shifting toward the unity as the reaction of the monomer charge-transfer complex becomes predominant.[25]

The VCZ-DEF system, the rate curve of which resembles b_1 or c, is understood that in this system the contribution of the monomer charge-transfer complex to the polymerization is almost negligible, and that the reaction consists of almost only the free monomers. Indeed, it was found that the initial rate of copolymerization in this system was almost independent of the concentration of the M_2(DEF) monomer for a fixed concentration of the M_1(VCZ) monomer within experimental errors (Table III). By contrast, the VCZ-FN system, the rate curve of which resembles d, is understood that in this system reactions of both the monomer charge-transfer complex and the free monomers are operative in the propagation process of the polymerization.[26] The fact that the initial rates of copolymerization in the VCZ-FN system were five to twenty times faster than those in the VCZ-DEF system may be explained as due to much higher reactivity of the monomer charge-transfer complex[16] as compared with that of the free monomers.

Moreover, we can discuss the expected rate features of other special situations in the alternating radical copolymerization. Quite a similar treatment can be made in the case where the rate constant k_{21} is much greater than the rate constant k_{12}. When the rate constants k_{12} and k_{21}, and k_{1c} and k_{2c}, are of comparable order of magnitude with each other, and most termination occurs by the cross-reaction between $m_1\cdot$ and $m_2\cdot$, the overall rate equation will be reduced to eq 24. In this case the rate will

$$R_p = (2k_{21}k_{12}R_i/k_{t12})^{1/2}[M_1]^{1/2}[M_2]^{1/2} + (R_i/2k_{t12})^{1/2}\{(k_{21}/k_{12})^{1/2}k_{1c}K[M_1]^{3/2}[M_2]^{1/2} + (k_{12}/k_{21})^{1/2}k_{2c}K[M_1]^{1/2}[M_2]^{3/2}\} \quad (24)$$

maximize at the monomer feed molar ratio of 1:1 in both case 1 and case 2, respectively.[27]

Finally, it should be emphasized that all of the 1:1 alternating radical copolymerization can not be explained by the mechanism of homopolymerization of the monomer charge-transfer complex, which may be applied only to limited systems. In general, it is important to take account of the reactions of both the monomer charge-transfer complex and the free monomers. It is suggested that the degree of the contribution of each of them to the reaction, quantitative evaluation of which is left to a further study, varies greatly depending upon the reaction system. It can, therefore, be said that the regulation of 1:1 alternation in the polymer structure is not brought about solely by the participation of the monomer charge-transfer complex in polymerization, but rather stabilization of the transition state in the cross-propagation between a growing chain radical and a monomer including a monomer charge-transfer complex either by electrostatic interaction due to the different polarity or electron transfer is responsible for the regulation of the 1:1 alternating structure.

(25) If it is assumed that the reactivity of the monomer charge-transfer complex is β times greater than that of the free monomer, *i.e.*, $k_{2c} = \beta k_{21}$, we obtain

$$R_p = (R_i/k_{t22})^{1/2}k_{21}\{2[M_1] + \beta K[M_1][M_2]\}$$
$$= (R_i/k_{t22})^{1/2}k_{21}A\{2x + \beta Kx(1 - x)\}$$

where $[M_1] + [M_2] = A$ (mol/l.); $[M_1]/([M_1] + [M_2]) = x$. Differentiating the above equation, we obtain

$$dR_p/dx = (R_i/k_{t22})^{1/2}k_{21}A\{2 + \beta K - 2\beta Kx\}$$

The maximum of R_p will appear at

$$x = (2 + \beta K)/2\beta K = (1/2) + 1/\beta K \geqq (1/2)$$

(26) Although an attempt to evaluate the equilibrium constant K for the formation of the charge-transfer complex by means of nmr spectroscopy was not successful, the charge-transfer interaction may be stronger with the VCZ–FN system than the VCZ–DEF system in view of the greater electron-accepting strength of FN and the greater red shift in the electronic absorption spectra in the VCZ–FN system. It may also be possible that the VCZ–FN charge-transfer complex is much more activated in its reactivity than the VCZ–DEF complex.

(27) Substituting $(k_{21}/k_{12}) \approx (k_{12}/k_{21}) \approx 1$, and $k_{1c} \approx k_{2c}$, R_p in the case 2 is expressed as

$$R_p = (R_i/2k_{t12})^{1/2}k_{1c}K[M_1]^{1/2}[M_2]^{1/2}\{[M_1] + [M_2]\}$$

where

$$[M_1] + [M_2] = \text{const}$$

A ^{13}C Nuclear Magnetic Resonance Study of Alkane Motion

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ABSTRACT: Carbon-13 spin-lattice relaxation times (T_1) have been measured for resolved carbons in neat n-alkanes (n = 7, 10, 13, 15, 18, 20) and 2-methylnonadecane, and effective correlation times (τ_{eff}) have been calculated from the T_1 values. A self-consistent analysis of the τ_{eff} values is provided using a model which considers alkane carbon motion in terms of contributions from overall and internal rotations. This analysis yields values for the barriers to methyl rotation in the linear (2.6 kcal/mol) and branched (2.9 kcal/mol) alkanes that are in approximate agreement with previously reported values. One also obtains information on the effects of chain ends and branches on internal motion and an estimate of the number of carbons involved in segmental motion of long alkanes.

The measurement of nuclear spin–lattice relaxation times (T_1) provides information on the molecular dynamics of polymers.[2,3] The carbon-13 nucleus is particularly suited for such studies since the wide range of chemical shifts and the absence of spin–spin splittings, upon proton irradiation, normally enables T_1 values to be measured for many of the chemically distinct carbons of a polymer chain. The determination of ^{13}C T_1 values for individual main-chain and side-chain carbons makes it possible to probe directly segmental motion of the polymer backbone

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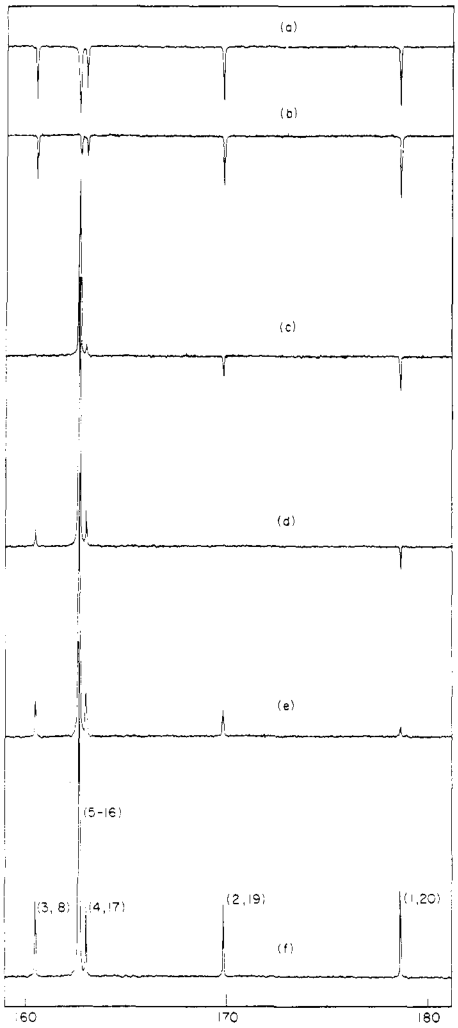

Figure 1. 15.08-MHz partially relaxed Fourier transform ^{13}C spectra of neat eicosane at 39° as a function of t—the time between 180 and 90° pulses. (a) t = 0.3 sec; (b) t = 0.5 sec; (c) t = 1.0 sec; (d) t = 1.5 sec; (e) t = 3.0 sec; (f) normal spectrum $t = \infty$. Sixteen decays are accumulated in each case. Chemical shifts are given in parts per million upfield from external CS_2. Assignments of carbon resonances are given in parentheses.

and localized motion of side-chain and terminal main-chain carbons. T_1 measurements have been made on a series of low molecular weight alkanes and the calculated correlation times have provided semiquantitative information on the nature of the motions in linear and branched alkanes. These results should prove useful in furthering our understanding of the motions in polyethylenes.

Results and Discussion

Carbon relaxation times (Table I) were determined for the n-alkanes, where n = 7, 10, 13, 15, 18, and 20, and for 2-methylnonadecane from inversion-recovery pulsed-Fourier transform spectra. Partially relaxed and equilibrium spectra of eicosane (n = 20) and 2-methylnonadecane are shown in Figures 1 and 2, respectively, along with chemical shift assignments based on the additivity parameters of Grant and Paul.[4] Similar spectra were obtained for the other alkanes studied.

The ^{13}CH nuclear Overhauser enhancement factor[2b] was determined for each resolved resonance and the maximum value (2.98 ± 0.3) was found in every case. The Overhauser enhancements are evidence that the alkane carbons relax predominantly by a CH heteronuclear dipolar relaxation mechanism and that the rotational reorientation is such that the extreme narrowing condition is valid; *i.e.*, $(\omega_C + \omega_H)^2\tau_r^2 \ll 1$, where τ_r is a reorientational correlation time and ω_C and ω_H are the respective Larmor precession frequencies of the ^{13}C and ^1H nuclei. Under these conditions an effective rotational correlation time, τ_{eff}, for the vector connecting the directly bonded C and H atoms is given by[5,6]

Table I
^{13}C Spin–Lattice Relaxation Times[a] for the Alkanes at 39°

	Carbon				
n-Alkane	*1, n*[b]	*2, n − 1*	*3, n − 2*	*4, n − 3*	Int[c]
C_7	10.9	13.2	12.8	12.0	
C_{10}	7.1	7.4	6.3	5.4	5.1
C_{13}	5.9	5.1	4.3	3.7	2.2
C_{15}	4.7	3.5	2.6	2.1	1.6
C_{18}	4.4	2.9	2.1	1.6	1.0
C_{20}	3.6	2.3	1.6	1.1	0.8
2-Me C_{19}	*1, 2-Me*[b]	*2*	*3*	*4*	*5*
	2.3	2.8	1.3	0.8	0.7
	19[b]	*18*	*17*	*16*	*15-6*
	3.6	2.3	1.6	1.2	0.7

[a] In seconds. [b] Italic numbers indicate carbon position in the chain. [c] Int designates the internal carbons having overlapping resonances.

$$\tau_{\text{eff}} = r_{\text{CH}}^6/KT_1N_{\text{H}} \qquad (1)$$

where r_{CH} is the internuclear distance (1.09 Å), T_1 is the spin-lattice relaxation time (Table I), N_{H} is the number of attached protons, and K is a constant equal to 3.56×10^{10} Å^6 sec^{-2}.

In a rigid spherical molecule a single correlation time characterizes the isotropic reorientation of the CH vector, and τ_{eff} calculated from eq 1 is equal to $(6R)^{-1}$, where R is the rotational diffusion coefficient of the sphere. In a polymer, a distribution of correlation times is required to describe the complex motion of a CH vector[7] because (a) the reorientation of a CH vector is due to motions which occur in a distribution of polymer conformations, (b) in a given conformation, the reorientation can be anisotropic,[8] and (c) reorientation is due, in part, to transitions between the different chain conformations.[9] Hence, the single correlation time calculated using eq 1 is in fact a weighted average of the correlation times τ_i which characterize the rotation of the CH vector,[10,11] *i.e.*, $\tau_{\text{eff}} = \Sigma c_i\tau_i$. The coefficients, c_i, depend upon (a) the probability that the motion associated with τ_i occurs and (b) the orientation of the CH vector with respect to the rotation axes.

It follows from the above discussion that a rigorous analysis of the alkane τ_{eff} values (Table II) requires a detailed model of the chain motion. Since such models are not yet available, the present analysis is limited to a simplified model of alkane motion, suggested by the system-

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Table II
Calculated τ_{eff} Values[a] for the Alkanes at 39°

		Carbon			
n-Alkane	*1, n*[b]	*2, n − 1*	*3, n − 2*	*4, n − 3*	Int[c]
C_7	1.4	1.7	1.8	2.0	
C_{10}	2.2	3.2	3.7	4.3	4.6
C_{13}	2.7	4.6	5.5	6.4	10.7
C_{15}	3.4	6.7	9.1	11.3	15.2
C_{18}	3.6	8.1	11.3	14.4	23.1
C_{20}	4.3	10.4	14.8	20.7	30.2
2-Me C_{19}	*1, 2*-Me[b]	*2*	*3*	*4*	*5*
	6.8	16.8	18.6	28.4	33.7
	19[b]	*18*	*17*	*16*	*15-6*
	4.4	10.1	14.9	19.0	33.7

[a] In picoseconds. [b] Italic numbers indicate carbon position in the chain. [c] Int designates the internal carbons having overlapping resonances.

atic behavior of the τ_{eff} values (Table II) as summarized below.

First, for a particular resolved carbon (C_1, C_2, etc.) the correlation time progressively increases as the chain length increases. Second, the correlation times increase from the chain ends toward the center of each alkane. (Similar observations of a gradation of correlation times along an alkyl side chain have been made by several authors.[12-14]) Finally, the ratio τ_{eff} for terminal methyl groups to τ_{eff} for methylenes in the interior of the hydrocarbon (designated Int in the tables) increases monotonically from *ca.* 1.5 in heptane to about 7 in eicosane. These results indicate that the rotational motion of an internuclear CH vector in the hydrocarbons can be analyzed in terms of: (a) an overall rotation of the molecule (considered rigid) with average rotational rate $(\tau_0)^{-1}$ which is expected to decrease as molecular weight and viscosity increase and, (b) internal motion due to rotation about individual carbon—carbon bonds in the chain with rate $(\tau_i)^{-1}$ which is largest at the chain ends. For molecules having segmental freedom but slow overall reorientation (*i.e.*, $(\tau_0{}^{-1})$ small), $(\tau_{\mathrm{eff}})^{-1}$ is approximately equal to $(\tau_i)^{-1}$. This is the case for carbons remote from the chain termini in polystyrene.[15] For rapid overall rotation (*i.e.*, $(\tau_0{}^{-1})$ large) such as occurs in small molecules, $(\tau_{\mathrm{eff}})^{-1}$ is approximately equal to $(\tau_0)^{-1}$.

The simplest expression for the rate of rotational reorientation of the *j*th carbon in the chain, $({}^j\tau_{\mathrm{eff}})^{-1}$, which reduces to the limits discussed in the previous paragraph, is a sum of rates for internal and overall rotations, *i.e.*

$$({}^j\tau_{\mathrm{eff}})^{-1} = ({}^j\tau_i)^{-1} + ({}^j\tau_0)^{-1} \qquad (2)$$

Although a rigorous justification for eq 2 is not available, this equation provides a self-consistent framework for analyzing the alkane data. This can be seen by considering the rate $[\tau(1,2)]^{-1}$, defined as the difference in the rates which characterize the motion of the terminal methyl and terminal methylene carbons in a given alkane, *i.e.*

$$[\tau(1,2)]^{-1} = ({}^1\tau_{\mathrm{eff}})^{-1} - ({}^2\tau_{\mathrm{eff}})^{-1} \qquad (3)$$

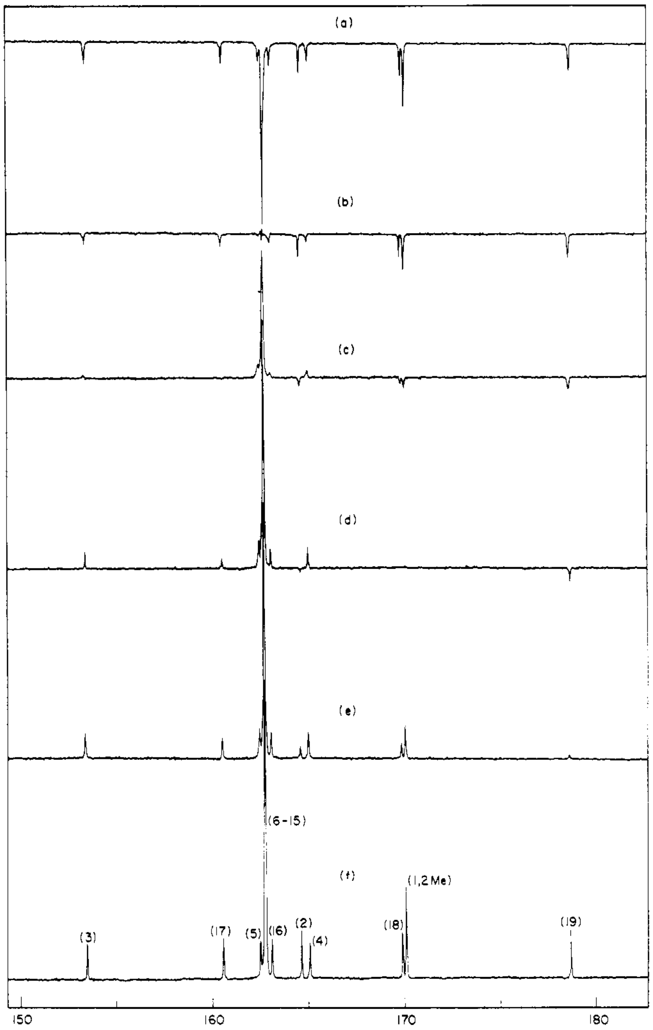

Figure 2. 15.08-MHz partially relaxed Fourier transform ^{13}C spectra of neat 2-methylnonadecane at 39° as a function of *t*—the time between 180 and 90° pulses. (a) t = 0.1 sec; (b) t = 0.5 sec; (c) t = 1.0 sec; (d) t = 1.5 sec; (e) t = 3.0 sec; (f) normal spectrum $t = \infty$. Sixteen decays were accumulated in each case. Chemical shifts are given in parts per million upfield from external CS_2. Assignment of carbon resonances are given in parentheses. According to standard nomencalture, the equivalent methyls are designated 1- and 2-Me. The assignment of the C_2 and C_4 carbon resonances were confirmed on the basis of their respective T_1 values (given that the T_1 values decrease toward the center of the chain).

The physical meaning of $\tau(1,2)$ becomes apparent on substituting eq 2 into 3 which yields

$$[\tau(1,2)]^{-1} = ({}^1\tau_i)^{-1} - ({}^2\tau_i)^{-1} \qquad (4)$$

The right side of eq 4 involves only internal correlation times since the overall correlation times of all carbons in a given alkane are equal (by definition) and the terms involving τ_0 cancel. Hence, in each alkane, the difference in internal rates $[\tau(1,2)]^{-1}$ should represent the rate of methyl group rotation alone, since the total methyl motion is the result of all rotations that affect its neighboring methylene plus its rotation about the terminal C_1—C_2 bond. Therefore, $\tau(1,2)$ should be independent of alkane molecular weight as should $[\tau(1,j)]^{-1}$ which represents the difference in internal rates (calculated according to eq 4) of the methyl carbon and carbon *j*. The calculated values of $\tau(1,j)$ are, in fact, approximately constant (Table III).

Since $\tau(1,2)$ represents the time characterizing methyl group rotation, it is related to the rotational potential barrier (V_r) for thermally activated rotation according

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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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