Table III
Correlation Times $\tau(1,j)^a$ Corresponding to Differences in Rates of Internal Rotation

Compound	$\tau(1,2)$	$\tau(1,3)$	$\tau(1,4)$	$\tau(1,\mathrm{Int})$
C_7	7.9	6.3	4.7	
C_{10}	7.0	5.4	4.5	4.2
C_{13}	6.5	5.3	4.7	3.6
C_{15}	6.9	5.4	4.9	4.4
C_{18}	6.5	5.3	4.8	4.3
C_{20}	7.3	6.1	5.4	5.0

[a] In picoseconds.

to[16]

$$\tau(1,2) = A \exp(V_r/RT) \tag{5}$$

When A (the preexponential factor) is taken as the $\tau(1,2)$ value for a methyl moiety in the gas phase, $(I_{\mathrm{Me}}/kT)^{1/2}$, a value of 2.6 kcal/mol is computed for V_r. This is the same value found by Anderson and Slichter[17] from proton magnetic resonance studies for the end methyl rotational barrier in thirteen alkanes ranging from C_6 to C_{40}.

The correlation times of the carbons at the linear terminus of 2-methylnonadecane and that of eicosane are equal (Table II) showing that these two alkanes have the same overall correlation times and that the methyl branch does not influence the local motion of the linear end of the nonadecane chain. By contrast the correlation times of carbons at the branched end of the chain are markedly different from those in eicosane. In 2-methylnonadecane, $\tau(1,2)$ is about 50% larger than in the n-alkanes and corresponds to V_r = 2.9 kcal/mol for the rotation of the branched methyls. This result is in agreement with previous reports of larger rotational barriers for branched methyls in hydrocarbons.[18] Differences in motion between linear and branched ends of the chain are also due to the slower methyl and methylene motions which result form the required rotation of two methyl groups about the C_2—C_3 bond. The additional carbon mass in the branch appears to explain the result that the C_2 and C_3 carbons in 2-methylnonadecane have τ_{eff} values which are equal to τ_{eff} values of the C_3 and C_4 carbons in eicosane, respectively.

In addition to influencing the motion of the chain terminus, the branch also perturbs the terminal carbon chemical shifts, and permits resolution of the C_5 carbon resonance of the nonadecane. It is seen (Table II) that this carbon has the same correlation time as the internal methylenes (C_6 to C_{15}) in the chain, suggesting that the segmental motion, which determines the correlation time of a carbon in a long-chain alkane (in solution), involves *ca.* 5–6 carbons on each side of the given carbon.

Conclusions

An analysis of alkane data in terms of a simple motional model has been found to account for individual alkane carbon correlation times in a self-consistent fashion. In this model, the rate of rotational reorientation of chain carbons is taken as a sum of rates corresponding to overall and internal rotations. The model provides semiquantitative information on several aspects of the internal chain motion, such as: (1) the barrier to internal methyl rotations, (2) the effects of chain ends and branches on rates of the internal motion, and (3) an estimate of the number of carbons involved in the segmental motion in long chains. However, the analysis provides limited insight into the details of molecular motion, since it involves averages of correlation times. Calculations of the detailed motion of small substituted hydrocarbons have been made in an effort to account for their dielectric relaxation.[9] Similar calculations, employing the appropriate nmr correlation functions,[10,11] would yield T_1 values of individual carbons in the alkanes. The present study provides data which checks the assumptions inherent in such calculations, and hence should aid in the effort to obtain realistic models of the molecular motion of polymers.

Experimental Section

The alkanes, obtained from commercial sources, were at least 95% pure. Samples were pipetted into 10-mm tubes, purged with dry nitrogen, and plugged (to prevent vortexing). Sample temperature was maintained at 39° in the probe using a commercial temperature controller. The experiments were performed on a homemade Fourier transform spectrometer, described previously[19,20] operating at 15.08 MHz and equipped with proton noise decoupling. Partially relaxed spectra were obtained using standard 180°-t-90° pulse sequences with a $5T_1$ recycle time, and 16 free induction decays were accumulated in each case. T_1 values were calculated from least-squares analysis of the integrated intensities. Reproducability of T_1 values is estimated to be ±10%.

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Carbon-13 Nuclear Magnetic Resonance Characterization of Heterogeneous Sequence Distributions in Styrene-Acrylonitrile Copolymers

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ABSTRACT: Average acrylonitrile sequence lengths have been obtained for a variety of high conversion styrene-acrylonitrile copolymers by the analysis of their ^{13}C nmr spectra. Assuming a homogeneous sequence distribution, different values for the average lengths are obtained, depending upon the way in which the nmr data are used. These discrepancies are interpreted in terms of the probable heterogeneity of the sequence distributions.

The ^{13}C nmr spectra of solutions of styrene-acrylonitrile copolymers are well enough resolved to be discussed in terms of chemical shifts associated with sequences of triad monomer-unit residues in the chain.[1] In favorable cases, resolution is sufficiently good that triad concentrations

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(1) J. Schaefer, *Macromolecules*, 4, 107 (1971).

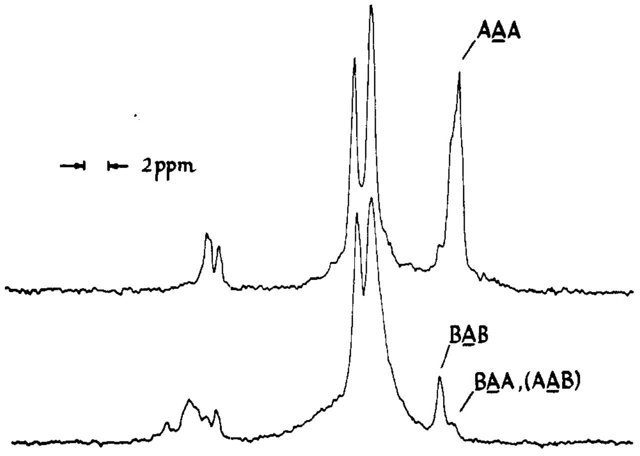

Figure 1. ^{13}C nmr spectra of the aromatic and nitrile-carbon regions of styrene-acrylonitrile copolymers A (upper) and F (lower).

can also be determined by ^{13}C nmr. These are in agreement with values calculated from simple kinetic considerations, at least for those copolymers prepared under carefully controlled conditions of conversion and reactant concentrations.[1] From a practical point of view, however, these controlled, or programmed, conditions are not always met in high-conversion styrene-acrylonitrile reactors. Furthermore, *the actual conditions within the reactor are not uniform, and in general, are not well known.* Under these circumstances, theoretical calculations designed to account for compositional heterogeneity are not of much value in predicting either the extent of the heterogeneity, or its effect on quantities such as average sequence lengths. In this paper we show that ^{13}C nmr is sensitive enough to distinguish between the sequence distributions of high-conversion, styrene-acrylonitrile copolymers, which vary in composition from one another by only a few mole per cent. The resulting experimentally determined sequence distributions can themselves be used to characterize, in part, the extent of compositional heterogeneity of a given high-conversion copolymer.

Experimental Section

Natural abundance ^{13}C nmr absorption spectra were obtained at 22.6 MHz by Fourier transform techniques using a Bruker spectrometer, some details of which have been described earlier.[2] Two recent changes have been made in the operation of this spectrometer. The first deals with the collection of valid data early in the free induction decay. The ^{13}C IF amplifier is now gated off for 120 μsec beginning with the rf pulse. The gate consists of two 30-dB balanced modulators in series. This gate (together with a diode short preceding the preamplifier first stage) eliminates distortions by preventing any part of the pulse and most of the ringdown resulting from the response to the pulse of the receiver coil and the narrow-banded preamplifier from reaching the low-pass active filters immediately preceding the Nicolet 1074 time-averaging computer. The 1074 is triggered simultaneously with the rf pulse, and so (using the 100-μsec dwell time of a SW-77 sweep control) makes its first sampling after 80 μsec and its second sampling after 180 μsec. If the first accumulation of the 1074 operating in the measure mode is erased, no subsequent spurious data appear in the first channel, which accumulates to zero because of the presence of the blanking gate. Valid data appear in the second channel of the 1074. The effect on the spectrum of the zero accumulated in the first channel is a simple shift in the level of the base line for the data acquisition outlined above. Free induction decays can therefore be collected (using tight filters and a narrow-banded preamplifier for a good signal to noise performance) and transformed with negligible distortion due to lost or invalid early information, at least for medium and high-resolution spectra.

The second change in the operation of the spectrometer involves the use of external ^{19}F field-frequency stabilization. An external lock permits time-averaging experiments on solid or irregular samples, and greatly simplifies and standardizes routine or repetitive measurements. To obtain this capability, a coil, 5 mm in diameter, was placed some 4 cm from the center of the analytical sample coil. This external lock coil was operated in a time-shared mode using hexafluorobenzene doped with a stable free radical to provide the lock signal. Typical 24-hr stability of the system is about ±1 Hz.

Fully relaxed, proton-decoupled, FT ^{13}C nmr spectra were obtained of five experimental styrene-acrylonitrile copolymers and of Lustran A-25. These polymers were prepared by free-radical techniques in high-conversion reactors. Details of the actual extent of conversion of the five experimental polymers, and of the variation of the reactants during the course of the polymerization, were not well characterized. Each of these polymers contained about 75 mol % acrylonitrile. Spectra were obtained at 35° from 15% solutions (by weight) of the polymers in dimethyl sulfoxide-d_6. Simulations of the observed spectra were made using a Du-Pont 310 curve resolver.

Results and Discussion

The ^{13}C nmr spectra of the aromatic and nitrile carbons of two styrene-acrylonitrile copolymers, (-CH$_2$CHC$_6$H$_5$-; -CH$_2$CHCN-)$_x$ which differ in composition by about 20 mol % are shown in Figure 1. (The spectra of the copolymer main-chain carbons are relatively poorly resolved and are not shown.) As discussed in detail elsewhere,[1] the lowest field group of lines is due to the quaternary carbons of the styrene units, and can be interpreted in terms of structural and steric sequences at least five units in length. (Chemical shifts for all lines, relative to tetramethylsilane, may be found in ref 1.) The two intense lines in the middle of the spectrum are due to all the remaining aromatic styrene carbons in various kinds of sequences. While the spectra of the styrene aromatic carbons are very detailed, it is not a simple matter to extract quantitative sequence concentrations from them. This is not true, however, of the nitrile-carbon spectra of the acrylonitrile units. The high-field nitrile-carbon line can be considered the sum of three bands, which are assigned to the three possible kinds of acrylonitrile structural triads, as shown in Figure 1. Since the relative chemical shifts of these bands is more than twice as large as those of the nitrile-carbon lines associated with the various stereochemical configurations in polyacrylonitrile homopolymer,[3] it seems reasonable to attribute these three bands predominantly to structural sequences. The effect on the AAA line in the copolymer (where A is acrylonitrile) of the stereochemistry of nearest neighbors is not resolved, unlike the situation for the homopolymer.[3] Apparently, the minor influence of different next-nearest structural neighbors is enough to average this information into a single band.

The spectra of two copolymers which differ in composition by 6 mol % are shown in Figure 2. The nitrile-carbon regions are clearly different, and yield different triad concentrations following computer simulation and decomposition. The simulations were based on the presence of only three lines, of identical widths, which vary only in relative intensities. A slightly sloped base line was also assumed. The spectra of two copolymers which differ in composition by only 1 mol % are shown in Figure 3. Despite the virtually identical total compositions, the nitrile-carbon spectra are distinguishable. (In the 75 mol % acrylonitrile composition range, each styrene unit has almost exclusively acrylonitrile nearest-, and next-nearest neighbors, and so the aromatic-carbon spectra are not much different from one polymer to the next.) In terms of the sequence distributions, copolymer E of Figure 3b contains as many

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

(3) J. Schaefer, *Macromolecules*, **4**, 105 (1971).

Table I
Triad Concentrations and Average Sequence Lengths for Some High-Conversion Styrene–Acrylonitrile Copolymers

Copolymer	M_A	[BAB]	[BAA, (AAB)]	[AAA]	$\langle A\rangle^a$	$\langle A\rangle^b$	$\langle A\rangle^c$
A	0.794	0.065	0.317	0.619	3.44	4.91	3.89
B	0.768	0.075	0.298	0.627	2.98	5.21	3.34
C	0.754	0.098	0.378	0.646	2.93	4.42	3.10
D	0.737	0.073	0.404	0.523	3.76	3.59	2.84
E	0.728	0.074	0.464	0.462	4.13	2.98	2.71
F	0.388	0.883	0.117	0.000	1.07	1.00	1.07

[a] Based on R_1. [b] Based on R_2. [c] Based on the final composition.

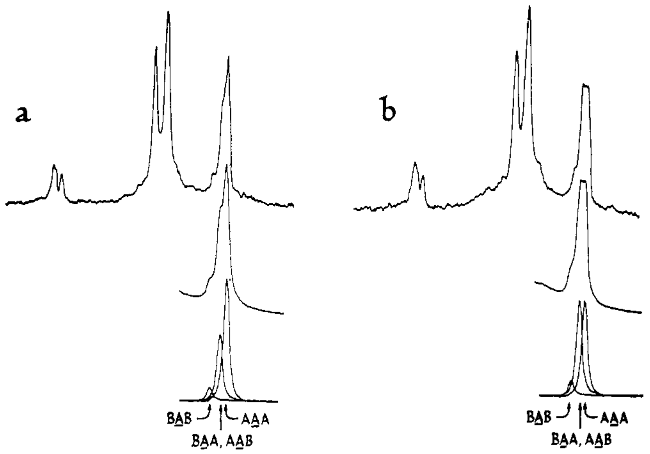

Figure 2. ^{13}C nmr spectra of the aromatic- and nitrile-carbon regions of styrene–acrylonitrile copolymers A (a) and E (b). Computer simulations, spectral decompositions and line assignments are shown for the nitrile-carbon region.

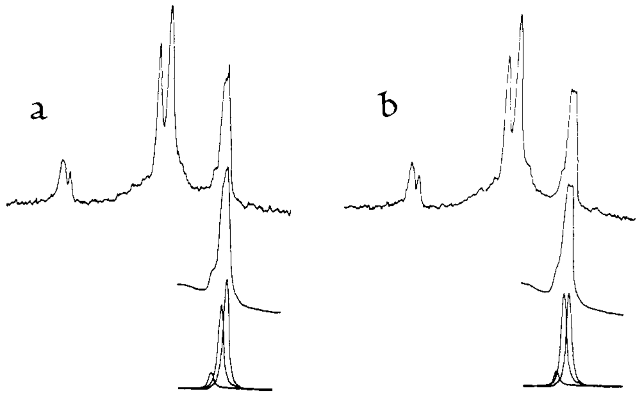

Figure 3. ^{13}C nmr spectra of the aromatic- and nitrile-carbon regions of styrene–acrylonitrile copolymers D (a) and E (b). Computer simulations and spectral decompositions are shown for the nitrile-carbon region.

short sequences of acrylonitrile as that of copolymer D of Figure 3a, but fewer longer sequences. Triad concentrations for all the copolymers are presented in Table I, as well as total compositions, the latter determined by comparison of the integrated intensities of the quaternary-carbon lines of styrene units to those of the nitrile-carbon lines of the acrylonitrile units. Complications from variations in nuclear Overhauser enhancements were considered safely ignored.[4]

Assuming the applicability of a first-order Markoff description of the sequence distribution,[5] the average acrylonitrile sequence length can be determined in any of three ways. Thus

$$\langle A\rangle = 1 + (2R_1)^{-1} \qquad (1)$$

and

$$\langle A\rangle = 1 + 2R_2 \qquad (2)$$

where

$$R_1 = [BAB]/[BAA,(AAB)] \qquad (3)$$

and

$$R_2 = [AAA]/[BAA,(AAB)] \qquad (4)$$

Furthermore[6]

$$\langle A\rangle = 1 + \frac{2r_1r_2M_A/M_B}{[(M_A/M_B - 1)^2 + 4r_1r_2M_A/M_B]^{1/2} - (M_A/M_B - 1)} \qquad (5)$$

where M_A is the mole fraction of acrylonitrile, and M_B the mole fraction of styrene in the final copolymer. The product r_1r_2 is the reactivity ratio product and is taken equal to 0.021 for styrene–acrylonitrile.[7] Values of the acrylonitrile average sequence length obtained from comparisons of triad concentrations and from the total composition are presented in Table I. They are all substantially different. Since the theoretical applicability of the statistical analysis has already been established on well-characterized low-conversion styrene–acrylonitrile copolymers,[1] the discrepancy here must be attributed to the heterogeneity of the sequence distribution of the high-conversion copolymers.

Equations 1, 2, and 5 are only strictly applicable for a homogeneous copolymerization in which the ratio of reactants is constant, or approximately constant, throughout the whole polymerization process. For the polymers of Table I, this has not, in general, been the case. Thus, if at some point during a styrene–acrylonitrile copolymerization the abundance of styrene, for example, is sharply depleted, some acrylonitrile homopolymer will be added to the existing copolymer chains. The net result is a heterogeneous sequence distribution. Estimates of acrylonitrile average sequence lengths will accordingly differ depending on whether one uses R_1 (which does not strongly depend upon long sequences of acrylonitrile), the total composition (which does depend upon their presence), or R_2 (which is actually rather sensitive to the presence of long sequences of acrylonitrile).

We emphasize that it is no surprise that these copolymers are compositionally heterogeneous, or that the heterogeneity has an effect on the appearance of the ^{13}C nmr spectrum. What may be surprising is that despite the various complications of styrene–acrylonitrile ^{13}C nmr spectra, detailed analysis can produce three different, independent estimates of acrylonitrile sequence length, even for high-conversion copolymers. This means that the very nature of the discrepancy between these three estimates can

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(5) J. Schaefer, *J. Phys. Chem.*, **70**, 1975 (1966).
(6) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 180.
(7) See ref 6, p 188.

be used as an approximate measure of the extent of an otherwise difficult to characterize compositional heterogeneity.

For example, copolymers A, B, and C of Table I probably contain some relatively longer sequences of acrylonitrile since the estimate of the average acrylonitrile sequence length based on R_2 is much larger than those based either on R_1 or the final composition. Naturally, this kind of measure is more accurate for that range of copolymer composition in which very long sequences are not likely (which is the case for the copolymers of Table I). This is true since the actual nmr measurement is in terms of triads. Thus, the measure of deviations from theoretical predictions of average sequence lengths is most sensitive for those lengths which are on the order of about 2–4, or approximately the length of a triad.

Simulation of Reactions with Lignin by Computer (SIMREL). I. Polymerization of Coniferyl Alcohol Monomers[1]

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ABSTRACT: A computer program was written to simulate the formation of a dehydrogenation polymer of coniferyl alcohol starting with a monomer of the type $C_9H_9O_2OCH_3$ with another monomer of the same type, forming a polymer of up to 100 units (aglomerated monomers). Coupling reactions are selected according to a statistical distribution of predetermined values found in the literature. Coupling modes include combinations of any of four radical species leading to previously reported interunit bonds. Tables are printed out giving the reaction sequence and the percentage figures of the reaction types at the time of simulation. A summary with the final configuration of the polymer is printed at the end of the simulation run, also listing a modified Rydholm diagram and other tables. The simulation mechanism is based on code numbers of molecule positions in C_9 units that identify chemical elements and reactivity coefficients and that decide upon the possibility of a molecule position to perform a reaction. Three states of reactivity are possible: reactive, not reactive, and "latent." A "latent reactivity" classifies a reaction as possible with the exception that a statistical percentage figure does not permit further reaction with this particular position because a prescribed analytical value is lower or equal to one being computed. The SIMREL program searches for a reactive position in the polymer under formation and performs a reaction with a new monomer unless it is statistically impossible; then, the reactive position is converted into a latent one. A limit on the number of units in the polymer or exhaustion of reactive positions terminates the simulation.

1. Introduction

Lignin is known to be a three-dimensionally branched polyphenol, synthesized by some plants from phenylpropenoid precursors (for review, see ref 3–6). Enzymatically triggered phenolic coupling has been recognized as the motor of polymerization. Although this mechanism is widely believed to proceed in a random manner, some schemes have been proposed to the contrary.[7,8] However, one way or the other, there seems to be no doubt as to the initial enzymatic control of its formation from coniferyl alcohol and related phenylpropanes. If there is a control mechanism that would cause lignin to form in "repeating units," it would be unique to the biochemistry of plants, as other natural polyphenols such as tannins and phlobaphenes are considered to be disordered polymers. Also, the existence of such a control mechanism would probably have little effect on the overall chemical makeup of lignin and its reactions. The concept of lignin as a completely ordered molecule might be as erroneous as that of lignin as an entirely homogeneous substance; recent indications obtained by several investigators are that lignin configuration varies with its location in the cell structure.[9-14] The assumption that a statistical polymer formed essentially randomly through a limited number of oxidative coupling reactions of one, two, or three p-hydroxycinnamyl alcohol-type phenols makes this substance well suited for mathematical simulation by computer. Such mathematical models have previously been used in the field of pulp and paper technology to simulate pulping processes in terms of such process parameters as liquor: wood ratio, chemical charge, and reaction rates.[15-22] These models allowed to make reasonable predictions as to yields and lignin contents of resulting pulps. However, no attempts have been

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(1) Part of the results have been presented in a paper given at the 4th Canadian Wood Chemistry Symposium, held in Quebec, Canada, July 4–6, 1973.

(2) (a) Assistant Professor of Wood Chemistry; (b) M. S., formerly a Research Associate, College of Forest Resources, University of Washington, Seattle, Wash.

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