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A Carbon-13 Spin-Lattice Relaxation Study of Side Chains of Poly(alkyl methacrylate)

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The carbon-13 spin-lattice relaxation times (T_1) of the carbons in the alkyl side chains of poly(alkyl methacrylate) (butyl, octyl, dodecyl, and octadecyl), including poly(butyl methacrylate) of low molecular weights, were determined from partially-relaxed Fourier transform spectra. The T_1 for polymers of high molecular weights were found to be determined by the internal motion of the side chains, and not by the overall motion of the polymer molecules. The relaxation data indicate that the internal motion of the short side chains (butyl and octyl) is restricted by interactions between the side chains, although this effect was ineffective near the free ends of long chains (dodecyl and octadecyl). These observations are interpreted in terms of the local environment around the side chains.

The measurements of carbon-13 spin-lattice relaxation times (^{13}C-T_1) have been applied to investigations of the molecular dynamics of polymers in solutions.[1] Many of those investigations were concerned with the segmental mobility of backbone chains. On the other hand, a few papers have been published on localized motion, such as the internal motion of side groups, the internal motion of methyl groups of polypropyrene[2] and the ring motion of pyrrolidine residues of polypeptides.[3]

In a previous study, Hirai *et al.* evaluated the internal motion of the side groups of polyacrylamides having various molecular weights using ^{1}H-NMR spectroscopy and discussed the change in the local environment around the side groups arising from increase in molecular weight.[4] In the present investigation, samples of poly(normal alkyl methacrylate), including poly(butyl methacrylate) of low molecular weights, were studied. In these polymers, one end of the alkyl side chains is attached to the polymer backbone; such alkyl chains are termed anchored chains. In such cases, a marked gradation of the ^{13}C-T_1 along the alkyl chains was observed.[5] The gradation of T_1 reflects a change in internal motion along the side chains. Therefore, poly(alkyl methacrylate) is an ideal sample for discussing the internal motion of side groups.

The ^{13}C-T_1 for the side chains of poly(alkyl methacrylate) (butyl, octyl, dodecyl, and octadecyl) were determined from partially-relaxed Fourier transform spectra, and the correlation times were estimated. The internal motion of the side chains and the local environment around these chains is discussed on the basis of the relaxation data.

Experimental

Samples of poly(butyl methacrylate), poly(octyl methacrylate), poly(dodecyl methacrylate), and poly(octadecyl methacrylate) were prepared by polymerization of 10 g of the respective monomers in 20 ml of carbon tetrachloride for 5 h at 70 °C, using about 0.1 g of α,α'-azobisisobutyronitrile as an initiator. Samples of poly(butyl methacrylate) of various molecular weights were also prepared by changing the amount of the initiator (over the range from 0.3 to 3 g). The polymers were precipitated in a large amount of methanol in order to free them from any residual monomer, and were dried *in vacuo*. The number-average molecular weights of these polymers were determined using a Kunauar membrane osmometer and a vapor-pressure osmometer in chloroform solutions at 37 °C. The average molecular weights of the polymer samples were as follows: poly(butyl methacrylate) 1.36×10^3—7.95×10^4, poly(octyl methacrylate) 13.4×10^4, poly(dodecyl methacrylate) 8.26×10^4, and poly(octadecyl methacrylate) 11.3×10^4.

Polymer solutions for ^{13}C-NMR spectral measurements were prepared by dissolving of 0.3 g of the polymers in 0.7 ml of chloroform-*d*; the concentration of the polymers was 30% (wt/vol). The solutions were transferred to 8 mm o.d. NMR tubes, which were sealed after the air had been replaced with nitrogen gas. The sample volume was confined to a volume which was designed to be about 15% less than that of the rf sample coil, since it has been pointed out by Farrar and Becker[6] that, in order to avoid systematic errors introduced in T_1, the sample volume should not extend above or below the rf sample coil.

The carbon-13 NMR spectra were measured using a JEOL JNM PS-100 spectrometer equipped with a PFT-100 Fourier transform system operating at 25.03 MHz, and a EC-100 computer with a memory capacity of 16 kirowords. The 90° pulse width was about 23 μs. The apparatus was equipped with an internal ^{2}D field-frequency lock and a noise-modulated proton decoupler. The time-domain signal was digitized in 8192 channels, to provide 4096 data points after Fourier transformation. The recycle times of the 90° pulse were chosen to be at least four times the longest spin-lattice relaxation time. The experiments on spin-lattice relaxation were restricted to a spectral width of 2000 Hz. Over this widths, the ^{13}C rf field is sufficiently effective. All spectra were observed at 27 °C.

The T_1 were calculated, for six significant time intervals in the range from 30 ms to 6.0 s, using the least-squares method. The error in T_1 was estimated from the values of $\lim_{t\to0} \ln\{A_0-A(t)\}/A_0$; the maximum error was within ±10%.

Results and Discussion

^{13}C-NMR Spectra of Poly(alkyl methacrylate). Figure 1 shows the proton-decoupled ^{13}C-NMR spectra of poly(alkyl methacrylate) (butyl, octyl, dodecyl, and octadecyl). In examining these spectra, attention is called to the peaks of the side chain carbons.

The chemical shifts of the carbons of alkyl chains can be estimated from the empirical equation of Grant and Paul[7] or that of Lindeman and Adams;[8] these equations are often used for spectral assignments. The chemical shifts of the carbons of the alkyl side chains were estimated using the equation of Lindeman and Adams.[8] In the calculations, the effect of substitution

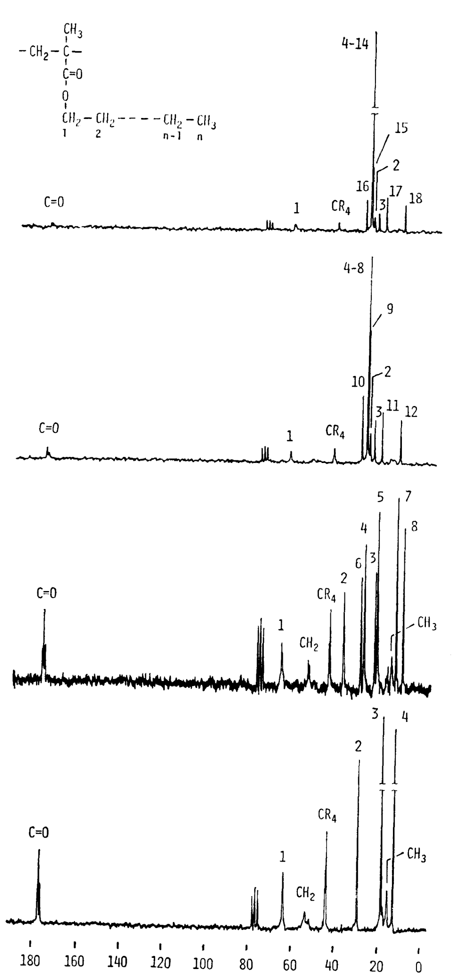


Fig. 1. Proton-decoupled natural-abundance ^{13}C Fourier transform NMR spectra of poly(alkyl methacrylate) in chloroform-*d* (30% (w/v)), at 25.03 MHz and 27 °C. From the top, poly(octadecyl methacrylate), poly(dodecyl methacrylate), poly(octyl methacrylate), and poly(butyl methacrylate). Assignments are indicated near the top of each peak. The numbering system for the alkyl chain starts at the O-CH_2 carbon. The horizontal scale is ^{13}C chemical shifts (ppm) relative to tetramethylsilane.

by –OCOR groups[9] was also taken into account. The calculated values are listed in the column marked "Calcd" in Table 1.

The values of the observed chemical shifts are given in the column marked "Obsd". For carbons near the anchored end, the chemical shifts of the peaks yielding short spin-lattice relaxation times are given (the ^{13}C-T_1 values are given in the following section). The basis for this arrangement of the observed chemical shifts is as follows. The ^{13}C-T_1 values for various anchored chains (one end of alkyl chains is anchored to massive materials or to some solvent matrix) have been measured by various investigators.[5,10–14] The ^{13}C-T_1 for all anchored chains increases along the chain from the carbon at the anchored end toward the terminal methyl carbon; there are no exceptions to this rule. One end of each of the alkyl side chains of poly(alkyl methacrylate) is anchored to the polymer backbone; the T_1 for the side chains should be similar to those for the anchored chains already examined.[5,10–14]

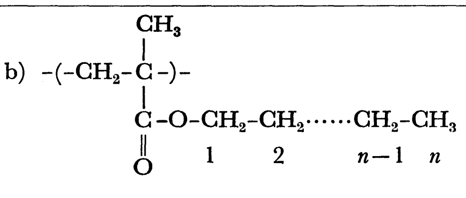
For poly(butyl methacrylate), poly(dodecyl methacrylate), and poly(octadecyl methacrylate), the calculated values are in fair agreement with the observed values. Only for poly(octyl methacrylate), is the agreement poor. The origin of this disagreement is obscure; in the assignment of the octyl chain the rule of chemical shifts for linear alkanes was also taken into account. However, it is evident that the assignments for carbons 7 and 8, which have long relaxation times, can be made without error. This means that the disagreement for the octyl chain does not affect the main discussion of the present study given in the following section.

Internal Motion of Alkyl Side Chains. The spin-lattice relaxation times of ^{13}C nuclei in polymers are determined predominantly by ^{13}C–H dipolar interactions.[15] Other possible relaxation mechanisms can be ignored.[1,15] Therefore, only the intramolecular dipolar interactions between a carbon and nearby completely saturated spin-spin decoupled protons are assumed here. If the "extreme narrowing condition" is satisfied, the relaxation time T_1 is given as follows (this condition is valid for side-chain carbons having moderately long spin-lattice relaxation times):

TABLE 1. OBSERVED AND CALCULATED CHEMICAL SHIFTS[a] FOR SIDE CHAINS OF POLY(ALKYL METHACRYLATE)

	Butyl			Octyl			Dodecyl			Octadecyl	
n[b]	Obsd	Calcd	*n*	Obsd	Calcd	*n*	Obsd	Calcd	*n*	Obsd	Calcd
1	64.8	65.4	1	67.1	65.7	1	65.0	65.7	1	65.3	65.7
2	30.3	32.8	2	38.4	30.4	2	28.2	30.4	2	28.3	30.4
3	19.4	21.4	3	23.8	28.7	3	26.1	28.7	3	26.2	28.7
4	13.8	13.9	4	28.8	30.0	4—8	29.7	30.0	4—14	29.9	30.0
			5	22.8	29.7	9	29.4	29.7	15	29.5	29.7
			6	30.3	32.4	10	32.0	32.4	16	32.0	32.4
			7	13.9	22.7	11	22.7	22.7	17	23.0	22.7
			8	10.8	13.9	12	14.2	13.9	18	14.2	13.9

a) ppm relative to tetramethylsilane. b)



$$-(-CH_2-\overset{CH_3}{\underset{C-O-CH_2-CH_2\cdots\cdots CH_2-CH_3}{C}}-)-$$

$\overset{\Vert}{O}$ 1 2 $n-1$ n

$$1/T_1 = \hbar^2\gamma_C^2\gamma_H^2\tau\sum_N r_N^{-6}, \qquad (1)$$

where $\hbar$ is Planck's constant divided by 2π, γ_C and γ_H are the carbon and proton gyromagnetic ratios, respectively, τ is the correlation time (τ is often expressed as τ_{eff}, the "effective correlation time"), and r_N is the internuclear C–H distance for the N-th proton. In the calculation of $\sum_N r_N^{-6}$, account is taken of the directly bonded protons only.

T_1 of Butyl Chains and Molecular Weights: Table 2 shows the T_1 values for the side chains of poly(butyl methacrylate) of various molecular weights. The effective correlation times (τ_{eff}) were calculated from Eq. 1 using these T_1 values and are listed in Table 3.

Tables 2 and 3 indicate the typical behavior of T_1 and τ_{eff} for anchored chains: the values of T_1 increase steeply from the 1-CH$_2$ carbon to the terminal carbon (of course, τ_{eff} decreases steeply). These findings are similar to the observations of Levy.[5] The gradation of T_1 and τ_{eff} reflects increasing internal motion toward the terminal methyl groups. Tables 2 and 3 also indicate that the values of T_1 and τ_{eff} for each carbon depend on the molecular weight in the region of low molecular weights. The values of T_1 for each carbon decrease with increasing molecular weight, while τ_{eff} increases with increasing molecular weight. For polymers of high molecular weight, T_1 and τ_{eff} are independent of the molecular weight. Similar results have also been reported for the ^{13}C-T_1 of polystyrene[16] and polyisobutylene[17] in solutions. These findings indicate that T_1 and τ_{eff} for polymers of high molecular weight (in the present experiment, $\overline{M}_n \geq 24900$) are determined by the internal motion of the side chains and not by the overall motion of the polymer molecules. The reciprocal of the correlation time $(\tau_{eff})^{-1}$ can be taken as the sum of the rates for internal and overall motion, *i.e.*, $(\tau_{eff})^{-1} = (\tau_o)^{-1} + (\tau_i)^{-1}$. For polymers having $\overline{M}_n \geq 24900$, the condition $(\tau_o)^{-1} \ll (\tau_i)^{-1}$ is valid, and $(\tau_{eff})^{-1}$ is approximately equal to $(\tau_i)^{-1}$.

TABLE 2. CARBON-13 SPIN-LATTICE RELAXATION TIMES FOR SIDE CHAINS OF POLY(BUTYL METHACRYLATE)

DP[b)]	T_1[a)]			
	1-CH$_2$	2-CH$_2$	3-CH$_2$	4-CH$_3$
10	0.083	0.36	0.84	1.54
38	0.080	0.29	0.85	1.55
175	0.081	0.26	0.68	1.29
560	0.071	0.25	0.73	1.30

a) In seconds, error ±10%.
b) Average degrees of polymerization.

TABLE 3. EFFECTIVE CORRELATION TIMES FOR SIDE CHAINS OF POLY(BUTYL METHACRYLATE)

DP[b)]	τ_{eff}[a)]			
	1-CH$_2$	2-CH$_2$	3-CH$_2$	4-CH$_3$
10	2.8	0.66	0.28	0.10
38	2.9	0.83	0.28	0.10
175	2.9	0.91	0.34	0.12
560	3.3	0.95	0.32	0.12

a) In 10^{-10} s. b) Average degrees of polymerization.

T_1 of Alkyl Side Chains: Table 4 shows the values of T_1 for the side chains of poly(butyl methacrylate), poly(octyl methacrylate), poly(dodecyl methacrylate), and poly(octadecyl methacrylate). From these values of T_1, the effective correlation times (${}^j\tau_{eff}$, where j is the j-carbon) for each carbon of the side chains can be calculated. Table 5 shows the reciprocals of the correlation times, ${}^j\tau_{eff}^{-1}$. ${}^j\tau_{eff}^{-1}$ reflects only the rate of internal motion of the j-carbon in the chain, because, as described in the preceding section, the condition $(\tau_o)^{-1} \ll (\tau_i)^{-1}$ is valid for these polymer samples. Figure 2 shows a plot of ${}^j\tau_{eff}^{-1}$-j for the side-chain carbons of poly(alkyl methacrylate).

The values of ${}^j\tau_{eff}^{-1}$ for the butyl and octyl chains increase progressively toward the free end. The ${}^j\tau_{eff}^{-1}$ curves for the dodecyl and octadecyl chains have flat regions (dotted lines in Fig. 2), which contain carbons 4 to 8 and carbons 4 to 14. The ${}^j\tau_{eff}^{-1}$ values for the last four carbons (the four carbons near the free end) of these chains increase sharply. Figure 2 also indicates that the ${}^j\tau_{eff}^{-1}$ for the last four carbons depends on the chain length of these side chains. The ${}^j\tau_{eff}^{-1}$ values for the butyl chain are small, and those for the octyl chain are comparably small. The ${}^j\tau_{eff}^{-1}$ values for the last four carbons of the dodecyl and octadecyl chains are rather large. This ${}^j\tau_{eff}^{-1}$ behavior resembles that of the anchored chains discussed below.

Figure 3 shows the ${}^j\tau_{eff}^{-1}$ curves for various anchored

TABLE 4. CARBON-13 SPIN-LATTICE RELAXATION TIMES[a)] FOR SIDE CHAINS OF POLY(ALKYL METHACRYLATE)

Butyl		Octyl		Dodecyl		Octadecyl	
n[b)]	T_1	n	T_1	n	T_1	n	T_1
1	0.071	1		1		1	
2	0.25	2	0.14	2	0.087	2	0.071
3	0.73	3	0.14	3	0.22	3	0.32
4	1.30	4	0.26	4—8	0.56	4—14	0.64
		5	0.48	9	0.58	15	0.64
		6	0.32	10	1.21	16	1.91
		7	1.24	11	2.34	17	2.78
		8	1.55	12	3.32	18	3.98

a) In seconds, error ±10%.
b) See footnote b) of Table 1.

TABLE 5. ${}^j\tau_{eff}^{-1}$:[a)] THE RATES OF ROTATIONAL REORIENTATION OF THE j-CARBON IN SIDE CHAINS OF POLY(ALKYL METHACRYLATE)

Butyl		Octyl		Dodecyl		Octadecyl	
n[b)]	$({}^j\tau_{eff})^{-1}$	n	$({}^j\tau_{eff})^{-1}$	n	$({}^j\tau_{eff})^{-1}$	n	$({}^j\tau_{eff})^{-1}$
1	0.3	1		1		1	
2	1.1	2	0.6	2	0.4	2	0.3
3	3.1	3	0.6	3	0.9	3	1.3
4	8.3	4	1.1	4—8	2.4	4—14	2.7
		5	2.0	9	2.5	15	2.7
		6	1.4	10	5.1	16	8.1
		7	5.3	11	9.9	17	11.8
		8	9.9	12	21.2	18	25.4

a) In 10^{10} s^{-1}. b) See footnote b) of Table 1.

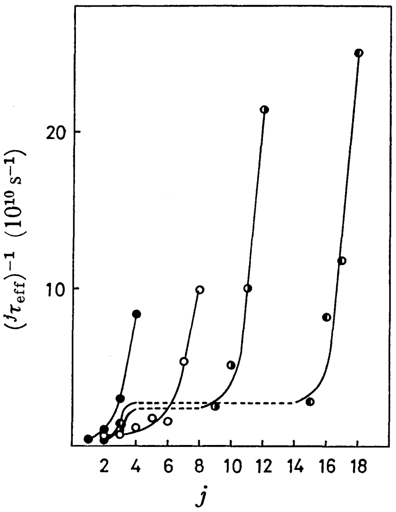


Fig. 2. The plots of $({}^j\tau_{\rm eff})^{-1}$-$j$ for the carbons of the side chains of poly(alkyl methacrylate). ●: Butyl chain, ○: octyl chain, ◑: dodecyl chain, ◐: octadecyl chain.

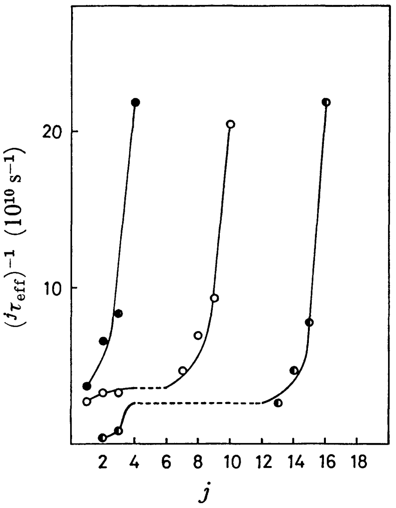


Fig. 3. The plots of $({}^j\tau_{\rm eff})^{-1}$-$j$ for various anchored alkyl chains. ●: Butylammonium ion, ○: 1-decanol, ◐: dipalmitoyllecithin.

chains (the alkyl chains of the butylammonium ion, 1-decanol, and dipalmitoyllecithin). These curves were prepared from ^{13}C-T_1 data for these chains.[10,13,14] The ${}^j\tau_{\rm eff}{}^{-1}$ behavior of the last four carbons of these alkyl chains is different from that of the side chains of poly(alkyl methacrylate). In the case of these anchored chains, the ${}^j\tau_{\rm eff}{}^{-1}$ values for the four carbons is large and give quite similar curves, in spite of the very different properties of these alkyl chains (the curves for *N*,*N*-di-*n*-butyl formamide[12] and lecithin derivatives[11] are also similar to these curves). This constancy of ${}^j\tau_{\rm eff}{}^{-1}$ for the last carbons is called the "limiting microviscosity effect."[18,19] The ${}^j\tau_{\rm eff}{}^{-1}$ values for the last four carbons of these chains do not depend on the chain length or on the type of molecular anchor.

However, the change of ${}^j\tau_{\rm eff}{}^{-1}$ for anchored chains shown in Fig. 3 results only from the restriction of the motion of the anchored end (the anchoring effect). For the side chains of poly(alkyl methacrylate), in addition to this "anchoring effect", the effect of intramolecular packing of the side chains[4] should also be considered. The local environment of the alkyl side chains of poly(alkyl methacrylate) differs from that of the anchored chains in Fig. 3 only in the existence of this intramolecular packing of chains. Therefore, the difference in the ${}^j\tau_{\rm eff}{}^{-1}$ behavior for the last carbons of the side chains of poly(alkyl methacrylate) from those for the various anchored chains, namely the dependence of the ${}^j\tau_{\rm eff}{}^{-1}$ curves on the chain length, can be attributed to this intramolecular packing effect.

The relaxation data presented above indicate that the intramolecular packing effect is ineffective for the last four carbons of the dodecyl and octadecyl chains, although it is effective for the butyl and octyl chains.

The effect of intramolecular packing on internal motion should become measurable when the side chains are unable to escape each other due to the increase in the backbone-chain length[4,20] (this requires that side groups be bulky and rigid). Such examples, in fact, have been observed for the internal rotation of amide groups of polyacrylamide[4] or the tumbling motion of phenyl groups of polystyrene.[21]

The side chains of poly(alkyl methacrylate) differ considerably from the side groups of polyacrylamide and polystyrene in the degree of freedom for interanl motion. Evidently, the degree of freedom for internal motion of alkyl side chains is larger than that of the side groups of polyacrylamide and polystyrene. The degree of freedom of the alkyl side chains is very large at carbons remote from the anchored end. In such cases, the carbons of the side chains can easily exchange equilibrium positions, even if intramolecular packing of the side chains occurs for the polymer chains. As a result, the packing effect is ineffective for restricting internal motion; the side chains behave similarly to the anchored chains, for which the intramolecular packing effect is absent.

From these considerations, the ${}^j\tau_{\rm eff}{}^{-1}$ behavior for the alkyl side chains of poly(alkyl methacrylate) can be interpreted as follows. The internal motion of the last four carbons of the dodecyl and octadecyl chains is not affected by the intramolecular packing of the side chains, because these chains can easily exchange positions with each other. On the other hand, the degrees of freedom of the internal motion for the butyl and octyl chains are less than those for the carbons near the free ends of the dodecyl and octadecyl chains. The butyl and octyl chains are not long enough to permit relaxation of the packing effects, and reduced ${}^j\tau_{\rm eff}{}^{-1}$ values, which arise from the intramolecular packing of the side chains, can be observed. The observations for the side chains of poly(alkyl methacrylate) are interpreted well using the above considerations.

It is concluded that the internal motion of the short side chains (butyl and octyl) is restricted by the intramolecular packing of the side groups, but that this effect is ineffective near the free ends of long chains (dodecyl and octadecyl).

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