*Nuclear Magnetic Resonance Spectra of Polymethyl Methacrylate in Solution. I. An Attempt to make Stereoregularity Measurements**

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Recent studies by Bovey et al.[1-3] of polymethyl methacrylate have demonstrated that high resolution nuclear magnetic resonance methods are applicable to the determination of the stereochemical configurations of polymer chains. The stereoregular polymerizations of methacrylic acid esters have been investigated[4,5] since 1958. The crystal structure of isotactic polymethyl methacrylate was proposed by Stroupe et al.[6] on the basis of the X-ray fiber pattern, and in order to measure the degree of stereoregularity of the polymer, an infrared spectrometer was employed by several workers.[7-10] The latter method gave a rather qualitative description of the chain structure. By the use of this method, however, we can not find out the difference between the syndiotactic and the atactic polymers. For this purpose, the nuclear magnetic resonance method would be the most powerful one, because new information about the stereochemical configuration of the polymer chains can be obtained from the spectra.

An attempt is made in this paper not only to estimate the tacticity of the polymer but also to find out the relation between the polymer and the polymerization mechanism by means of an analysis of the spectra.

Experimental

Since a detailed description of the polymerization was given by Watanabe et al.,[4,11] only a brief summary of the methods will be given here.

Free Radical Polymerization.—Each polymerization from −35°C to 0°C was carried out in a flask containing 8.0 ml. of methyl methacrylate in 20 ml. of toluene and 2.0 g. of benzoin by means of photosensitization by ultraviolet light. Dry nitrogen was introduced into the flask during the polymerization. Benzoyl peroxide (B.P.O.) was used as the initiator between 20°C and 70°C. Together with amounts of methyl methacrylate and toluene the same as those mentioned above, 0.1 g. of B.P.O. was sealed in a reaction vessel which had previously been flushed with nitrogen. Then the vessel was kept turning round in a constant temperature bath. At temperatures higher than 100°C, thermal polymerizations were employed. After an appropriate reaction time, the polymerization was stopped and the polymer products were poured into methanol. Then the precipitates were reprecipitated from an acetone solution and was dried in vacuo at about 50°C.

Polymerization Using Grignard's Reagent Catalysts.—*n*-Butylmagnesiumbromide and isobutylmagnesiumbromide were prepared as solutions in

TABLE I. POLYMERIZATION CONDITIONS OF METHYL METHACRYLATE POLYMERS

Sample No.	Catalyst	Solvent for polymerization	Polymerization temp., °C.
1	Benzoin+UV	Toluene	−35
2			−25
3			−15
4	B.P.O.	Toluene	0
5			20
6			40
7			70
8	—	Toluene	100
9			150
10	Di-*n*-butylmagnesium	Toluene	−50
11	Isobutylmagnesiumbromide		−50
12	*n*-Butylmagnesiumbromide		−50

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* Part of this paper was presented at the Annual Meeting of the Physical Society of Japan, Sapporo, September, 1960.

[1] F. A. Bovey and G. V. D. Tiers, *J. Polymer Sci.*, **44**, 173 (1960).

[2] A. Nishioka, H. Watanabe, I. Yamaguchi and H. Shimizu, ibid., **45**, 232 (1960).

[3] U. Johnsen and K. Tessmar, *Kolloid Zeits.*, **168**, 160 (1960).

[4] H. Watanabe and Y. Sono, paper presented at the Local Meeting of the Chemical Society of Japan, Nagoya, November, 1958.

[5] T. G. Fox, W. E. Goode, S. Gratch, C. M. Huggett, J. F. Kincaid, A. Spell and J. D. Stroupe, *J. Polymer Sci.*, **31**, 173 (1958).

[6] J. D. Stroupe and R. E. Hughes, *J. Am. Chem. Soc.*, **80**, 2341 (1958).

[7] T. G. Fox, B. S. Garrett, W. E. Woode, S. Gratch, T. F. Kincaid, A. Spell and J. D. Stroupe, ibid., **80**, 1768 (1958).

[8] U. Baumann, H. Schreiber and K. Tessmar, *Makromol. Chem.*, **36**, 81 (1960).

[9] H. Watanabe, K. Abe, Y. Sono and A. Nishioka, paper presented at the International Symposium on Macromolecular Chemistry, Moscow, June, 1960. A. Nishioka, H. Watanabe, K. Abe and Y. Sono, *J. Polymer Sci.*, **48**, 241 (1960).

[10] W. E. Goode, F. H. Owens, R. P. Fellman, W. H. Snyder and J. E. Moore, ibid., **46**, 317 (1960).

[11] H. Watanabe, Y. Kato and A. Nishioka, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **65**, 270 (1962)

toluene. For the former, for instance, polymerization was carried out by adding it (along with 2.54×10^{-3} mol. of bromine) to a mixture of 40 ml. of toluene and 20 ml. of methyl methacrylate at −50°C. A similar polymerization was made using di-*n*-butylmagnesium as a catalyst to examine the effect of the chemical components of the catalyst on the structure of the polymer. The polymerization conditions of methyl methacrylate are shown in Table I.

NMR Spectra.—The instrument employed for these measurements was a Varian Model V-4300-C spectrometer operating at 56.4 Mc./s. Spectra were taken at 20°C, using about 0.5 ml. of the solution of the polymer in ethanol-free chloroform (3% W/V). Since tetramethylsilane as an internal standard was not available, the scale of the abscissa of Fig. 1 is expressed in parts per million, with reference to the peak due to the methoxy group ($-OCH_3$). Three characteristic peaks at the right of the spectrum are assigned to α-methyl groups of the polymer. Since their relative intensities play an important role in our discussion, the spectra were exactly traced on section paper and were decomposed into three symmetrical peaks one by one, while the total area of the three peaks was kept unchanged. These trials should be repeated until a satisfactory similarity among the corresponding isolated peaks of all spectra is attained. Once a reasonable decomposition is accomplished for one spectrum, the results may be applied to another. It seems that for our spectra the values of the relative area thus obtained are more accurate than those measured with a planimeter.

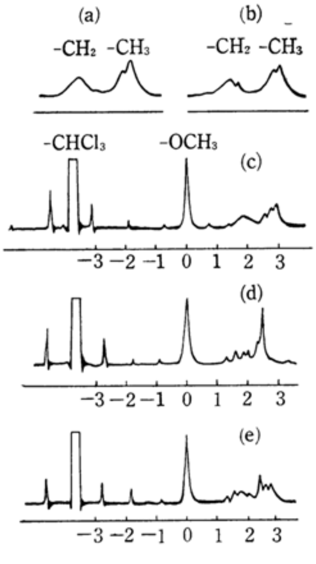

Fig. 1. NMR spectra of 3 per cent chloroform solutions of polymethyl methacrylates, obtained at 56.4 Mc./sec. and 20°C.

(a) sample 6 (b) sample 8
(c) sample 10 (d) sample 11
(e) sample 12

Results and Representation

Some examples of the results are shown in Fig. 1. There are remarkable changes in both the $-CH_2$ and α-CH_3 regions. Especially, the relative intensities of the three peaks at the right vary with the conditions of polymerization, while their peak positions remain unchanged. As one of the authors[2,4] and other workers[1,3] have already mentioned, these changes in spectra are caused by an magnetic anisotropy effect of the ester carbonyl groups in combination with the conformation and stereochemical configuration of these polymer chains. Every monomer unit in a polymer chain of methyl methacrylate has an asymmetric carbon atom, and its placement may be designated as *d* or *l*. For the sake of convenience, they will be replaced in this paper by 0 and 1 respectively. It doesn't matter whether an arbitrary monomer unit in the polymer chain is represented by 0 (or 1). Assuming that any one of these monomer units corresponds to 0 (or 1), all the other monomer units may be classified without ambiguity. Assume two operators "⊕" and "⊜", similar to logical symbols, as follows:

a	b	⊕ $\{ab\}$,	⊜ $\{ab\}$
0	0	0	I
0	1	1	D_1
1	0	1	D_2
1	1	0	S

where the letters *a* and *b* represent either 0 or 1, and *ab* represents two consecutive digits formed in a binary sequence of 0's and 1's. The bottom row of this table, for instance, means that every pair of 1's (.... 1 1 ....) in the binary sequence must be replaced by 0 after the operation "⊕." Therefore, a binary sequence of ten digits long (for example,

$A=1\,1\,0\,0\,0\,1\,0\,1\,0\,0$),

is transformed into:

$B=$⊕$\{A\}=0\,1\,0\,0\,1\,1\,1\,1\,0$,

where *A* denotes the sequence *A*, the length of which is always reduced by one digit after the operation. In a like manner, every pair of 1's in the binary sequence must be changed to *S* by the operation "⊜." When the above-mentioned meaning of 0 and 1 is taken into account, the binary sequence *A* may be recognized as a partial model of the polymer chains we are concerned with, and sequence *B* represents the states of the bonds of the monomer units which together construct the polymer chain. Applying operation "⊜" to the sequence *B* yields a sequence

$$C = ⊜\{B\} = ⊜⊕\{A\} = D_1D_2ID_1SSSD_2,$$

where *D*'s are the units which break *I*- or *S*-sequences. We have called them "ditactic" (or di-syndiotactic) units in the meaning of the sequence *A*, because they themselves alone are constructed to the sequence as follows:

..... 1 1 0 0 1 1 0 0 1 1 0 0 .....

D-units as defined here are exactly the same as Bovey's *h*-units,¹⁾ which were called "heterotactic configurations" (i. e., *ldd*, *dll*, *ddl*, or *lld*). It is apparent that in the sequence ⊜ ⊕ $\{A\}$, D_1's and D_2's appear in couples, sometimes by turns, and sometimes at both ends of *I*- or *S*-subsequences. Therefore, in an infinite sequence, both D_1 and D_2 should have the same probability of occurrence. In addition to this, it may be pointed out that even *D*'s appear between two *I*- or *S*-subsequences, while odd *D*'s are allowed to exist between *I*- and *S*-subsequences.

The facts that the α-methyl peak in general splits into three peaks and that the relative intensitites vary noticeably, suggest that every successive three-monomer unit in the polymer chains contributes to their peak intensities. From the viewpoint of nuclear magnetic resonance phenomena, the α-methyl group of any monomer unit is not affected very much by the other monomer units, except by the nearest neighbors on both sides. From the same point of view, we may explain that D_1- and D_2-units are essentially the same and that the α-methyl groups of polymethyl methacrylate are now classified into three species symbolized by *I*, *D* and *S*. It is conceivable that there exists a close relationship between these three species of α-methyl groups and the three α-methyl peaks in Fig. 1. The much useful information[4,5,12] so far obtained about the polymerization of methyl methacrylate leads to the following conclusion: The three α-methyl peaks are due to *I*-, *D*- and *S*-units, from left to right, respectively. The relative area of each peak is proportional to the ratio of the corresponding units to the whole polymer chain. Figure 1 shows that the left peak, ascribed to *I*-units, is very high in the spectrum of polymers using isobuthylmagnesiumbromide as a catalyst. On the contrary, for samples prepared with free radical initiators, the other two peaks are moderately high, and a tendency towards decreasing *S*-units can be observed as the polymerization temperature increases. The spectrum of the sample polymerized with di-*n*-butylmagnesium is a typical one; in it these three peaks are competitively high. It should be noticed that the *D*-unit of the polymer chains has been detected for the first time; no method except high resolution NMR is available at present for the direct measurement of the unit.

In order to facilitate the representation of the fractions of three units which appear in a sequence ⊜ ⊕ $\{A\}$, a ternary diagram as shown in Fig. 2 was employed. Any point plotted in the ternary diagram represents only one type of stereochemical configuration of the polymer chain, because the corresponding *I*-, *D*- and *S*-units are always unique in their proportions. The apex at the top of the diagram is assumed to correspond to the configuration of polymer chains including only *D*-units; the others give, respectively, the configurations of pure isotactic and syndiotactic polymer chains in the meaning of Natta.[13] Making use of a geometrical theorem, the relation:

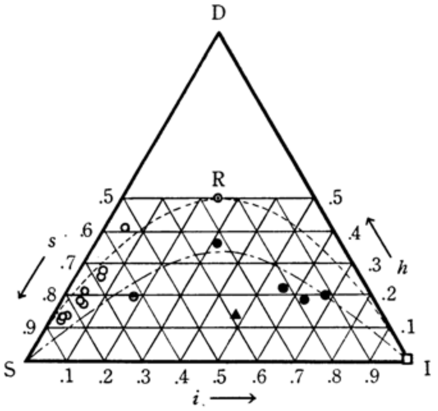

Fig. 2. Ternary diagram illustrating the stereochemical configuration of molecular chains of polymethyl methacrylate.

$$i + h + s = 1 \tag{1}$$

is valid for any point in the ternary diagram, where *i*, *h* and *s* represent the probabilities of finding *I*-, *D*- and *S*-units respectively in a sequence ⊜ ⊕ $\{A\}$. The dotted curve, *S R I*, and the point, *R*, will be discussed in the following section. Table II presents the results of quantitative measurements of the relative contributions due to three α-methyl peaks of the polymers prepared in various polymerization conditions. They correspond to the plots shown in Fig. 2.

For the methylene peaks of polymethyl methacrylate, a striking difference is found between the spectra of isotactic and syndiotactic polymethyl methacrylates. A quartet

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[12] R. G. J. Miller, B. Mills, P. A. Small, A. Turner-Jones and D. G. M. Wood, *J. Chem. Ind.* (*London*), **1958**, 1323.

[13] G. Natta, *J. Polymer Sci.*, **34**, 3 (1959).

due to the methylene protons of the polymer can be observed in the former, while there is only a single, though rather broad peak in the latter. This point may be explained on the basis of the NMR spectrum of AB system.[14] Two protons of a methylene group are thought to be non-equivalent when they are just on the "0" bond in an infinite sequence, ⊕ $\{A\}$. They, therefore, give rise to absorption lines which consist of a pair of doublets. In case they are on the "1" bond, they are equivalent and yield a single absorption peak. The values of the chemical shift, $(\delta_A - \delta_B)$, and the coupling constant, J_{AB}, as estimated from the spectrum of sample 11 in Fig. 1, are 37.0 c/s and 15.5 c/s respectively. These values are well in accordance with those obtained by Bovey et al.[1,3] In view of the above discussion, it is apparent that the configuration of the polymer chains can be determined in this case, not in the meaning of the sequence ⊜ ⊕ $\{A\}$, but in that of the sequence ⊕ $\{A\}$. That is, the information about D-units can not be obtained, at least explicitly, by the analysis of the methylene peaks in the NMR spectrum of polymethyl methacrylate.

Polymer Characterization

In the preceding section, a short description was given of how the D-units behave in the sequence ⊜ ⊕ $\{A\}$. The sequence without a D-unit represents an isotactic or syndiotactic polymer chain, which is essentially the same as defined by Natta. In this case, the number of isotactic or syndiotactic sequences is only one, and its length is two units shorter than that of the original sequence, A; in other words, the number of the units in the sequence is less by two than that of the monomer units in the polymer chain. When any D is contained in the sequence, the situation is quite different. Some of the units belonging, in a sense, to the isotactic or syndiotactic part are counted this time in the sequence of D-units. This apparently indicates that a molecular chain in which isotactic and syndiotactic parts both exist contains one D-unit or more. A stereoblock polymer may be defined as one for which h, the proportion of D's in the sequence ⊜ ⊕ $\{A\}$, is properly small in contrast with the large proportion of both I's and S's. As a general rule, the larger the proportion of D's, the shorter the average length of I- and S-sequences becomes. Each average length of sequences is a characteristic measure of the polymer chain. On some assumptions in the polymerization steps, let us consider two cases:

Case 1. A Polymer with a Probability of a Specified Bond.—As was explained in the previous section, the states of bonds may be specified by two digits, "0" and "1", in the meaning of the sequence ⊕ $\{A\}$. Let us assume that the probability of the occurrence of 0-digits in the sequence ⊕ $\{A\}$ is designated by p. In terms of polymerization, it may be defined as the probability that the monomer unit at the end of a growing chain will add another monomer of the same designation, that is, of the same placement. The expected number of times that a sequence ⊜ ⊕ $\{A\}$ of the length N will contain the subsequence of I-units of the length k is given by:

$$\overline{X}_{I,k}=(N-k-1)p^{k+1}(1-p)^2+2p^{k+1}(1-p) \tag{2}$$

for $k \leqq N-1$, and

$$\overline{X}_{I,N}=p^{N+1} \tag{3}$$

which are easily derived from the calculation of the number of times that a binary sequence ⊕ $\{A\}$ of the length $(N+1)$ includes consecutive 0-digits of the length $(k+1)$. Hence, the number of I-units in the sequence ⊜ ⊕ $\{A\}$ is:

$$\begin{aligned}[I] &= \sum_{k=1}^{(N+1)p-1} k\{(N-k-1)p^{k+1}(1-p)^2 \\ &\quad +2p^{k+1}(1-p)\}=p(1-p)\{(N-1)(1-p) \\ &\quad +2\}\sum_{k=1}^{(N+1)p-1} kp^k-p(1-p)^2\sum_{k=1}^{(N+1)p-1} k^2p^k\end{aligned} \tag{4}$$

The number of successive I-units of the length k included in the sequence ⊜ ⊕ $\{A\}$ is also given by:

$$\begin{aligned}[\{I\}] &= \sum_{k=1}^{(N+1)p-1} \{(N-k-1)p^{k+1}(1-p)^2 \\ &\quad +2p^{k+1}(1-p)\}=p(1-p)\{(N-1)(1-p) \\ &\quad +2\}\sum_{k=1}^{(N+1)p-1} p^k-p(1-p)^2\sum_{k=1}^{(N+1)p-1} kp^k\end{aligned} \tag{5}$$

When N is very large, Eqs. 4 and 5 are approximated as follows:

$$[I] \approx p(1-p)^2N\sum_{k=1}^{\infty}kp^k=p^2N \tag{6}$$

$$[\{I\}] \approx p(1-p)^2N\sum_{k=1}^{\infty}p^k=p^2(1-p)N \tag{7}$$

For an infinite sequence, it is necessary to take the limit of Eqs. 4 and 5. Thefore, the average length of successive I-units in the sequence ⊜ ⊕ $\{A\}$ is given by

$$\langle I\rangle=\lim_{N\to\infty}\frac{[I]}{[\{I\}]}=\frac{1}{1-p} \tag{8}$$

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[14] H. J. Bernstein, J. A. Pople and W. G. Schneider, *Can. J. Chem.*, 35, 65 (1957).

In like manner, results are obtained for S-units:

$$[S]=(1-p)^2N \tag{9}$$

$$\langle S\rangle=1/p \tag{10}$$

The summations, however, of even and odd D's must be taken separately, since even D's come into existence only between two I- or S-subsequences, while odd D's come into existence between I- and S-subsequences. Thus, the number of D-units can be obtained straightforwardly:

$$\begin{aligned}[D]=&\\ &\{p^3+(1-p)^3\}\sum_{k=1}^{(N+1)p-1}\{2k(N-2k-1)p^k(1-p)^k\}\\ &+2\{p^2+(1-p)^2\}\sum_{k=1}^{(N+1)p-1}2kp^k(1-p)^k\\ &+2p(1-p)\sum_{k=1}^{(N+1)p-1}\{(2k-1)(N-2k)p^k(1-p)^k\}\\ &+2\sum_{k=1}^{(N+1)p-1}(2k-1)p^k(1-p)^k\end{aligned} \tag{11}$$

and

$$\begin{aligned}[\{D\}]=&\\ &\{p^3+(1-p)^3\}\sum_{k=1}^{(N+1)p-1}(N-2k-1)p^k(1-p)^k\\ &+2\{p^2+(1-p)^2\}\sum_{k=1}^{(N+1)p-1}p^k(1-p)^k\\ &+2p(1-p)\sum_{k=1}^{(N+1)p-1}\{(N-2k)p^k(1-p)^k\}\\ &+2\sum_{k=1}^{(N+1)p-1}p^k(1-p)^k\end{aligned} \tag{12}$$

where it is assumed that $p\leqq 1/2$. For $p>1/2$, the results do not differ from Eqs. 11 and 12 except that p and $(1-p)$ replace each other. Taking the limit of the summations in Eqs. 11 and 12 gives the final results:

$$[D]\approx 2p(1-p)N \tag{13}$$

$$[\{D\}]\approx p(1-p)N \tag{14}$$

It is very interesting that the average length of successive D-units becomes equal to two units; that is,

$$\langle D\rangle=2 \tag{15}$$

If we divide the number of units of each species by the total number of units in the sequence, we get the probability of the occurrence of the unit in the sequence; therefore, for this case Eqs. 6, 9 and 13 give:

$$i=p^2 \tag{16}$$

$$s=(1-p)^2 \tag{17}$$

$$h=2p(1-p) \tag{18}$$

where i, s and h are the same probabilities that appeared in Eq. 1. Eliminating the parameter, p, from Eqs. 16 to 18, we find that

$$h/2=\sqrt{i\cdot s} \tag{19}$$

This relationship can be seen in Fig. 2 as a dotted locus $S\,R\,I$. When the probability of making a 0-digit in a sequence ⊕ $\{A\}$ is given, the structure of the sequence ⊜ ⊕ $\{A\}$ is always represented by one of the points just on the locus $S\,R\,I$. In terms of our experiments, this may be explained as follows. If the manner of the monomer addition, that is, the state of the bond, is specified by a single probability, p, the α-methyl groups of the polymethyl methacrylate so obtained give a spectrum which can be represented by a point on the curve $S\,R\,I$. The point "R" in the ternary diagram is of great interest because the value of p just equals one-half. This means that it exactly corresponds to the so-called random polymerization, and that, if the above mentioned probability is applicable, it may be considered as a special case of this model.

Case 2. The Stereoblock Polymer.—It is very difficult to put bounds to "stereoblock" polymers. According to the designation of the placements, they are composed of two kinds of blocks, such as 00000 and 111, which are formed alternately in the polymerization steps. When the lengths of these subsequences are rather too short, the polymer is no longer a stereoblock one. In all cases, however, the sequence lengths of D-units in the sequence ⊜ ⊕ $\{A\}$ should remain short. For the sake of simplicity, it is assumed that any D-unit appears "solo" throughout this section; two special cases, corresponding to two different mechanisms of polymerization, will be treated below.

First, we assume an infinitely long polymer chain in which isotactic and syndiotactic blocks appear "alternately" and in which the number of monomer units in the blocks varies from three to infinity. As an example, all sequences of "specified bonds" including any single 0-digit, such as

...... 1 1 1 1 0 1 1 1 ......

are excluded, since it is transformed by the operator "⊜" into:

...... $I\,I\,I\,D\,D\,I\,I$ ......

Then, for the I- and S-parts of the stereoblock polymer chain, it is found that

$$[\{I\}]=[\{S\}]=$$
$$(i+s)N\sum_{k=1}^{\infty}\left(\frac{i}{i+s}\right)^{k}\left(\frac{s}{i+s}\right)^{2}=\frac{is}{i+s}N \tag{20}$$

for the very large integer, N, which equals the number of monomer units contained in the polymer chain. The other notations in Eq. 20 are exactly the same as those mentioned in the preceding section. By using the relation:

$$[\{I\}]+[\{S\}]=[\{D\}] \tag{21}$$

which holds for infinite sequences, the number of subsequences of D-units is given by:

$$[\{D\}]=\frac{2}{1/i+1/s}N \tag{22}$$

which leads to:

$$h=\frac{2}{1/i+1/s} \tag{23}$$

since it is assumed that $[D]=[\{D\}]=hN$. $\langle I\rangle$ and $\langle S\rangle$ in this case can be represented by i, h and s:

$$\langle I\rangle=2i/h \tag{24}$$

$$\langle S\rangle=2s/h \tag{25}$$

The chain curve plotted in Fig. 2 exhibits the relation among i, h and s given by Eq. 23. If we accept the above model, this curve represents the spectra of the α-methyl groups of the methyl methacrylate polymer chains which would be formed in a manner that alternations from an isotactic chain growth to a syndiotactic one and vice versa occur quite at random.

In the second place, let us discuss the polymer chain designated by the following sequence:

$$\cdots\cdots D\,\overbrace{I\,I\cdots\cdots I\,I}^{\langle I\rangle}\;D\,\overbrace{S\,S\cdots\cdots S}^{\langle S\rangle}\;D\cdots\cdots$$

in which isotactic blocks of length $\langle I\rangle$ and syndiotactic blocks of length $\langle S\rangle$ are formed alternately, leaving single D-units at every change. Then, we have

$$i=\langle I\rangle/(\langle I\rangle+\langle S\rangle+2) \tag{26}$$

$$s=\langle S\rangle/(\langle I\rangle+\langle S\rangle+2) \tag{27}$$

$$h=2/(\langle I\rangle+\langle S\rangle+2) \tag{28}$$

and Eqs. 24 and 25 again hold. In this case, if the values of $\langle I\rangle$ and $\langle S\rangle$ are given, Eqs. 26 to 28 correspond to the definite plot in the ternary diagram.

Discussion

We have now reached the point where we can discuss the relation between our models and the experimental results.

If a polymerization of methyl methacrylate occurs quite at random in the meaning of stereochemical placements of the monomer units, the polymers so obtained give the spectrum of α-methyl groups which may be represented by the point R in Fig. 2. All the experimental results, however, are scattered far from the point. This apparently indicates that the random polymerization in the strict sense can not be achieved, even if a free radical polymerization at a high temperature is employed. We may also conclude from Fig. 2 that essentially different mechanisms of polymerization give polymers of different structures. For polymers prepared with free radical initiators, the model described in the previous section (see Case 1) seems to be applicable. The probability, p, can be calculated by Eq. 17; the results are shown in Table II. It is conceivable that p depends almost entirely upon the polymerization temperature of the sample.

TABLE II. CHARACTERISTIC PARAMETERS OF FREE RADICAL POLYMETHYL METHACRYLATE AS A FUNCTION OF THE POLYMERIZATION TEMPERATURE

Sample No.	Proportion of α-methyl peak area			p	$\langle I\rangle$	$\langle S\rangle$*
	i	h	s			
1	0.02	0.13	0.85	0.08	1.1	14.1
2	0.02	0.14	0.84	0.08	1.1	13.0
3	0.03	0.14	0.83	0.09	1.1	12.9
4	0.05	0.18	0.77	0.12	1.1	9.6
5	0.04	0.19	0.77	0.12	1.1	9.1
6	0.04	0.21	0.75	0.13	1.1	8.1
7	0.06	0.26	0.68	0.18	1.2	6.2
8	0.05	0.28	0.67	0.18	1.2	5.8
9	0.05	0.41	0.54	0.27	1.4	3.6

* Calculated from Eq. 34.

According to the procedure of Fordham,[15] the probability, p, may be written in the form:

$$p=\frac{k_i}{k_i+k_s} \tag{29}$$

where k_i and k_s are the rate constants for the addition of monomer units to the chain to form isotactic and syndiotactic placements respectively. We have, then,

$$\frac{k_i}{k_s}=\frac{p}{1-p}$$
$$=\exp\{\Delta(\Delta S)/\boldsymbol{R}\}\exp\{-\Delta(\Delta H)/\boldsymbol{R}T\} \tag{30}$$

where $\Delta(\Delta S)=\Delta S_i-\Delta S_s$ and where $\Delta(\Delta H)=\Delta H_i-\Delta H_s$, which are the differences in activation entropies and in activation enthalpies

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[15] J. W. L. Fordham, *J. Polymer Sci.*, 39, 321 (1959).

respectively between an isotactic placement and a syndiotactic one. Equation 30 shows that the logarithm of $p/(1-p)$ is linear in reciprocal temperature and that the values of $\Delta(\Delta H)$ and $\Delta(\Delta S)$ can be found from the slope and the intercept at $1/T=0$ respectively. In Fig. 3 are plotted the results from which we obtain :[11]

$$\Delta(\Delta H)=(1.58\pm0.07)\,\text{kcal.}$$

$$\text{and } \Delta(\Delta S)=(0.67\pm0.24)\text{ e. u.}$$

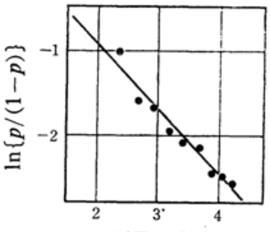

Fig. 3. $\ln\{p/(1-p)\}$ vs. $1/T$ for polymethyl methacrylate prepared in free radical polymerization.

These results are considerably larger than those obtained by other workers.[16,17] Substituting these values into Eq. 30, we find

$$\frac{k_i}{k_s}=1.95\exp(-1580/\boldsymbol{R}T) \tag{31}$$

so that from Eqs. 17 and 29, the proportion of S-units will be :

$$s=\left\{\frac{1}{1+1.95\exp(-1580/\boldsymbol{R}T)}\right\}^2 \tag{32}$$

Since the melting point of toluene is −95°C, Eq. 32 shows that the proportion of S-units attainable in practice in the polymer chain is less than 95 per cent. On the other hand, the random polymerization could be obtained, if it were possible, at about 1000°C. As a matter of fact, however, the polymerization would occur only below the ceiling-temperature[18] of the system.

Even the polymer made at room temperature contains fairly long sequences of S-units. The average sequence lengths of I- and S-units can be calculated from the equations given below:

$$\langle I\rangle=1+h/2s \tag{33}$$

$$\langle S\rangle=1+2s/h \tag{34}$$

The results are shown in Table II.

As we have seen in Fig. 2, the mechanism of anionic polymerization can not be explained by the model used for free radical polymerization. Let us now consider the applicability of the two models developed in the previous section for the stereoblock polymer. Of course, there are a few points to be clarified beforehand. First, it is very difficult to define the term "stereoblock" exactly, but no further discussion is needed here. Secondly, the polymer prepared with an anionic initiator might consist of molecular chains formed in several polymerization mechanisms, which could each perhaps be described in the same manner as the free radical polymers. The observations, however, on the difference in activation energies between isotactic and syndiotactic placements of a monomer-unit would not seem to support this assumption. The distribution range in the ternary diagram is too narrow to cover the cases of anionic polymerization. In case a sample is a mixture of polymer chains of different tacticities, its apparent i, h and s values can be calculated from these values of the componenents. In terms of the ternary diagram, this may be explained as follows. Just on each point of the ternary diagram we assume a material particle of the same mass as the corresponding component. Then, the overall structure of the sample can be represented by the center of gravity for the system of these material particles. It seems, therefore, impossible to deduce the plots for anionic polymerization products from the experimental results for free radical polymers.

As has been mentioned earlier, two models developed in the previous section for stereoblock polymers are special ones, because of their assumption that $\langle D\rangle=1$. One is a random-sequence-length model for its I- and S-parts, while the other is a constant-sequence-length model. The former is represented by the chain curve in Fig. 4. Some of the experimental results seem to satisfy Eq. 23 approximately when Bovey's data[1] are taken into account. One of our plots, however, deviates considerably from the curve. This may be partly due to the separation of three

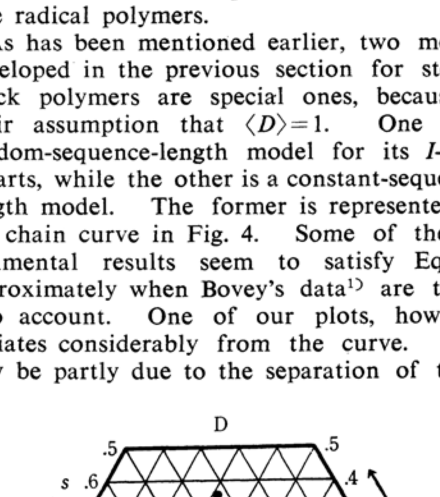

Fig. 4. Ternary diagram illustrating the stereochemical configuration of methyl methacrylate polymers prepared with anionic initiators : sample 10 ◓, sample 11 □, and sample 12 ▲, Bovey's data ●.

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[16] F. A. Bovey, *J. Polymer Sci.*, **46**, 95 (1960).

[17] T. G. Fox and H. W. Schnecko, *Polymer*, 3, 575 (1962).

[18] R. D. Snow and F. E. Frey, *Ind. Eng. Chem.* (*Industr.*), 30, 176 (1938).

rather poorly resolved α-methyl peaks, since it is attended with a little difficulty. Mainly, however, it seems to arise from the fact that the mechanism of polymerization is more complicated.

For the latter model, the avrerage sequence lenghths $\langle I\rangle$ and $\langle S\rangle$ are introduced as the parameters, but as yet we have not sufficient information to evaluate them. Using the values of samples 10 and 12, we obtain $\langle I\rangle=1.8$ and $\langle S\rangle=6.2$ for the former and $\langle I\rangle=7.5$ and $\langle S\rangle=5.8$ for the latter. We might say that the steric hindrance for each stereochemical configuration of molecular chains would be one of the origins that make blocks of a constant length. It seems, however, rather improbable that such a long and constant sequence length as calculated above could be ascribed to this origin. On the contrary, it seems possible that in anionic polymerizations the behavior of metallic counterions brings us stereoblock polymers.(1) One example is that a metallic counterion contributes to the isotactic chain growth for a certain period, and then leaves from the chain end for the following period, allowing the syndiotactic chain growth. Alternation between these two states yields a stereoblock polymer chain, but this case would preferably be included in our former model. In actual fact, the mechanism of anionic polymerization is beyond our depth because of its complexity.

In the course of the decomposition of spectra, we found that, at room temperature, the *I* part of methyl methacrylate polymer chains gives a somewhat narrower resonance peak of α-methyl groups than that ascribed to the *S* part. Recently, at a higher temperature, we have observed the inversion of apparent peak heights between *I*- and *S*-peaks in some of the stereoblock polymers. This probably corresponds to the remarkable difference in glass temperature between isotactic and syndiotactic polymethyl methacrylates.(7) The detailed investigation of these problems must be the subject of future research.

Summary

The NMR spectra of polymethyl methacrylates prepared with various initiators have been examined. Three resonance peaks of α-methyl protons observed with an increasing magnetic field correspond to three species of the monomer units, i. e., *I*-, *D*- and *S*-units respectively. The proportion of each peak area may be used to characterize the stereoregularity of the polymer chain. A ternary diagram has been proposed to represent the stereochemical configuration of the polymers. Together with the average sequence lengths of the units, the possible polymerization mechanisms are considered. Free radical polymers of methyl methacrylate seem to be describable with a single parameter which depends only on the polymerization temperature. Some polymers prepared with anionic initiators show a stereoblock character. The polymerization mechanism has also been discussed in some idealized cases.

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