*A High Resolution Nuclear Magnetic Resonance Study of the Styrene-Methylmethacrylate Copolymer**

By Yoshinori KATO, Nobuyuki ASHIKARI and Atsuo NISHIOKA

(Received June 9, 1964)

Since Bovey et al.[1] drew attention to the fact that new information about the configuration of polymer chains can be obtained from the high resolution nuclear magnetic resonance spectra, it has been a matter of great concern to us to find some direct evidence for the "copolymer structure" by means of the NMR method. In a preceding paper[2] it was shown that the microstructure of the methyl methacrylate polymer chains can be analyzed to a great extent by the aid of the NMR spectra. In that case the discovery of the *D*-unit (or the heterotactic unit) remarkably improved our knowledge about the stereo regularity of polymer chains. Especially by making use of the concept of the *D*-unit, the difference between

---

* This paper was read at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.

[1] F. A. Bovey, G. V. D. Tiers and G. Filipovich, *J. Polymer Sci.*, **38**, 73 (1959).

[2] Y. Kato and A. Nishioka, This Bulletin, **37**, 1614 (1964).

random and stereoblock polymers can be difined more distinctly. Stereoreglar polymers may be regarded as a kind of copolymer in the sense that they consist of two different species of monomer placements, isotactic and syndiotactic. Therefore, some of the problems we considered in our previous study of polymethyl methacrylate may be applicable to the case of the copolymer.

On the other hand, it is well-known that a benzene ring placed in a magnetic field exhibits a long-range shielding effect which arises from the diamagnetic circulation of the π-electrons.[1,3] Therefore, in polymers such as polystyrene, which contains aromatic rings, some anomalies may be observed in the NMR resonance peaks of the α-protons, methylene protons, and the like. In such cases we may consider the aromatic ring as "a probe" to obtain some valuable information concerning the microstructure of the polymer. For these reasons we have studied the styrene-methyl methacrylate copolymer in solution by means of the NMR method.

At first we expected that the resonance peak due to α-methyl groups of methyl methacrylate would be separated into three peaks, as is the case with polymethyl methacrylate. If so, the dependence of the stereoregularity on the mole per cent of methyl methacrylate in the copolymer could have been obtained. Contrary to our expectations, however, the α-methyl peak does not separate explicitly, but quite a new anomaly can be found in the resonance region due to the methoxy groups.[4] A similar result could be obtained from the NMR spectra of the paraxylylene-methylmethacrylate copolymer.[5]

It is the purpose of this paper to interpret the NMR spectra of the styrene-methylmethacrylate copolymer in order to obtain some information concerning the copolymer structures Using this information it will be possible to study the kinetics of the radical copolymerization.

Experimental

Each sample was prepared in free radical polymerization at 40°C with triisopropylboron as a catalyst. Details of the polymerization conditions are listed in Table I. Proton magnetic resonance measurements were made at 20°C using a Varian V-4300-C spectrometer operating at 56.4 Mc/s. The concentration of the sample in carbon tetrachloride was varied within the range of 6~11% so as to make easy the observation of the minor component of each copolymer sample. The side band technique was employed to estimate the chemical shifts. However, since tetramethylsilane as an internal reference was not available, we could not express the peak positions in the τ-scale.

TABLE I. PREPARATION OF STYRENE-METHYLMETHACRYLATE COPOLYMERS

Sample No.	Mol. % of MMA charged	% conv.
1	81.2	11.21
2	61.9	8.35
3	51.9	7.93
4	41.9	7.08
4′	41.9	7.66
5	20.8	7.56

Results and Discussion

Figure 1 shows the NMR spectra of a polystyrene sample, a polymethyl methacrylate smple and of a mixture of these two polymers. The significance of these spectra is that we can not find any particular change in the NMR spectrum when these two polymers are mixed in the solution. The observed spectra of the copolymer samples are shown in Fig. 2. The sharp peaks at the extreme left may be due to a small quantity of an impurity such as benzene or chloroform. We examined this point and confirmed that the peak appears at the same position as the resonance peak of chloroform within the range of experimental error. Therefore, chemical shifts are expressed in parts per millon referred to this peak. The nearest peak to this is the aromatic proton resonance. In the spectra of samples 1 to 3 the phenyl resonance gives rise to a

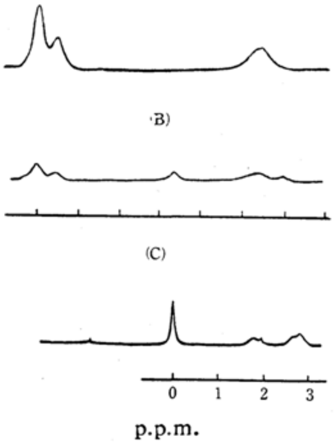


Fig. 1. NMR spectra of (A) polystyrene, (C) polymethyl methacrylate, and (B) the mixture of these two polymers in the ratio of 1 : 1.

---

3) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London (1959).

4) A. Nishioka, Y. Kato and N. Ashikari, *J. Polymer Sci.*, **62**, S10 (1962).

5) A. Nishioka, Y. Kato and H. Mitsuoka, ibid., **62**, S9 (1962).

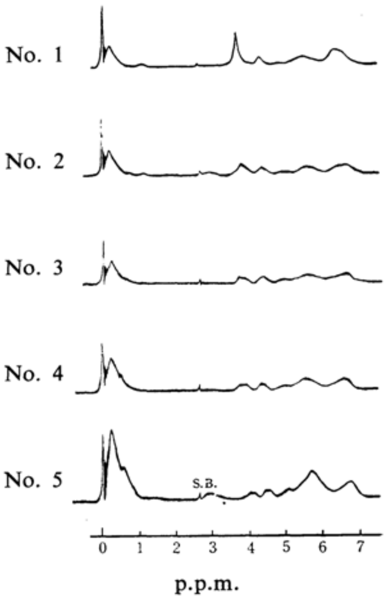


Fig. 2. NMR spectra of styrene-methylmethacrylate copolymers.

broad but single peak, whereas in the rest two separate peaks can be observed. A similar change of spectra has already been found by Bovey et al.[1] in their study of the styrene-butadiene copolymer. They attributed this change to the steric restriction of the phenyl groups. In the copolymer the average sequence length of styrene blocks may base short as several styrene monomer units. According to Bovey's criterion, these short styrene blocks give rise to a single resonance peak at 3.0 τ. Howewer, if the average sequence length is longer than ten styrene units, the phenyl resonance always splits into two peaks. It was also confirmed by Bovey et al. that the smaller phenyl peak is due to the ortho-protons.

The comparison of the spectrum of sample 1 with that given in Fig. 1 (C) clearly shows that some remarkable changes have taken place in the resonance region of the methoxy groups contained in methyl methacrylate. For the sake of convenience, let us denote the three peaks at (3.8±0.2), (4.4±0.1) and 5.0 p.p.m. in our scale of the chemical shift as A-, B- and C-peaks respectively. It is then evident that the A-peak is due to the methoxy groups of methyl methacrylate, but that the relative peak area is considerably smaller than the corresponding peak of Fig. 1 (C). Here, we shall leave the B and C peaks untouched for the moment.

Next, the peak at about 5.6 p.p.m. can be assigned to the methylene protons. Since these protons are equally contained in styrene and methyl methacrylate, the relative area of this peak remains constant independently of the mole per cent of methyl methacrylate in the copolymer. Therefore, the normalization factor of the spectrum may be obtained as the reciprocal peak area of the methlene resonace. The peak at about 6.6 p.p.m. may be the α-methyl resonance. If so, the methyl peak area must be equal to that due to the methoxy groups of methyl methacrylate. The α-proton resonance of styrene is perhaps embedded on the left side of the methylene peak. In addition, the unknown peak C defined above overlaps with the methylene resonance. In order to settle these problems we measured the relative area of each peak. The results are shown in Fig. 3. In the measurement the α-proton peaks could not be separated from the methylene peaks explicitly. We separated them by remembering that the fraction of the peak area of the methylene resonance is invariable. Therefore, the results may include small errors. However, it may safely be concluded from Fig. 3, that both the A- and B-peaks can be ascribed to the methoxy groups of methyl methacrylate. The sum of the A- and B-peak areas seems to be less than the peak area of the α-methyl resonance. This implies that there exist some other resonance peaks due to the methoxy groups. Judging from the possible configurations of the copolymer in connection with the long-range shielding effect of aromatic rings,[6,7] these unknown peaks may be found in the vicinity of the C-peak. Recently Bovey[8] has reported on this copolymer. Since his interpretations were based

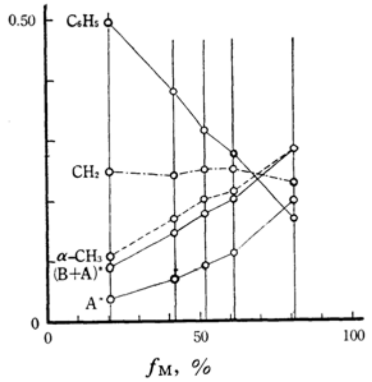


Fig. 3. Fraction of peak area (f_M) obtained from the NMR spectrum of styrene-methylmethacrylate copolymer plotted against mole per cent of methyl methacrylate charged (f).
* See text.

---

6) J. A. Pople, *J. Chem. Phys.*, **24**, 1111 (1956).
7) J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957).
8) F. A. Bovey, *J. Polymer Sci.*, **62**, 197 (1962).

TABLE II. CHEMICAL SHIFTS FOR STYRENE-METHYLMETHACRYLATE COPOLYMERS AND HOMOPOLYMERS IN CARBON TETRACHLORIDE

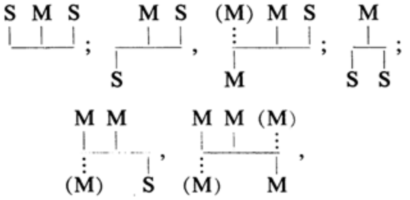
Sample No.	Aromatic	Chemical shift (p.p.m.)* $-OCH_3$* A*	B*	C*	$-CH_2$	α-CH_3
1	0.22	3.72	4.34	5.05	5.60	6.42
2	0.23	3.81	4.37	5.13	5.58	6.64
3	0.23, 0.49	3.84	4.45	5.02	5.62	6.67
4	0.27, 0.48	3.93	4.44	5.03	5.64	6.72
5	0.28, 0.62	4.06	4.51	5.04	5.64	6.73
6**	0.28, 0.74		—	?	5.64	—
7***	—	(3.83)	—	—	(5.63)	(6.34~6.73)

* See text.
** Styrene homopolymer.
*** Three per cent stereoblock PMMA in chloroform.

on the well-resolved NMR spectra observed at 90°C, many interesting results have been obtained. Especially the change in the resonance region of methoxy groups with the mole per cent of methyl methacrylate in the monomer feed seems to offer a key to the analysis of the microstructure of the polymer chains. Introducing some assumptions, we may treat this problem in a way analogous to that used in the case of polymethyl methacrylate.[2)]

In the case of this copolymer it is evident that not the stereoregular placement, but the placement of the styrene monomer unit referred to that of the neighboring methyl methacrylate unit is very important. On the assumption that any methyl methacrylate monomer unit in the copolymer chain can be classified only by its relative placement to the neighboring styrene monomer units on one or both sides, it may readily be seen that there are six configurations of three consecutive monomer units. In principle they may be expected to give rise to six different resonances of methoxy groups in the central methyl methacrylate units.

The configurations may be symbolically illustrated thus:



where S and M stand for styrene and methyl methacrylate monomer units respectively. A vertical line above (or below) the horizontal one represents a so-called *d*- or *l*-unit, and a broken line stands for one equivalent alternate. Perhaps the first configuration will give rise to a resonance at a higher magnetic field than the others. The resonance due to the second configuration will appear close to that due to the third. Though the fourth contains a styrene units at the each end, its resonance magnetic field may be very little different from those of the last two. The spectra of samples 3 to 5 shown in Fig. 1 seem to be in accordance with our interpretation, especially in the methoxy resonance region. However, because of the poor resolution, we can not discuss the problem further at present.

Another evidence of copolymer structure is provided by the interpretation of the chemical shifts. As is shown in Table II, the peak position of the α-methyl resonance shifts towards a higher magnetic field as the styrene component of the polymer chain increases. This is also in accordance with the results obtained by Bovey et al.[1,8)] from the styrene-butadiene and methylmethacrylate-styrene copolymers. However, the exact stereochemical information which was available in the case of polymethyl methacrylate can no longer be obtained from this copolymer. In fact, only a slight change in the line shape of the α-methyl resonance can be observed. The same is true for the resonance line shapes of the styrene component.[9)] In short, the methoxy resonance plays an important role in the NMR spectra of this copolymer.

As an example of a quantitative analysis of NMR spectra, the monomer reactivity ratio[10-13)] was estimated from the measurements of the peak areas of both phenyl and α-methyl resonances. The copolymer composition curve is shown in Fig. 4.

---

9) R. J. Kern and J. V. Pustinger, *Nature*, **185**, 236 (1960).

10) T. Alfrey, Jr. and G. Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).

11) F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).

12) F. T. Wall, ibid., **66**, 2050 (1944).

13) C. H. Bamford, W. G. Barb, A. D. Jenkins and P. F. Onyon, "The Kinetics of Vinyl Polymerization by Radical Mechanisms," Butterworths Publications Ltd., London (1958).

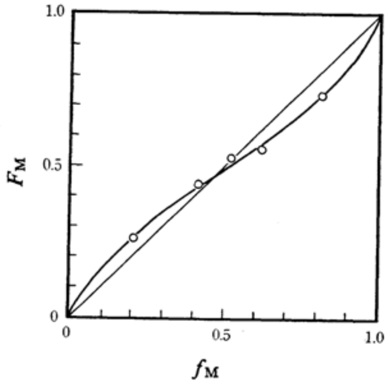


Fig. 4. Copolymer composition curve for the styrene-methylmethacrylate system. F_M, f_M are the mole fractions of MMA in copolymer and in monomer mixture. The heavy line is the theoretical curve for $r_1=0.56$, $r_2=0.50$; ○ : experimental results.

The results,

$$r_1 \text{ (styrene)} = 0.56 \pm 0.01$$

$$r_2 \text{ (MMA)} = 0.50 \pm 0.03$$

are in good agreement with the values given by Lewis et al.:[14]

Monomer reactivity ratio	Polymerization temp.	
	60°C	131°C
r_1 (styrene)	0.52±0.026	0.590±0.026
r_2 (MMA)	0.46±0.026	0.536±0.026

Summary

The information concerning *D*-units in methyl methacrylate polymer chains has inproved our knowledge about the stereoregularity of the polymer.[2] As an extension of the study, we have examined styrene-methylmethacrylate copolymers prepared under various polymerization conditions. In these cases, the α-methyl resonance of methyl methacrylate does not change, except that the peak position shifts towards a higher magnetic field as the styrene component of the polymer chain increases. A direct evidence of the copolymer structure has been obtained by the analysis of the methoxy resonance. A total of six methoxy resonance lines can be observed if any methyl methacrylate monomer unit in the copolymer chain can be classified only in terms of its placement relative to the neighboring styrene monomer units.

Monomer reactivity ratios have been estimated from the NMR spectra. The results are r_1 (styrene) $=0.56\pm0.01$ and r_2 (MMA) $=0.50\pm0.03$.

The authors are indebted to Dr. Naohiro Hayakawa for his kind help in the NMR measurement.

The Electrical Communication Laboratory
Musashino, Tokyo

---

14) F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 1519 (1948).