur, M. E.; Stockmayer, W. H. *J. Chem. Phys.* **1965**, *43*, 4319.
(7) Stockmayer, W. H. *Pure Appl. Chem.* **1967**, *15*, 539.
(8) Heatley, F. *Polymer* **1975**, *16*, 493.
(9) Fawcett, A. H.; Fee, S. *Macromolecules* **1982**, *15*, 933.
(10) Cole, R. H.; Winsor, P., IV; Fawcett, A. H.; Fee, S. *Macromolecules* **1987**, *20*, 157.
(11) Matsuo, K.; Mansfield, M. L.; Stockmayer, W. H. *Macromolecules* **1982**, *15*, 935.
(12) Mansfield, M. L. *Macromolecules* **1982**, *15*, 1587.

Macromolecules **1989**, *22*, 3667-3674

(13) Fawcett, A. H.; Ivin, K. J. *Polymer* **1972**, *13*, 439.

(14) Stockmayer, W. H.; Matsuo, K.; Guest, J. A.; Westphal, W. B. *Makromol. Chem.* **1979**, *180*, 281.

(15) Ivin, K. J.; Navrátil, M. *J. Polym. Sci., Polym. Chem. Ed.* **1970**, *8*, 3373.

(16) Kessler, H.; Gehrke, M.; Griesinger, C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 490.

(17) Chemical shifts actually are correctly obtained by extrapolating the diagonal intersections on the midaxis (corresponding to $J = 0$) perpendicularly downward to the lower horizontal axis. J values are given by spacings along the vertical axis, not along the diagonals. In practice, slices (not shown) are generated along the diagonals and J values estimated from their spacings, corrected for slant.

(18) If discrimination occurs in both directions, one will resolve 16 pentad sequences. In general, for chains such as these, having a directional sense and with a single chiral center per monomer unit, the number of tactic sequences observable in principle is 2^{n-1}, where n is the number of monomer units in each tactic sequence, dyad, triad, etc. If equal or comparable discrimination does in fact prevail in both directions, only "odd-ads" will have observational significance no matter what group is being observed.

(19) It has been suggested[12] that the generation of helical conformations may require the existence of substantial syndiotactic sequences, embracing as many as four olefin units. But in a random chain, an *RSRS* (or *SRSR*) sequence has a probability of only $(1/2)^4$ or 0.0625.

(20) (a) Karplus, M. *J. Chem. Phys.* **1959**, *30*, 11; (b) *J. Am. Chem. Soc.* **1963**, *85*, 2870; (c) *J. Chem. Phys.* **1960**, *33*, 1842.

NMR Transverse Relaxation Function Calculated for the Rouse Model

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ABSTRACT: The relaxation of the transverse components of magnetization, due to dipolar interactions between a spin pair on an isolated bond along a polymer chain, has been calculated by using the Rouse model for the chain dynamics. Explicit expressions for the relaxation function are given in terms of a suitably defined NMR time scale Δ, the fastest Rouse relaxation time τ, and the degree of polymerization of the chain N. For times t greater than the longest Rouse mode $\sim \tau N^2$ we show that the relaxation function is given by the real part of an exponential form: $\exp(-\lambda^*(\Delta\tau,N)t)$. The functional dependence of λ^* on $\Delta\tau$ and N shows a variety of different behaviors depending on whether the combinations $\Delta\tau$ and $N\Delta\tau$ are greater or less than 1. For $\Delta\tau \ll 1$, λ^* is real, whereas for $\Delta\tau \gg 1$, λ^* is complex and the relaxation function is modulated by a cosine term. The decay of the relaxation function is determined by the real part of λ^*, which can be identified with the inverse of the spin-spin relaxation time T_2. We show that λ^* increases linearly as τ for $\Delta\tau \ll 1$, reaches a maximum for $\Delta\tau \sim 1$, and decreases as $\tau^{-1/2}$ for $\Delta\tau \gg 1$. The molecular weight dependence of λ^* shows a ln (N) dependence when $\Delta\tau \ll 1$ up to a maximum value $N_{\max} \sim 1/\Delta\tau$ and for $N > N_{\max}$ is independent of molecular weight. The frequently used second moment approximation is shown to be valid only when $\Delta\tau \ll 1$ and $N \ll N_{\max}$. For times $t < \tau N^2$ the relaxation function no longer has a simple exponential form. An algebraic expression is available for $\tau \rightarrow \infty$.

1. Relaxation Function

The simplest theoretical model with which to study the NMR phenomena in polymer molecules consists of two spin-$^1/_2$ nuclei a distance d apart, fixed to a single bond in a chain of identical bonds. Dipolar interactions between this spin pair are considered, while those with spins pairs on other bonds are neglected.[1]

For a single spin in a magnetic field B along the z direction, the transverse components of the magnetization m_x and m_y can be considered as precessing with an angular frequency ω_0 (the Larmour frequency):

$$m_x(t) = m_x \cos(\omega_0 t) \qquad m_y(t) = m_y \sin(\omega_0 t)$$

The combination of transverse components of the magnetization given by

$$m(t) = m_x(t) + i m_y(t)$$

can be described by the oscillator equation

$$\mathrm{d}m(t)/\mathrm{d}t = i\omega_0 m(t) \tag{1.1}$$

The presence of the other spin contributes a dipolar field at the site of the first spin and leads to an additional interaction energy of $\hbar\Delta\omega(\alpha)$, where

$$\Delta\omega(\alpha) = \frac{3\gamma^2\hbar}{4d^3}(3\cos^2\alpha - 1) \tag{1.2}$$

γ is the gyromagnetic ratio, d is the distance apart of the two spins, and α is the angle that this makes with the magnetic field B.

The system can now be regarded as an oscillator with a natural frequency $\omega_0 + \Delta\omega(\alpha)$. For a mobile bond, the angle α is a function of the time $\alpha = \alpha(t)$ and is determined by the dynamics of the main-chain bond. The oscillator equation (1.1) integrates to give

$$m(t) = m(0)\exp(i\omega_0 t)\exp\int_0^t i\Delta\omega(\alpha(t'))\,\mathrm{d}t' \tag{1.3}$$

The dephasing of the transverse components of the magnetization due to the dipole interaction is described by the term

$$\exp\int_0^t i\Delta\omega(\alpha(t'))\,\mathrm{d}t'$$

and the transverse relaxation function $G(t)$ is defined to be[2]

$$G(t) = \left\langle \cos\int_0^t \Delta\omega(\alpha(t'))\,\mathrm{d}t' \right\rangle \tag{1.4}$$

where the averaging is done over all the dynamic configurations of the bond angle $\alpha(t)$.

In this paper we will present an analytical calculation of $G(t)$ for a chain where the dynamical behavior of the bonds is governed by the Rouse model.[3] Since the use of this model is really only applicable to a scaled invariant version of the original polymer chain, we must consider

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