

SHORT COMMUNICATIONS

Molecular Motion of Poly(acrylate)s Having Mesogenic Side Chains in Deuterated Chloroform Solution Studied by High-Resolution ^{13}C Nuclear Magnetic Resonance

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It has been known that the polymers composed of rigid and anisotropic mesogenic groups and soft spacers form the liquid crystal in the solid state.¹⁻⁵ The length and the structure of the flexible spacer composed of a methylene chain greatly affect the molecular order, molecular motion, and conformation of a polymer, and give complexed effect on the features of liquid crystal phase and its transition temperature. It is therefore very important to clarify the dependence of the molecular motion of these polymers on the spacer length. We have a great interest to examine the molecular motion of the polymers having the mesogenic group in the side chain. In this work, the molecular motion in the solution has been investigated in order to obtain information about fundamental properties of such a liquid crystalline polymer. It has been well established that the high-resolution nuclear magnetic resonance (NMR) gives us detailed informations about microscopic molecular structure and motion.⁶⁻¹¹ The ^{13}C NMR relaxation of three acrylate polymers shown below with different spacers in length connecting the mesogenic group to

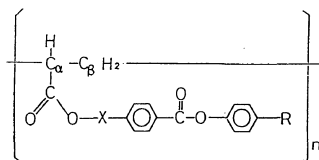
the main chain have been investigated, and molecular motions are discussed in terms of the spacer length.

EXPERIMENTAL

Samples used in this work are three kinds of acrylate polymers having the mesogenic side groups which are kindly supplied by Prof. F. Cser, in Research Institute for Plastics, Budapest, Hungary.¹² Their chemical structures are shown in Table I, where *X* is the spacer and *R* is the side chain end group. In

Table I. Chemical structure and abbreviations for poly(acrylate)s

R	X		
	—	(CH ₂) ₂ O	(CH ₂) ₆ O
O(CH ₂) ₃ CH ₃	BPAB	BPAEB	BPAHB



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the order of spacer length, they are abbreviated as BPAHB, BPAEB, and BPAB, respectively.

^{13}C NMR measurements were carried out in 5.5% w/v CDCl_3 solution at 30°C . Spin-lattice relaxation time T_1 under the complete decoupling condition and nuclear Overhauser enhancement NOE at 50 MHz were measured by a Varian XL-200 spectrometer. T_1 at 100 MHz was measured by a Bruker MSL-400 spectrometer. T_1 was estimated by the inversion recovery method. NOE was calculated as the ratio of the peak intensities with and without ^1H random noise decoupling.

RESULTS

Figure 1 shows the values of NT_1 for protonated carbons at 50 MHz where N is the number of protons attached to the carbon. The transverse axis indicates the skeletal structure of BPAHB residue, where two main chain carbons are in the left side. Main chain, mesogenic and end group carbons give almost similar NT_1 values in three samples. On the other hand, for the spacer carbons, NT_1 is greater in BPAHB than BPAEB. The trend as a whole is that NT_1 value increases as nearer to the end of the side chain. The results of NT_1 at 100 MHz indicated that the tendency of the dependence on each carbon is similar to those at 50 MHz.

The values of NOE at 50 MHz are plotted in Figure 2. The main chain has relatively smaller values of nearly 1, and the side chain has larger values between 2 and 3.

DISCUSSION

When the ^{13}C magnetization is relaxed by dipolar interactions with ^1H at a constant separation r , T_1 , and NOE are given by⁶

$$\frac{1}{NT_1} = \frac{1}{4r^6} \gamma_{\text{H}}^2 \gamma_{\text{C}}^2 \hbar^2 (J_0(\omega_{\text{H}} - \omega_{\text{C}}) + 3J_1(\omega_{\text{H}}) + 6J_2(\omega_{\text{H}} + \omega_{\text{C}})) \quad (1)$$

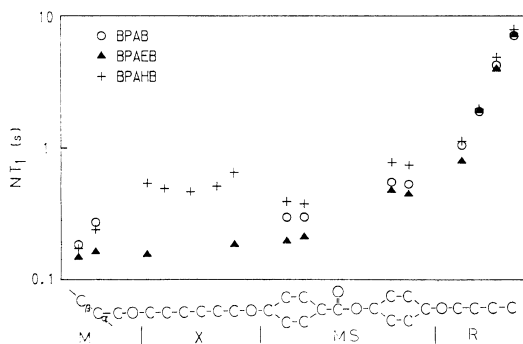


Figure 1. Spin-lattice relaxation time NT_1 (s) at 50 MHz for carbons having protons in poly(acrylate)s, where N is the number of protons attached to each carbon. \circ , BPAB; \blacktriangle , BPAEB; $+$, BPAHB. Skeletal structure of BPAHB is shown at the bottom, where M indicates the main chain including the carboxyl group in the side chain, X the spacer group, MS the mesogenic group, and R the side chain end group.

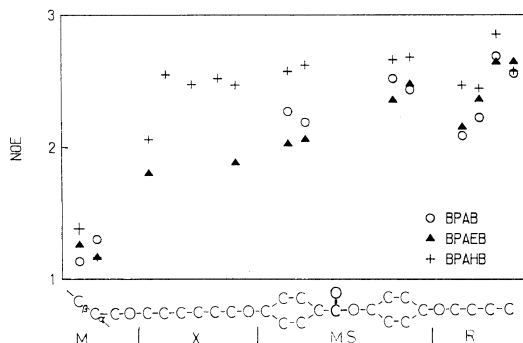


Figure 2. Nuclear Overhauser enhancement (NOE) at 50 MHz for each carbon in poly(acrylate)s. \circ , BPAB; \blacktriangle , BPAEB; $+$, BPAHB.

$$\text{NOE} = 1 + \frac{\gamma_{\text{H}}}{\gamma_{\text{C}}} \frac{6J_2(\omega_{\text{H}} + \omega_{\text{C}}) - J_0(\omega_{\text{H}} - \omega_{\text{C}})}{J_0(\omega_{\text{H}} - \omega_{\text{C}}) + 3J_1(\omega_{\text{H}}) + 6J_2(\omega_{\text{H}} + \omega_{\text{C}})} \quad (2)$$

where $J_q(\omega)$ is the spectral density, γ_{H} and γ_{C} the gyromagnetic ratios, and ω_{H} and ω_{C} the angular resonance frequencies of ^1H and ^{13}C , respectively. \hbar is the Planck constant divided by 2π . Using these relations, we can obtain informations about the molecular motions in polymers when $J_q(\omega)$ is expressed with a proper motional model. So far many models including

the multiple internal rotation have been proposed.^{8-11,13-15} In this work, we have used the relation on the basis of the Model Free treatment^{14,15} in order to investigate the rate and the amplitude of the molecular motion at the same time.

$J_q(\omega)$ is given by

$$J_q(\omega) = \frac{2}{5} \left(\frac{S^2 \tau_M}{1 + \omega^2 \tau_M^2} + \frac{(1 - S^2) \tau^*}{1 + \omega^2 \tau^{*2}} \right) \quad (3)$$

$$\tau^* = (\tau_M^{-1} + \tau_1^{-1})^{-1} \quad (4)$$

here τ_M and τ_1 are the correlation times for motion of a molecule as a whole and the internal motion, respectively. S is the order parameter concerning the spatial spread of the internal motion. When $S=1$, ¹³C-¹H spin pair undergoes no internal motion and $S=0$ corresponds to the completely isotropic internal motion. On practice of the analysis, it is assumed that the main chain undergoes the segmental motion with the correlation time τ_M and $S=1$, and that the internal motion with the correlation time τ_1 superimposed on the segmental motion occurs in the side chain.

Table II. Correlation times τ_M of main chain carbons in unit of 10^{-8} (s)

	BPAB	BPAEB	BPAHB
C_α	1.95	1.11	1.70
C_β	1.48	1.00	1.19

In Table II are shown the estimated correlation times τ_M of the segmental motion in the main chain which fairly well explain the experimental values of NT_1 at 50 and 100 MHz and NOE at 50 MHz at the same time. The value of τ_M is the order of 10^{-8} s, and there is little difference among three samples. It has been reported that randomly coiled polymers undergo segmental motion in solution with correlation time 10^{-8} — 10^{-11} s.^{6-11,13-15} The present results indicate that the main chain undergoes isotropic and relatively slower segmental motion in solution presumably due to having large pendant mesogenic group in the side chain.

For the internal motion in the side chain, the internal correlation time τ_1 and the order parameter S were estimated using eq 1 and 2 after introduction of τ_M values obtained above into eq 3 and 4. In Figure 3 thus obtained τ_1 values which explains experimental results are shown for protonated carbons in the side chain. τ_1 is in the range of 10^{-11} — 10^{-10} s except for the side chain end group where further decrease to 10^{-12} s occurs. For the mesogenic and end groups, τ_1 values of the three samples are almost same. However, for the spacer, BPAHB has shorter τ_1 than BPAEB. This means that the internal motion in the spacer part is faster for the longer spacer.

In Figure 4 the estimated S is shown for each carbon in the side chain. There is a remarkable difference between the values of S at

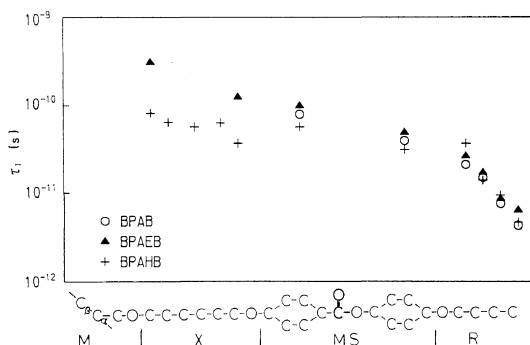


Figure 3. Correlation times τ_1 (s) of internal motions for poly(acrylate)s. ○, BPAB; ▲, BPAEB; +, BPAHB.

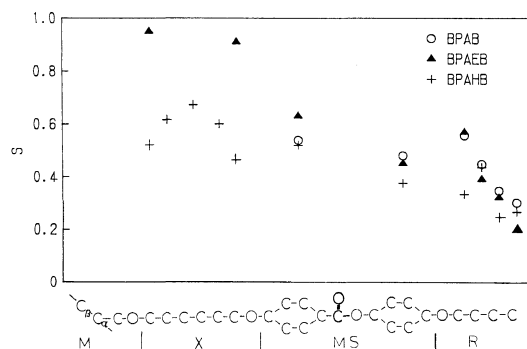


Figure 4. Order parameters S of internal motions for poly(acrylate)s. ○, BPAB; ▲, BPAEB; +, BPAHB.

the spacer part; 0.9 and 0.6 for BPAEB and BPAHB, respectively. As S is defined by $S = \langle (3 \cos^2 \Delta\theta - 1)/2 \rangle_t$, we can estimate the angular amplitude $\Delta\theta$ of the internal motion. Let $S = (3 \cos^2 \Delta\theta - 1)/2$ simply here to see the order of magnitude of $\Delta\theta$. In the mesogenic group and end groups, $\Delta\theta$ is estimated to be 40° and there is no difference among the three samples. However, in the spacer, values of $\Delta\theta$ are 30° and 10° for BPAHB and BPAEB, respectively. The angular amplitude increases with increase of the spacer length. In the solid state, mobility and orientation distribution for the mesogenic group are reported to be lower and narrower, respectively, than other portions of polymer.¹⁷ In solution, correlation time of internal rotation τ_i and order parameter S are rather rapid and smaller, respectively, in the mesogenic group (this work). Similar results were reported for polymers having side chains, where internal motion of the side chain becomes more rapid as nearer to the end of the side chain.^{10,15} Noticeable result obtained in this work is that internal motion of mesogenic group is not depending on the spacer length.

In conclusion, we can see that the main chain undergoes isotropic segmental motion in the solution, and the internal motion in the spacer is more rapid and isotropic with increase of spacer length. On the other hand, the internal motion of the mesogenic group does not depend on the spacer length. Exact reason is not clear at this stage. However, it may be considered that the internal motion of the mesogenic group is not influenced by the mobility of main chain and the spacer due to its large size and high bulkiness. Only 2 or 3 internal bonds between main chain and mesogenic group may be sufficient for mesogenic group to undergo a certain extent of internal motion relative to main chain, and internal motion becomes independent of main chain. In such a case mobility will be determined by the interactions with surrounding media (solvent), and strongly depend on

the size and anisotropy of the mesogenic group.

Similar studies on the samples with different side chain end group are in progress, and the results will be published soon elsewhere. Preliminary results on the molecular motion in the solid state observed by the spin-probe technique for all of the above samples appear in ref 16.

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