Carbon-13 Nuclear Magnetic Resonance Study of the Microstructure and Molecular Dynamics of Poly(styrene peroxide)

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ABSTRACT: This is the first reported study of a polyperoxide by NMR. Styrene was copolymerized with oxygen at 55 °C, with oxygen pressures of 1 and 0.0197 atm, to yield copolymers with 50 and 55 mol % styrene, respectively. The equimolar copolymer contained an average of 40 styrene and peroxide units. The backbone ^{13}C resonances revealed dyad tacticity, with equal probability of *m* and *r* placements. The styrene-rich copolymer contained 9 mol % ether units, as well as variable-length styrene sequences and peroxide units. The monomer sequence distribution could not be described accurately by first-order Markov statistics (i.e., the Lewis–Mayo copolymerization model) and indicated that the copolymerization involved a penultimate-unit effect in the propagation reactions. The equimolar copolymer had a variety of end-group structures, the most frequent being carbonyl and hydroperoxide. A study of the solution dynamics of this copolymer by ^{13}C NMR showed that an isotropic motional model, with a single effective correlation time for the main chain, satisfactorily fits the data. Three types of motion were considered: overall tumbling of the chain, internal segmental reorientation, and phenyl group rotation. The correlation times for the combined motion of tumbling and segmental reorientation, and for phenyl rotation, were obtained for three temperatures and gave activation energies of 20 and 27 kJ/mol, respectively. A comparison of the dynamic results with those obtained for polystyrene with equivalent molecular weight showed that the polyperoxide is a substantially more flexible polymer.

^{13}C NMR has become a technique of major importance in the quantitative examination of the structure and dynamic behavior of macromolecules, for reasons which have been well documented.[1] The primary NMR parameters related to structure are the chemical shift (δ) and the spin–spin coupling constant (J), whereas dynamic information is obtained from the spin–lattice and spin–spin relaxation times (T_1 and T_2) and the nuclear Overhauser enhancement factor (NOEF), η. Identification and measurement of various structural features, e.g., chain branches,[2] configurational sequences in homopolymers,[3] or monomer sequences in copolymers,[4] have provided detailed insight into mechanisms of chain propagation. Recently, increasing interest has been focused on the use of ^{13}C NMR in studying the dynamic aspects of macromolecules, both from the theoretical and experimental viewpoints.[5–20] These studies complement relaxation measurements made by other techniques, e.g., neutron scattering,[21] electron spin resonance of spin-labeled polymers,[22] fluorescence depolarization,[23] dielectric response,[24] and mechanical[25] and acoustic[26] absorption, and are of fundamental importance in advancing our understanding of structure–property relationships for polymeric materials.

At present, detailed modeling of chain dynamics, as applicable to nuclear relaxation, is still in development.[13,15,16,20,27] Although a simple motional model of isotropic reorientation, characterized by a single effective correlation time, has been found adequate to explain T_1 data obtained for several polymers over a limited range of experimental variables (i.e., temperature, solvent, concentration, and magnetic field strength),[7,9–12] the same model often does not account satisfactorily for either η or T_2. This discrepancy has been attributed to anisotropic chain motion[28] or to a distribution of correlation times.[13,15,20]

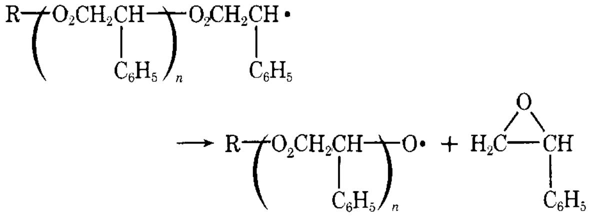
Relatively few studies have appeared to date concerning synthetic polymers of the type $\left(\!\!-\mathrm{CH_2{-}CHR{-}X}-\!\!\right)$, i.e., those incorporating a heteroatom unit X and an asymmetric center in their backbone. These polymers may be formed in various ways, e.g., by the ring-opening polymerizations of substituted oxiranes (X = O), thiiranes (X = S), and aziridines (X = NH), or by the alternating copolymerizations of suitable α-olefins with sulfur dioxide (X = SO_2) or molecular oxygen (X = O_2). The effect of the heteroatom unit on the transmission of configurational information (as detected by NMR) and the chain dynamic behavior, particularly in relation to the hydrocarbon-backbone analogues $\left(\!\!-\mathrm{CH_2{-}CHR}-\!\!\right)$, are the principal features of interest in these systems. Although the structural isomerism in polythiiranes {common name: poly(alkyl ethylene sulfide)s},[29–31] poly(but-2-ene sulfone),[32] poly(methylaziridine) {poly(propyleneimine)},[33] and poly(methyloxirane) {poly(propylene oxide)}[1a] has been examined by ^{13}C NMR, dynamic results have been reported only for poly(methyloxirane)[17,20] and poly(methylthiirane).[34]

In this paper we report the first NMR investigation of poly(styrene peroxide), the first of a series of studies of polymers of the above type with R = $-C_6H_5$. Here, X = O_2; future reports will concern the copolymers in which X = O, S, SO (sulfoxide), and SO_2 (sulfone). There are several reasons for choosing this series. (a) The various heteroatom units can be expected to impart a wide range of flexibilities to the backbone, from the highly mobile polyperoxide to the relatively stiff polysulfone. (b) The carbons of the phenyl group allow us to monitor the reorientation of this group about its C_1–C_4 axis, which will also depend on the steric influence of the heteroatom unit. (c) The chain dynamics of polystyrene has been the subject of several ^{13}C NMR reports in the literature,[7,9,20] and data from the heteroatom analogues may prove useful for comparative studies and tests of current motional models. (d) The attenuation (or enhancement) of the configurational sensitivity of the carbons in the styrene unit by the intervening heteroatom unit is of interest and may provide some rationale for tacticity effects in the ^{13}C spectra of polymers.

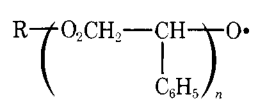
It has been known for some 30 years that styrene will copolymerize with molecular oxygen by a free-radical mechanism. The alternating equimolar copolymer was first prepared and identified by Bovey and Kolthoff.[35] The copolymerization was conducted at 50 °C in aqueous emulsion with potassium persulfate initiator to yield a polyperoxide with a molecular weight of about 5000 (estimated by viscosity measurements). Subsequently, Barnes et al.[36] produced the copolymer by bubbling pure oxygen through bulk styrene at 60 °C; they attributed initiation in the latter stages of the experiment to the thermal homolysis of the polyperoxide.

The kinetics and products of the reaction between styrene and oxygen were examined in detail over a wide range of oxygen pressures by Mayo and co-workers,[37,38] as part of a comprehensive study of the free-radical autoxidation of hydrocarbons.[39] The decomposition pathways of the polyperoxide were also investigated.[40] The composition of the copolymer and the yield of nonpolymeric products (principally benzaldehyde, formaldehyde, and styrene oxide) depended on the oxygen pressure. At atmospheric oxygen pressure or above, the major product was the equimolar copolymer, whereas at low oxygen pressures sequences of two or more styrene units were formed and increased yields of the nonpolymeric products were observed. Formation of styrene oxide was attributed to the rearrangement and scission of a propagating styryl radical with a penultimate oxygen unit (eq 1a). Benzaldehyde and formaldehyde were formed in equal amounts by thermal depolymerization (eq 1b).

Light-scattering measurements[37] indicated that the equimolar copolymer had a molecular weight of 8000. This result implied a number-average value of 4000 (degree of polymerization or DP = 30), since it was demonstrated that termination occurred almost exclusively by chain transfer (a material balance gave 20 chains for every molecule of AIBN which decomposed). The presence of ether units in the copolymers was deduced, especially for those prepared at low oxygen pressures; these were related to the yield of styrene oxide, according to the scheme:



$$R\left(O_2CH_2\underset{C_6H_5}{CH}\right)_n O_2CH_2\underset{C_6H_5}{CH}\cdot \longrightarrow R\left(O_2CH_2\underset{C_6H_5}{CH}\right)_n O\cdot + H_2C\overset{O}{—}\underset{C_6H_5}{CH} \quad (1a)$$



$$R\left(O_2CH_2—\underset{C_6H_5}{CH}\right)_n O\cdot \longrightarrow RO\cdot + nCH_2O + nC_6H_5CO \quad (1b)$$

The depolymerization of alkoxy radicals (eq 1b) was believed to proceed until a styrene unit preceded by another styrene unit or an ether group was exposed; addition of styrene to the stable alkoxy radical (RO·) then forms a new ether unit.[38] However, no quantitatively reliable analytical method was found by which to analyze the proportion of ether and peroxide units in these polymers. Further, infrared evidence pointed to the presence of a hydroxyl and a carbonyl end group in only one in every six and eight chains, respectively, and the remaining end groups could not be identified.[37]

The present work has shed some light on these points by direct analysis of the polymer microstructure by NMR and has also allowed the monomer sequence distribution to be determined, providing insight into the copolymerization mechanism.

Experimental Section

Reagents. Styrene (Eastman, stabilized with *tert*-butylpyrocatechol) was used immediately after fractional distillation at reduced pressure (53.9 °C, 30 Torr) in an argon atmosphere. The oxygen (Air Products) had a specified purity of 99.6%, the principal contaminants being nitrogen and hydrocarbons. Azobisisobutyronitrile (AIBN) was obtained from Polysciences Inc., and purified by recrystallization from methanol followed by drying in vacuo. *tert*-Butyl peroxybenzoate (practical grade, 95%) was obtained from Matheson Coleman and Bell.

Copolymerization. Two copolymers were prepared, which differed in their styrene contents. The first (hereafter designated as the equimolar copolymer) was prepared at 55 °C in a Morton type flask fitted with a high-speed stirrer (Labline STIR-O-VAC), oxygen bubbler, and reflux condenser. AIBN (1.23 mmol, based on styrene) was added after the styrene had been saturated at the reaction temperature with oxygen supplied at atmospheric pressure. The oxygen flow rate was adjusted to be at least fivefold greater than the rate of removal of this monomer by copolymerization. After a reaction time of 20 h, the homogeneous mixture was rapidly transferred to ten times its volume of ice-cold methanol, from which the copolymer precipitated as a tacky gum. This gum was reprecipitated three times from benzene solution into fresh methanol, with all methanol-soluble products being discarded in each case. Volatile products were removed from the copolymer by vacuum drying at ambient temperature for ca. 15 h, and the sample was then stored in the dark at −40 °C.

The second copolymer (hereafter designated as styrene rich) was prepared by a similar procedure, except that a 9 h reaction time was employed with the partial pressure of oxygen adjusted to 0.0197 atm (total pressure atmospheric), and the copolymer was reprecipitated from chloroform solutions. To attain the partial pressure above, the oxygen was diluted with the appropriate amount of nitrogen. The flow rates of the two gases were individually set with needle valves and checked by a soap-bubble flow meter. The gases were mixed in a large flask before entering the reaction vessel.

Characterization. The equimolar copolymer had a weight-average molecular weight of 10 900. This determination was made using a Sofica light-scattering photometer calibrated with benzene. Measurements were made at 24 °C with unpolarized light (546 nm), utilizing butanone as solvent. All solutions were clarified by filtration through a Metricel filter with 0.20 μm nominal pore diameter. The scattering data exhibited no significant depolarization or dissymmetry. A Zimm plot was made for seven concentrations (0.02 to 0.0019 g/ml) each at 11 angles. A value of dn/dc of 0.178 ml/g at 24 °C and 546 nm was obtained using a Brice-Phoenix differential refractometer calibrated with aqueous potassium chloride solutions.

The NMR spectra were recorded in the pulsed Fourier transform mode using a Bruker HX-360 and a modified Varian XL-100 spectrometer.[41] Spin-lattice relaxation times were measured by the standard inversion-recovery (180–τ–90–T) pulse sequence, with T at least five times the longest T_1 of interest. The polymer solutions were not deoxygenated, but the vapor space was flushed with nitrogen. Due to an unknown contribution from unresolved configurational broadening, T_2 values could not be measured from line widths. NOEF values were determined from peak areas obtained first with complete, broad-band proton decoupling and then with the decoupling unit turned off. In the latter case, the probe temperature was increased to compensate for the heating effect of the decoupler. Areas were obtained by cutting and weighing peaks which had been traced onto drawing paper. All chemical shifts are referenced to internal tetramethylsilane (TMS). Copolymer decomposition, which was monitored by the intensity of benzaldehyde resonances, was never a problem during data acquisition over the temperature range studied. Further details pertaining to individual spectra are given in the appropriate figure captions.

Results and Discussion

Copolymer Composition and Microstructure. Carbon-13 Spectra. Figure 1 shows the 25.16 MHz ^{13}C–{^1H} spectrum of the equimolar copolymer (I), the styrene-rich copolymer (II), and, for comparison purposes, the positions of the backbone and quaternary carbon resonances in atactic polystyrene (III). The assignment of methylene, methine, and quaternary carbons was made from the corresponding proton-coupled spectra, obtained at 90.52 MHz in order to minimize multiplet overlap.

(a) Equimolar Copolymer. The assignments are shown in Figure 1, spectrum I. The observed $J_{^{13}C-^1H}$ values were: methylene, 146 Hz; methine, 150 Hz; and ortho, meta, para (phenyl ring carbons 2, 3, and 4), 160 Hz. The couplings of the backbone carbons are considerably larger than those observed in polystyrene, i.e., 120 Hz.[42] We assign the high-field pair of aromatic carbons to ortho, on the basis of the aromatic carbon chemical shifts in the model compound α-methylbenzyl alcohol (ortho, 125.3; meta 128.2; and para, 127.0 ppm).[43] This may be contrasted with the spectrum of polystyrene, in which the para carbon appears at higher field than the ortho and meta carbons.[7]

Only the main-chain α and β carbons in the polyperoxide exhibit resolved fine structure. They give doublets of equal intensity (resolved almost to the baseline at 90.52 MHz), indicating that there are two magnetically nonequivalent environments for these nuclei. These must reflect configurational dyad placements of equal probability.[44] In the copolymer sequence

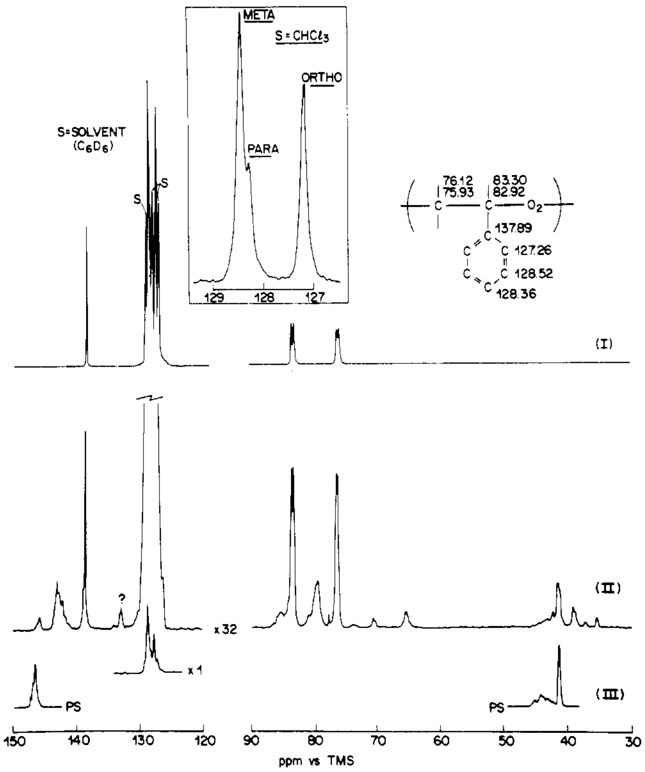
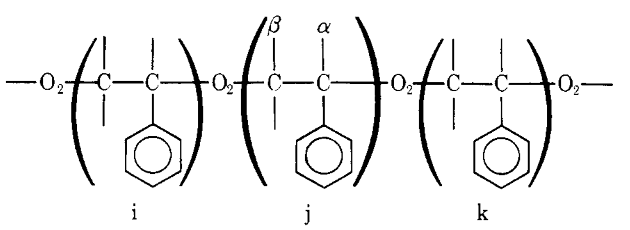


Figure 1. ^{13}C spectra (25.16 MHz) of poly(styrene peroxide)'s in benzene-d_6 observed at 55 °C. Concentration 22% by weight, 18 000 scans, 20 μs pulse width (90° flip angle), 4.0 s pulse delay, pulse positioned 2.78 ppm upfield from TMS, 5000 Hz spectral window, 8K data points (FID), 1.5 Hz digital broadening. Styrene content of copolymers: (I) 50 mol %, (II) 55 mol %. Spectrum of polystyrene (PS) shown in (III). Inset: expanded spectrum of aromatic ortho, meta, and para carbons obtained in chloroform solution to avoid solvent overlap observed with benzene-d_6 solutions.



it is reasonable, from proximity considerations, that the β carbon in the central unit j should be sensitive to the relative configuration of the α carbons in units i and j. It is somewhat less evident which pair of configurational dyads (ij or jk) affects the α-carbon resonance in unit j, for the second asymmetric center is equidistant in either case. This asymmetrical configurational sensitivity clearly reflects the directional properties of the chain. A similar situation has been observed in the ^{13}C spectrum of poly(methylthiirane).[29,45] In the present case, the almost identical configurational sensitivity of the backbone carbons, the aromatic carbons being insensitive, is in contrast to what is observed for polystyrene, where only the quaternary and β carbons show configurational splitting.[46-49]

The equal probability of m and r dyad placements indicates that the configurational propagation statistics for the equimolar polyperoxide follow the "ideal" Bernoullian case, i.e., $p(m) = p(r) = 0.5$, where $p(m)$ and $p(r)$ are the unconditional probabilities for the formation of meso and racemic dyads, respectively.[50] All known free-radical vinyl homopolymerizations exhibit biassed Bernoullian statistics, with $p(r) > p(m)$.[50] In the present system, the increased spacing of the asymmetric centers, introduced by the peroxide unit, removes any such bias, which is normally steric in origin.

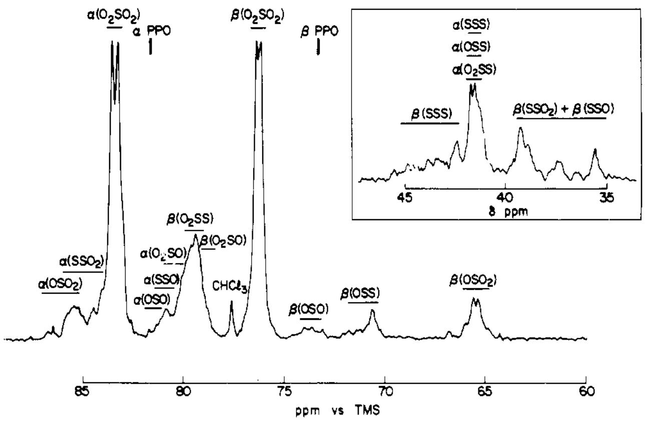


Figure 2. Backbone ^{13}C resonances of the styrene-rich polyperoxide at 25.16 MHz. Instrumental parameters as indicated in the caption to Figure 1. PPO = poly(phenyloxirane); S = styrene unit in the directional sense $-CH_2-CH(C_6H_5)-$; O_2 = peroxide unit, O = ether unit. Polymer observed as 22 wt % solution in benzene-d_6 at 55 °C, 18 000 scans.

(b) Styrene-Rich Copolymer. The ^{13}C spectrum of the styrene-rich copolymer (Figure 1, spectrum II) exhibits quaternary-, α- and β-carbon resonances which are identical in chemical shift to those observed for the equimolar copolymer, and which can be assigned therefore to alternating sequences of styrene (S) and peroxide (O_2) units. Since these resonances are the most intense, this polyperoxide does not deviate very widely from an equimolar composition. Small peaks for the quaternary and backbone carbons are also observed, with chemical shifts almost identical with those in polystyrene (Figure 1, spectrum III). These resonances must arise from sequences of styrene units long enough to contain carbon nuclei removed from the perturbing influence of the peroxide units.[51] However, there are backbone resonances (e.g., the β carbons at 65.59 and 70.69 ppm) which, because of their chemical shifts, cannot arise from any possible sequence of styrene and peroxide units. We attribute these to the presence of *ether* units (O),[52] using the ^{13}C spectrum of poly(phenyloxirane) {poly(styrene oxide)} as a model.[42] The styrene-rich polyperoxide can be regarded therefore as a terpolymer, consisting of styrene sequences and peroxide and ether units.[53]

The assignments of the backbone resonances to the various possible monomer sequences in the styrene-rich polyperoxide are shown in detail in Figure 2. After identifying the carbon *type* (i.e., methylene, methine, or quaternary) from the ^{1}H-coupled spectrum, we must assign the multiple resonances for each carbon.[44] There are too many peaks for a simple dyad analysis, and too few for tetrad effects. The spectral multiplicity therefore requires an interpretation in terms of monomer triad sequences.[54] By reference to the ^{13}C spectra for the equimolar copolymer, poly(phenyloxirane), and polystyrene, as discussed above, the resonances of carbons in O_2SO_2, OSO, and SSS sequences, respectively, can be unambiguously identified.

There then remains the problem of assigning resonances to the six distinct unsymmetrical sequences, i.e., O_2SS, OSS, O_2SO, and their reverse (the directional sense of S is always defined here as $C_\beta \rightarrow C_\alpha$), for which we did not have any suitable model compounds. It is reasonable, however, to assign the low-field group of resonances (65 to 85 ppm) to backbone carbons directly bonded to oxygen, i.e., α carbons in triad sequences derived from SO_2 and SO dyads and β carbons in triads derived from O_2S and OS dyads. Similarly, the back-

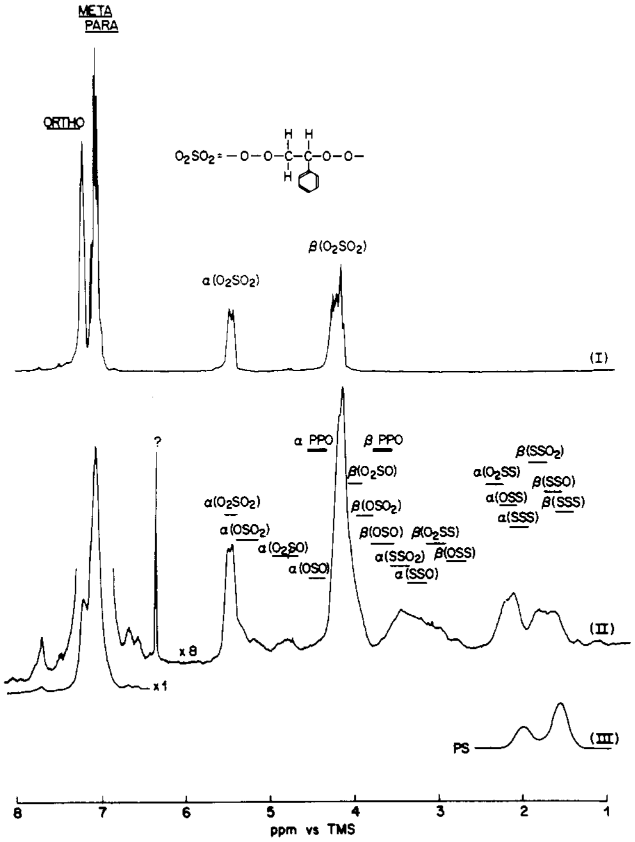


Figure 3. ^{1}H spectra (360 MHz) of poly(styrene peroxide)'s in benzene-d_6 (ca. 10% w/v) observed at 45 °C. FT mode, 100 scans, 13 μs pulse width (90° flip angle), 4348 Hz spectral window, 32K data points (FID). Styrene content of polymers: (I) 50 mol %, (II) 55 mol %. Backbone protons of polystyrene shown in III. PPO = poly(phenyloxirane).

bone carbons responsible for the high-field group of resonances (35 and 45 ppm) must be in triad sequences derived from SS dyads. Further, by comparison of the chemical shifts of the backbone carbons in the equimolar polyperoxide and poly(phenyloxirane), it is evident that the peroxide unit has a stronger deshielding effect on a directly bonded carbon than the ether unit. Another consideration in making the assignments was the effect on a carbon chemical shift of a γ substituent (i.e., that removed by three bonds). A γ oxygen was assumed to impart a larger shielding than a γ carbon, as is known for linear alcohols.[55] As a final aid in arriving at the assignments, two relations between peak areas were observed: (i) the area of an α-carbon resonance in any specified sequence must be identical with the area of the β-carbon resonance from the same sequence, and (ii) areas of carbon peaks in the unsymmetrical triad sequences OSS and O_2SS must be equal to the peak areas of their reverse sequences SSO and SSO_2.[56,57]

The quaternary carbon resonances (Figure 1, spectrum II) also show triad monomer sequence splittings, for which we make the assignments: O_2SO_2, O_2SO, and OSO_2 centered at 138.4 ppm, O_2SS, SSO_2, OSS, and SSO at 142.9 ppm, and SSS at 145.6 ppm.[58] A sharp peak at 77.6 ppm is assigned to residual chloroform, from which this polyperoxide was reprecipitated, on the basis of its chemical shift and the doublet splitting in the ^{1}H-coupled spectrum, with J = 209 Hz. The only peak we are unable to assign convincingly occurs at 132.6 ppm. This peak was also a doublet (J = 169 Hz) in the ^{1}H-coupled spectrum, and so corresponds to a C–H carbon. The complete ^{13}C spectrum of the styrene-rich polyperoxide shows that the sensitivity of carbons to their environment is in the increasing order $C_{2,3,4} < C_1 \simeq C_\alpha < C_\beta$.

Proton Spectra. Figure 3 shows the 360 MHz ^{1}H spectrum of the equimolar copolymer (I), the styrene-rich polymer (II), and, for comparison, the backbone protons in atactic polystyrene (III).

(a) Equimolar Copolymer. The backbone protons do not show a simple ABX spin-system pattern, as might be expected from isolated styrene units, because of the effect of random configurational dyad placements, discussed above. This dyad tacticity gives rise to ca. 0.08 ppm splitting of the resonances in the ^{1}H spectrum, which (at 360 MHz) is larger than the maximum possible vicinal coupling constant of ca. 10 Hz. Even at 60 MHz, the α-proton resonance is a broad, poorly resolved quartet, which does not allow the measurement of the vicinal coupling constants.

(b) Styrene-Rich Polyperoxide. The ^{1}H spectrum of this polymer (Figure 3, spectrum II) shows backbone proton resonances arising from structural features other than the regular alternation of styrene and peroxide units. These we attribute to ether units and sequences of several styrene units. We arrive at the assignments shown for the backbone region by employing a rationale similar to that used in interpreting the corresponding ^{13}C spectrum.

Copolymerization Statistics. In the following statistical analysis of the monomer sequence distributions we make the implicit assumption that the chains are of sufficient length so that end effects are negligible,[59] i.e., the principle of statistical stationarity is valid.[60] Following the treatments by Ito and Yamashita[57] and Pyun,[61] we denote the following.

The *unconditional* probability of occurrence of a sequence of n units, X^n, is $p(X^n)$. Since the polyperoxides contain three distinguishable chain units (S, O_2, and O), there are three ways to select a single unit (sequence with n = 1) at random. Thus,

$$p(S) + p(O_2) + p(O) = 1 \tag{2}$$

Further, for any sequence X^n,

$$p(X^nS) + p(X^nO_2) + p(X^nO) = p(X^n) \tag{3}$$

and

$$p(SX^n) + p(O_2X^n) + p(OX^n) = p(X^n) \tag{4}$$

We denote the *conditional* probability that a randomly selected chain unit be an A, under the constraint that the preceding sequence is X^n, by $P(X^n,A)$, where A can be any specified chain unit (i.e., S, O_2, or O). Thus,

$$P(X^n,S) + P(X^n,O_2) + P(X^n,O) = 1 \tag{5}$$

and

$$p(X^nA) = p(X^n)\cdot P(X^n,A) \tag{6}$$

Given a first-order Markovian description of the copolymerization (Lewis-Mayo model),[62]

$$P(X^n,A) = P(X^1,A) \tag{7}$$

where X^1 is the single unit preceding A; whereas for a second-order Markovian description, the conditional probabilities depend on the identities of the two preceding chain units:

$$P(X^n,A) = P(X^2,A) \tag{8}$$

The normalized unconditional probabilities of occurrence of all possible monomer triad sequences (excluding any sequences derived from successive placements of O_2 or O units[53]) were obtained by measurements of peak areas in both ^{13}C and ^{1}H spectra. These values are listed in Table I for the styrene-rich polyperoxide. The agreement between both sets of data is good, although the ^{1}H data could not be analyzed fully without using the relation $p(O_2SS)/p(OSS)$ = 2.17 from

Table I
Unconditional Probabilities of Occurrence of Triad Monomer Sequences in the Styrene-Rich Polyperoxide, Determined by Peak Areas from ^{13}C and ^{1}H Spectra, Given the Assignments in Figures 2 and 3 (Spectrum II), Respectively

	Unconditional probabilities	
Monomer triad sequence	^{13}C spectrum	^{1}H spectrum
SSS	0.027	0.028
O_2SS	0.056	0.057
OSS	0.026	0.026
SSO_2	0.056	0.057
SSO	0.026	0.026
O_2SO_2	0.251	0.236
O_2SO	0.047	0.054
OSO_2	0.047	0.054
OSO	0.017	0.018
SO_2S[a]	0.355	0.347
SOS[a]	0.091	0.098

[a] Not observable by ^{13}C or ^{1}H NMR. However, $p(SO_2S) = p(SO_2) = p(SSO_2) + p(OSO_2) + p(O_2SO_2)$, and similarly for $p(SOS)$, utilizing eq 3 and 4.

the ^{13}C data, due to the considerable degree of peak overlap in the ^{1}H spectrum. For this reason, the ^{13}C data are felt to be more reliable.[63]

From eq 2, 3, and 4, the macroscopic chain composition is then given by:

$$p(O_2) = p(O_2S) = p(SO_2S) = 0.355 \tag{9}$$

$$p(O) = p(OS) = p(SOS) = 0.091 \tag{10}$$

$$p(S) = 1 - \{p(O) + p(O_2)\} = 0.554 \tag{11}$$

Thus the molar styrene content of the styrene-rich polyperoxide is $100p(S)\%$, i.e., 55%, and the ratio R of styrene units to total oxygen units (i.e., peroxide and ether) is 1.24. This figure agrees well with Mayo's value, based on analytical results, of 1.18 for a polyperoxide prepared at 15 Torr of oxygen pressure.[38] Our data also show that the ratio of peroxide to ether units, $p(O_2)/p(O)$, is 3.91; i.e., ether units comprise only 20% of the total oxygen units (as peroxide and ether). This value is substantially lower than Mayo's figure of ca. 50% for a comparable polyperoxide, although this result was not considered reliable due to the uncertainty in chemical analysis of the polyperoxide.[38]

The copolymerization model we adopt is the penultimate (second-order Markov) case, as proposed by Mayo.[38] The unconditional dyad probabilities and second-order conditional probabilities appropriate to this case are derived from the unconditional triad probabilities in Table I by application of eq 5, 6, and 8. The values are shown in Table II; the conditional probabilities correspond to the state-transition probabilities discussed by Price for the penultimate copolymerization model.[64] It is evident that a simple, first-order Markov description of the polymerization is inaccurate, since the values of the state-transition probabilities depend on the identity of the terminal *and* penultimate chain units. This does not necessarily mean that the penultimate description is correct, however, since we do not have the tetrad monomer sequence data which would provide the quantitative test of this model.

Table II
Values for the Unconditional and Conditional Probabilities Appropriate to a Second-Order Markov Description of the Monomer Sequence Distribution in the Styrene-Rich Polyperoxide

Unconditional dyad probabilities		Conditional, second-order, state-transition probabilities	
$p(SO)$	0.091	$P(SO,S)$	1.0
		$P(SO,O)$	0.0
		$P(SO,O_2)$	0.0
$p(SO_2)$	0.355	$P(SO_2,S)$	1.0
		$P(SO_2,O)$	0.0
		$P(SO_2,O_2)$	0.0
$p(SS)$	0.109	$P(SS,S)$	0.245
		$P(SS,O)$	0.238
		$P(SS,O_2)$	0.517
$p(OS)$	0.091	$P(OS,S)$	0.287
		$P(OS,O)$	0.192
		$P(OS,O_2)$	0.521
$p(O_2S)$	0.355	$P(O_2S,S)$	0.159
		$P(O_2S,O)$	0.133
		$P(O_2S,O_2)$	0.708

Table III
Propagation Steps and Reactivity Ratios for the Description of the Copolymerization of Styrene with Oxygen by a Penultimate-Effect Model

Propagating chain radical	Monomer added	Rate constant	Reactivity ratio
$\sim SS\cdot$	S	k_{SSS}	$r_{SS} = k_{SSS}/k_{SSO_2}$
$\sim SS\cdot$	O_2	k_{SSO_2}	
$\sim OS\cdot$	S	k_{OSS}	$r_{OS} = k_{OSS}/k_{OSO_2}$
$\sim OS\cdot$	O_2	k_{OSO_2}	
$\sim O_2S\cdot$	S	k_{O_2SS}	$r_{O_2S} = k_{O_2SS}/k_{O_2SO_2}$
$\sim O_2S\cdot$	O_2	$k_{O_2SO_2}$	

Nevertheless, employing the penultimate model, we can derive the appropriate reactivity ratios, assuming that every ether unit in the polyperoxide originated from a peroxide unit in the penultimate position to a propagating styryl radical, as shown by eq 1. Thus we can equate the net conditional probability of addition of oxygen to a specified chain terminal dyad (X^2) as $\bar{P}(X^2,O_2)$, with:

$$\bar{P}(X^2,O_2) = P(X^2,O) + P(X^2,O_2) \tag{12}$$

Once the ether unit is built into the chain, however, three propagating styryl radicals must be distinguished with this model: $\sim SS\cdot$, $\sim OS\cdot$, and $\sim O_2S\cdot$. There are therefore six propagation steps with three nonzero reactivity ratios to be considered; these are defined in Table III. The conditional state-transition probabilities (Table II) are related to the monomer-feed composition and the reactivity ratios by Bayes's rule.[64,65] From this, and Mayo's data for the solubility of oxygen in styrene[66] (16×10^{-4} mol % at 15 Torr), we derive the following reactivity ratios:

$$r_{SS} = 5.2 \times 10^{-6}, r_{OS} = 6.4 \times 10^{-6}, \text{and } r_{O_2S} = 3.0 \times 10^{-6}$$

These results, based on the assumption of a penultimate model, indicate similar relative reactivities for $\sim SS\cdot$ and $\sim OS\cdot$ toward monomer but show that by comparison $\sim O_2S\cdot$ has an enhanced tendency to add oxygen or a reduced tendency to add styrene. This is contrary to Mayo's result, in which $\sim O_2S\cdot$ was believed to have an enhanced tendency to add styrene, compared to $\sim SS\cdot$. The reported reactivity ratios were $r_{SS} = 4.4 \times 10^{-8}$ and $r_{O_2S} = 1.8 \times 10^{-6}$, although in this treatment only two propagating styryl radicals were distinguished, $\sim SS\cdot$ and $\sim O_2S\cdot$.[38]

However, an examination of the equimolar copolymer (next section) shows that the penultimate model, with the reactivity ratios derived in this work, does not accurately predict the observed monomer sequence distribution. The predicted triad-sequence unconditional probabilities, with the oxygen

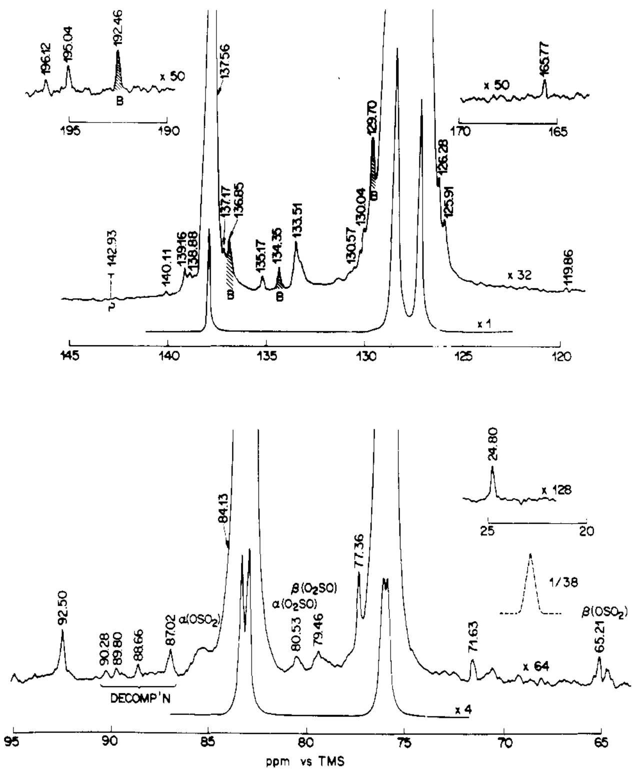


Figure 4. ^{13}C spectrum (25.16 MHz) of the equimolar polyperoxide in methylene-d_2 chloride observed at 33 °C. Concentration 44% by weight, 30 000 scans, 20 μs pulse width (90° flip angle), 3.0 s pulse delay, 5000 Hz spectral window, 8K data points (FID), 1.5 Hz digital broadening. Pulse positioned 150 Hz upfield from TMS. Carbonyl region observed under the same conditions, except pulse position moved downfield by 1000 Hz. B = benzaldehyde resonances; P = peak intensity for O_2SS and SSO_2 quaternary resonance predicted by penultimate model with reactivity ratios derived from the styrene-rich polyperoxide spectrum.

concentration at atmospheric pressure being 802×10^{-4} mol %,[38,66] are: SSS, 12×10^{-6}; $SSO_2 = O_2SS$, 19×10^{-4}; O_2SO_2, 0.497; and SO_2S, 0.499 (this calculation ignores ether units). The calculated chain composition is $p(S) = 0.501$, i.e., $p(O_2) = 0.499$ and $R = 1.004$. Although this macroscopic composition is experimentally indistinguishable from the one observed, we find that the predicted proportion of SSO_2 plus O_2SS sequences (i.e., one pair for every 130 O_2SO_2 sequences) is larger than the measured value (cf. predicted peak intensity for the quaternary carbon resonance at 142.93 ppm as shown in Figure 4). This finding is supported by an analysis of the ^1H spectrum of the equimolar copolymer (discussed in the following section).

The above discrepancy, if indeed significant, given the experimental error in determining such small reactivity ratios, may be due to effects during chain propagation other than those from penultimate units, such as the participation of molecular-association complexes. Litt and co-workers have considered the quantitative application of a complex-participation model to copolymer composition data and have shown that this model often provides a better treatment than the penultimate-effect model.[67,68] In the present instance, however, we do not have sufficient data (specifically that relating to the equilibrium constant for complex formation) for a quantitative test of this model. Styrene is known to form an association complex with oxygen,[69] although its concentration would be very low under the present copolymerization conditions.

Chain Irregularities and End Groups in the Equimolar Copolymer. For the remainder of this paper we will be concerned with the equimolar copolymer. In this section we consider the content and structure of irregular chain units and sequences and of end groups; in the final section the solution dynamics of this polyperoxide is discussed.

A variety of weak resonances (typically less than 1% of the backbone intensity) were observed in the ^{13}C and ^1H spectra of the equimolar copolymer. Most of these resonances appeared as shoulders on the intense backbone and aromatic peaks in the ^1H spectrum; the ^{13}C spectrum proved superior for observing and assigning minor structural features due to the much greater dispersion of chemical shifts. The 25.16 MHz ^{13}C spectrum of a methylene chloride solution of a freshly prepared equimolar polyperoxide is shown on an expanded scale in Figure 4. These peaks were all that were detected in the range 0 to 210 ppm.[70]

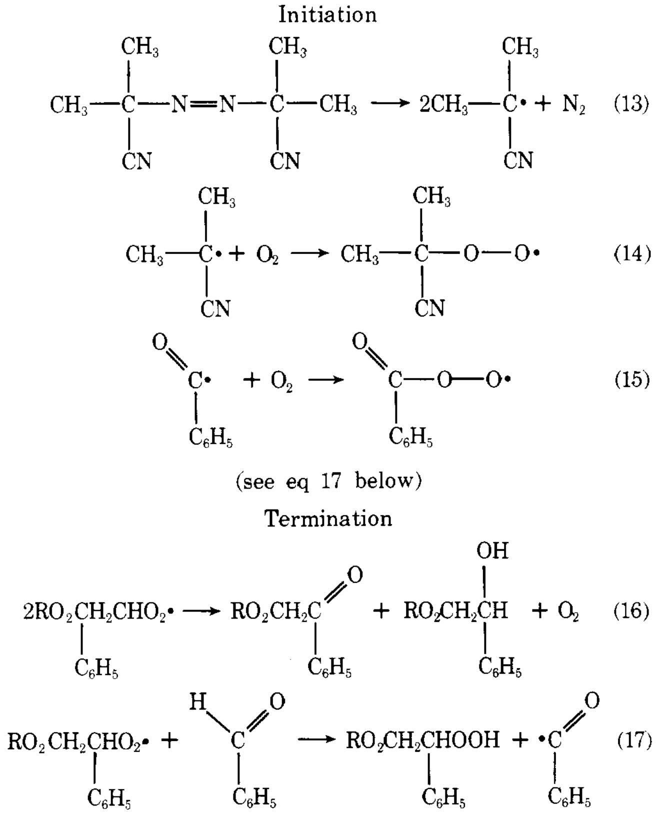
To identify more clearly products resulting from thermal depolymerization and from rearrangement of labile groups, a spectrum (not shown) was recorded (at 90.52 MHz) for a benzene solution of the polyperoxide which had been maintained at 65 °C for 4 h. Only two sets of resonances were noticeably affected, those for benzaldehyde (shaded in Figure 4) and those from 87.02 to 90.28 ppm; the relative intensities of these peaks increased after the thermal treatment. The benzaldehyde peaks were assigned by recording the spectrum of a polyperoxide solution to which ca. 2% benzaldehyde had been added. The intensities of the benzaldehyde resonances in Figure 4 show that the extent of depolymerization attained during data accumulation for this spectrum is small.

(a) Irregularities. In this class of structures we include ether units, which are observed as indicated in Figure 4 for the backbone region. No sequences derived from SS dyads (i.e., SSS, SSO_2, etc.) were detected at the signal-to-noise level of this spectrum, although these were observed in the ^1H spectrum at an approximate frequency of one for every 750 styrene units (cf. the level of one in 130 predicted by the penultimate model discussed above). Since ether units, and especially SS dyads, are so infrequent in the equimolar polyperoxide, SSO, OSS, and OSO sequences will be present only in vanishingly small amounts. Consequently, ether units will be observed only in OSO_2 and O_2SO sequences. They occur with frequencies of one for every 75 (from ^{13}C results) to 100 (from ^1H results) styrene units, i.e., about one in every two chains. This is much less than the value of one for every six styrene units in the styrene-rich polyperoxide and confirms the observation made by Mayo[38] of the inverse relationship between the ether content of the polyperoxide and the oxygen pressure at which it was prepared.[71] For the purpose of the dynamic study (Section 4), the content of irregular structures in the equimolar copolymer can be ignored.

(b) End Groups. We cannot make definitive assignments for all observable end-group resonances, since this would have required the prohibitively time consuming preparation and study of a large variety of model compounds. Nevertheless, the data allow us to establish the major initiation and termination steps. All weak resonances other than those due to benzaldehyde (192.46, 136.85, 134.35, and 129.70 ppm) ether units (65.21, 79.46, 80.53, and 85.26 ppm) and some unassigned decomposition products (90.28 to 87.02 ppm) are attributed to end groups.[59]

We make two assumptions. (i) No termination takes place by the bimolecular combination of two growing chains; and (ii) the lifetime of a peroxy radical greatly exceeds that for a styryl radical, so that only the former need be considered for the termination reactions. These assumptions have received justification in the literature.[37,38] If every chain were initiated by the same radical and terminated by a single step, we would expect to observe only two distinct end groups, each at the level of one in 38 backbone units.[72] The predicted intensity is shown in Figure 4 (on the scale appropriate to the backbone resonances). The number and intensity of weak resonances

Scheme I



Initiation

$$CH_3-\underset{CN}{\overset{CH_3}{C}}-N=N-\underset{CN}{\overset{CH_3}{C}}-CH_3 \longrightarrow 2CH_3-\underset{CN}{\overset{CH_3}{C}}\cdot + N_2 \tag{13}$$

$$CH_3-\underset{CN}{\overset{CH_3}{C}}\cdot + O_2 \longrightarrow CH_3-\underset{CN}{\overset{CH_3}{C}}-O-O\cdot \tag{14}$$

$$\underset{C_6H_5}{\overset{O}{C}}\cdot + O_2 \longrightarrow \underset{C_6H_5}{\overset{O}{C}}-O-O\cdot \tag{15}$$

(see eq 17 below)

Termination

$$2RO_2CH_2\underset{C_6H_5}{CHO_2}\cdot \longrightarrow RO_2CH_2\underset{C_6H_5}{C}{=}O + RO_2CH_2\underset{C_6H_5}{\overset{OH}{CH}} + O_2 \tag{16}$$

$$RO_2CH_2\underset{C_6H_5}{CHO_2}\cdot + H\underset{C_6H_5}{C}{=}O \longrightarrow RO_2CH_2\underset{C_6H_5}{CHOOH} + \cdot\underset{C_6H_5}{C}{=}O \tag{17}$$

demonstrate that there must be more than two types of end groups. Those which we have assigned are compatible with Scheme I.

In the initial stages of the copolymerization, the primary initiating radical must originate from the decomposition of AIBN (eq 13). The evidence for an AIBN fragment in the polyperoxide is the methyl resonance (24.80 ppm) and a probable nitrile resonance (119.86 ppm). Further, it appears that this primary initiating species is rapidly scavenged by oxygen (eq 14), for if it were to add styrene, a methylene carbon resonance would be observed at approximately 45 ppm, which is not the case. We have examined *tert*-butyl peroxybenzoate (5% in benzene-d_6 at 33 °C) as a suitable model, for which we observe: methyl carbons, 26.2 ppm, and the aliphatic quaternary carbon, 83.5 ppm (the latter is probably obscured by the backbone α carbon in the polyperoxide). The intensity of the methyl resonance (Figure 4) indicated one AIBN fragment in 16 chains, so eq 14 cannot represent the predominant initiation process.

The peak at 165.77 ppm provides good evidence for a peroxybenzoate end-group carbonyl resonance (for *tert*-butyl peroxybenzoate we observe: carbonyl, 164.1; C_1, 129.6; C_2 and C_3, 128.8 and 129.2 {or vice versa}; and C_4, 133.3 ppm). Equation 15 therefore represents a likely initiation step; the intensity of this carbonyl resonance (observed with a 20 s pulse interval) corresponds to one such group in three chains.

A probable termination step involves the Russell mechanism,[73] shown in eq 16. The evidence for this step is provided by one or the other of the carbonyl resonances at 196.12 and 195.04 ppm and the probable benzyl alcohol CH resonance at 71.63 ppm (cf. butyrophenone: carbonyl, 199.8; and α,α-dimethybenzyl alcohol, α-hydroxy carbon at 72.2 ppm; ref 43, compounds 373 and 354, respectively). A consideration of intensities shows that approximately one in seven chains has the benzyl alcohol end group but that nearly every chain has a benzoyl end group (either in phenylketo or peroxybenzoate structures). The latter conclusion is substantiated by the intensity of the resonance at 133.51 ppm, which can be assigned to the para carbon in benzoyl residues. Steps 15 and 16 account for only about half of these, so there must be other steps responsible for the remainder.

The final step for which we have good evidence is shown in eq 17, i.e., hydrogen-atom transfer from benzaldehyde, generated in situ during the reaction, to a peroxy radical. The peak at 77.36 ppm is reasonably assigned to the hydroperoxide group so formed (the methylene carbon would be expected at slightly lower field from the backbone β carbons, due to the lack of a shielding γ substituent); the intensity shows that half of the termination steps occur this way. Formaldehyde may also participate in a similar step. The only major end-group resonance we cannot assign satisfactorily is observed at 92.50 ppm and corresponds to one such carbon in every two chains. Carbons bearing two α-oxygen substituents have similar chemical shifts (cf. *sym*-trioxane, 93.5 ppm[42]). The presence of a methylene unit flanked by two peroxide units seemed unlikely;[71] structures with appropriate chemical shifts may involve epoxide or dioxetane rings following a peroxide unit, but these do not seem mechanistically plausible.

An infrared spectrum of the equimolar polyperoxide qualitatively supports the scheme outlined in eq 13 to 17. We observe hydroxyl and hydroperoxide (3530 and 3450 cm^{-1}, respectively), nitrile (2215 cm^{-1}), and three different carbonyl (1727, 1708, and 1690 cm^{-1}) characteristic frequencies.

The major conclusions we are able to draw are:

(i) Chain transfer to benzaldehyde, and possibly formaldehyde, terminates about one-half of the chains and regulates the degree of polymerization.

(ii) Initiation by addition of an AIBN fragment is not very frequent; the major initiation steps involve radical fragments generated by the transfer steps.

(iii) Every chain has a carbonyl end group of some type.

(iv) Half of the other end groups are hydroperoxide, with AIBN fragments and hydroxyl accounting for only 20% of the remainder. The balance is due to some unassigned structure with a carbon resonance at 92.50 ppm.

Solution Dynamics of the Equimolar Copolymer. General Features of Polymer Dynamics from ^{13}C Relaxation Measurements. The spin–lattice relaxation time of a ^{13}C nucleus arising from dipole–dipole interaction with bonded protons is given by

$$\frac{1}{NT_1} = \frac{1}{10}\cdot\frac{\gamma_H{}^2\gamma_C{}^2\hbar^2}{r_{C-H}{}^6}\cdot\chi(\tau_c) \tag{18}$$

where

$$\chi(\tau_c) = \frac{\tau_c}{1 + (\omega_H - \omega_C)^2\tau_c{}^2} + \frac{3\tau_c}{1 + \omega_C{}^2\tau_c{}^2} + \frac{6\tau_c}{1 + (\omega_H + \omega_C)^2\tau_c{}^2} \tag{19}$$

Here, τ_c is the single correlation time expressing an exponential decay of the motional autocorrelation function and prescribing the frequency spectrum of the motion concerned; γ_C and γ_H are the magnetogyric ratios for ^{13}C and ^{1}H, respectively; r_{C-H} is the C–H bond length (taken here as 1.10 Å); and N is the number of directly bonded protons. The NOEF of the carbon signal upon irradiation of the protons is given by:

$$\eta = \frac{1}{\chi(\tau_c)}\cdot\frac{\gamma_H}{\gamma_C}\left(\frac{6\tau_c}{1 + (\omega_H + \omega_C)^2\tau_c{}^2} - \frac{\tau_c}{1 + (\omega_H - \omega_C)^2\tau_c{}^2}\right) \tag{20}$$

In the "extreme-narrowing limit", when $\omega_C\tau_c \ll 1$, eq 18 and 20 simplify to give:[74,75]

$$\frac{1}{NT_1} = \frac{\gamma_H{}^2\gamma_C{}^2\hbar^2}{r_{C-H}{}^6}\cdot\tau_c = 2.03 \times 10^{10}\cdot\tau_c \tag{21}$$

Table IV
NOE Values for Equimolar Poly(styrene peroxide) in Benzene-d_6 Solution at 45 °C and 23.5 kG

Concn, wt %	NOE ± 10% (1 + η)		
	C_α	C_β	C_1
15	2.94	2.81	2.92
60	2.48	2.48	2.11

and

$$\eta = \frac{1}{2} \cdot \frac{\gamma_H}{\gamma_C} = 1.988 \qquad (22)$$

For small molecules, with tumbling times of the order of picoseconds, eq 21 is obeyed for dipole–dipole interactions, but other mechanisms of relaxation, principally spin rotation and chemical shift anisotropy, may contribute substantially.[76] For polymers, the position is rather different, owing to their relatively slow motions and rapid nuclear relaxation. For carbons with a directly bonded proton or protons, only the dipole interactions with these protons need be considered; even for quaternary and carbonyl carbons, dipole–dipole interactions with nearest-neighbor protons are normally dominant. In this respect, interpretation is simpler. On the other hand, eq 21 does not generally describe the relaxation, for the correlation time may well approach or exceed the reciprocal of the observing frequency. If this is the case, eq 22 will also fail and η will approach a minimum value of only 0.15. In this case, the more general eq 18 and 20 must be used (see ref 77, Figures 5.1 and 5.2, for particularly convenient plots of these equations).

Previous observations have established several other features of spin–lattice relaxation in polymer solutions: (a) For molecular weights above about 10 000 (typically 100 monomer units), T_1 is independent of molecular weight, local segmental motion being dominant; at lower molecular weights, T_1 increases as overall tumbling is manifested.[7,17] (b) T_1 is independent of polymer concentration up to about 10% but then begins to decrease owing to chain entanglement, provided τ_c^{-1} still exceeds the observing frequency.[17] (c) Side chains may have an additional degree of motional freedom by rotation. This rotation may be more rapid than the segmental motion of the main chain, in which case NT_1 will be longer for side chain carbons, as in polypropylene and poly(methyloxirane),[10,17] or, as observed for the phenyl groups of polystyrene, rotation may be so impeded by steric hindrance that the side chain and main chain carbon relaxation rates are comparable.[7] (d) The motion of the polymer chain may not be adequately described by a single correlation time. At sufficiently high temperatures, all polymer systems so far studied approach the limiting conditions described by eq 21 and 22, and this deficiency in the model is not evident. But as the temperature is lowered and T_1 approaches its minimum, it is found[1,20] that eq 18 and 20 do not yield concordant values of τ_c and that at its minimum T_1 is longer than the prescribed value (ca. 0.038 s for C–H in a 23.5 kG field; longer at higher fields). Heatley[20] has shown that all motional models in which a distribution of correlation times is proposed can be made to conform to experimental T_1 and η observations with suitable parameters for the distribution function.

Chain Dynamics of Polystyrene Peroxide. In Table IV are shown the nuclear Overhauser enhancements (η + 1) for 15 and 60% (w/w) solutions of the equimolar polyperoxide in benzene-d_6 at 45 °C. It is evident that in the more dilute solution the extreme narrowing condition for which eq 22 applies is fulfilled but that in the more concentrated solution chain entanglement retards segmental motion sufficiently so that this is not the case. It is noteworthy that even the quaternary carbon C_1 shows a full enhancement in the more dilute solution, indicating the strong dominance of ^{13}C–^1H dipole–dipole interaction.

T_1 values for all resolvable carbons are shown in Table V, together with those for atactic polystyrene of low molecular weight from this investigation and from the study of Heatley.[20] The 2:1 ratio of T_1 values for the α and β carbons confirms the dipole–dipole nature of the backbone carbon relaxation (this is true also for polystyrene and can be interpreted as indicating that chain motion is effectively isotropic[1]). The marked dependence of T_1 on temperature shows that the observations are on the high frequency side of the T_1 minimum, which in the simple one-τ_c treatment should be at 0.042 s in a 23.5 kG field, as we have seen. The data show that the polyperoxide is substantially more flexible than polystyrene, the main chain T_1 values being longer by a factor of ca. 2 under comparable conditions, but is less flexible than poly(methyloxirane) of comparable molecular weight,[20] for which the C_α carbons have T_1 values nearly fourfold longer.

For polystyrene, the relaxation of the phenyl C_2 and C_3 carbons is comparable to that of the C_α and C_4 carbons (the latter two being necessarily at least approximately equal since they share the same motion), indicating limited rotational motion, probably mainly libration.[78] In the polyperoxide, by contrast, the C_2 and C_3 relaxation times are 1.6 times those of C_α and C_4, showing that they enjoy a considerable measure of additional rotational freedom, a peroxide oxygen atom being less sterically restrictive than a β-methylene group.

An estimate of the phenyl group rotational time in relation

Table V
T_1 Values for Equimolar Polystyrene Peroxide and Polystyrene, Observed at 25 MHz

Concn %, (w/w)	Temp, °C	Solvent	T_1, s, ±10%				
			C_α[a]	C_β[a]	C_1	$C_{2,3}$	C_4
		Poly(styrene peroxide)					
22	55	$CHCl_3$	0.40	0.20		0.70	(0.40)[b]
22	45	$CDCl_3$	(0.30)[c]	(0.15)[c]	4.1	0.51	0.30
22	33	$CHCl_3$	0.24	0.12	3.2	0.39	(0.24)[b]
22	31	C_6D_6	0.18	0.095	3.0		0.18
60	31	C_6D_6	0.085	0.044			0.085
		Polystyrene					
(10)[e]	33	$CHCl_3$	0.058			0.078	
(22)[d]	33	$CHCl_3$	0.10	0.055	1.2	0.12	0.11

[a] No effect of stereochemical configuration was observed. [b] Not directly measured but assumed equal to value for C_α. [c] Not directly measured but taken from the C_4 value, assuming $T_1(C_\alpha) = 2T_1(C_\beta) = T_1(C_4)$. [d] Monodisperse with DP = 38 (Pressure Chemical Co., mol wt = 4000, $\overline{M}_w/\overline{M}_n \leq 1.1$). [e] Data from ref 20, for a monodisperse polymer of ca. 10 000 mol wt.

Table VI
Correlation Times (ns) for Chain Segmental Motion and Tumbling, $\tau_c(\Sigma)$, and Phenyl Group Rotation, $\tau_c(\phi)$, 22% Solution in Chloroform

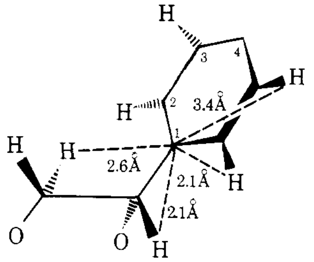
Temp, K	$\tau_c(\Sigma)$	$\tau_c(\phi)$
306	0.20	0.34
318	0.16	0.24
328	0.12	0.17

to chain segmental motion and overall tumbling may be made using the approximate relationship:[74]

$$\frac{1}{\tau_c(\phi,\text{obsd})} = \frac{1}{\tau_c(\sum)} + \frac{1}{\tau_c(\phi)} \tag{23}$$

here $\tau_c(\phi,\text{obsd})$ is the correlation time for the phenyl group calculated by eq 18 from the T_1 of the C_2, C_3 carbons, $\tau_c(\Sigma)$ is the correlation time for overall chain motion similarly calculated from the T_1 values for C_α and C_β, and $\tau_c(\phi)$ is the correlation time of the phenyl group, apart from the contribution of the main chain. In Table VI, values of $\tau_c(\Sigma)$ and $\tau_c(\phi)$ are given at three temperatures in chloroform. From these, we find approximate values of the activation energies for overall tumbling-plus-segmental motion and for phenyl group rotation of 20 and 27 kJ/mol, respectively. For poly(methyloxirane) of low molecular weight in chloroform, Heatley[17] has reported values of 21 kJ/mol for tumbling-plus-segmental motion and 11 kJ/mol for methyl group rotation.

An approximate calculation of the T_1 of the quaternary carbon C_1 can be carried out by generalizing eq 18 to include a summation over all nearest nonbonded protons. If the gauche conformation is assumed,[79] and the C_1–H distances given below are adopted, together with the assumption of $\tau_c(\Sigma)$ as appropriate for β-proton interactions and $\tau_c(\phi,\text{obsd})$ for the others,



it is found that at 33 and 45 °C the calculated T_1 values are 4.1 and 5.3 s, respectively, vs. observed values (Table V) of 3.2 and 4.1 s. Contributions from neighboring chain units may account for the discrepancy in part, but these must be much smaller than in polystyrene because of the spacing effect of the peroxide groups.

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(53) We consider the addition of oxygen to propagating peroxy or alkoxy radicals as highly improbable. A reviewer has pointed out that this polyperoxide may also contain "excess" $-CH_2-$ groups, arising from the addition of oxygen to $ROCH_2\cdot$ and $RCH_2C(C_6H_5)HCH_2\cdot$ radicals, which are

formed during the decomposition of terminal radicals. This would result in two types of "excess" methylene units: (i) –OCH_2O_2– and (ii) –SCH_2O_2–. We find no peaks corresponding to the first type (ref 71). The second type would have a ^{13}C resonance in almost the same position as $\beta(O_2SS)$ resonances, although its presence was not detectable within experimental error on the basis of the equality between α and β backbone carbon resonance areas.

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(59) It is unlikely that the resonances from the styrene unit removed from the end group by one peroxide unit will be noticeably perturbed in chemical shift from the positions of the main chain resonances, since at most only the γ substituent could vary with end-group structure. We therefore assume that all end-group resonances are due only to the carbons directly involved in this group.

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Constrained Anisotropic Motions of Cilia on Crystal Lamellar Surfaces in Polymers

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ABSTRACT: A model of flexible polymer chain ends, cilia, characterized by bend and twist between segments, is used to estimate motionally averaged NMR line widths for polyethylene, poly(vinylidene fluoride), and poly(chlorotrifluoroethylene). Comparison with existent data indicates that the model provides a simple format for qualitative discussion of the motion of cilia and loops.

I. Introduction

It is becoming increasingly evident from the interpretation of NMR relaxation data that there are often serious inadequacies in the use of the simple two-phase model[1] to describe a semicrystalline polymer. These conclusions are borne out in morphological studies which support the view that material, characteristic of the crystalline-amorphous boundary region, may be present in sufficient amounts as to constitute a separate macroscopic phase in model calculations.[2-14] This paper is the second in a series which deals with models of molecular motion applicable to molecules in this intermediate region.

The need for such refinements was recognized at an early stage in several studies that demonstrated the need for a third phase in the line shape analysis of broadline spectra from semicrystalline polymers.[15-20] More recently, Fujimoto and co-workers[21] utilized multiple pulse sequences to resolve three components in their T_2 and $T_{1\rho}$* measurements on Nylon and polyethylene which contrasted with the two-component decays usually observed.

Even with two-component T_2 decays there is an implicit need to invoke a third phase in order to arrive at an adequate description of certain features of the longer T_2 temperature curves; we specifically refer to the plateau which occurs at temperatures well in excess of the glass transition temperature T_g. Such behavior, which is typical of several polymers,[22-25] may be rationalized with ease when it is recognized that the longer T_2 in the two-component decay scheme is, in fact, a weighted average of the intermediate and long T_2's in the three-component analysis.

The third phase, identified as the boundaries between crystalline and amorphous regions, contains a preponderance of chain folds and unterminated chain ends or cilia.[2-14] These morphological entities exhibit motional behavior character-