*Nuclear Magnetic Resonance Spectra of Polymethyl Methacrylate in Solution. II. The Calibration of the Infrared Absorption Method and Some Applications to the Study of the Polymerization Mechanism**

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In the preceding paper,[1] it was shown that the degree of the stereoregularity of polymethyl methacrylate could be determined from the NMR spectrum by analyzing three peaks due to α-methyl protons. The proportions of their areas were represented in the ternary diagram with a single point. For free radical polymers, the plots were found to be in good accordance with a relationship that was represented by a unique curve in the diagram. It was also found that the manner of the growth of the molecular chains in free radical polymerization could be described by a single parameter, p, which depends only upon the polymerization temperature. On the other hand, polymers prepared in anionic polymerization exhibited quite different stereochemical configurations from those obtained in free radical polymerization, depending on the initiators employed.

It is the purpose of this paper to extend our method further and to apply it, as far as possible, to the investigation of the anionic polymerization mechanisms. As a matter of convenience, the infrared method[2] calibrated by our NMR method has been frequently employed for the measurement of the stereoregularity. The same notations as have been discussed in the previous paper will be used here.

Experimental

The preparation of samples and the NMR spectra have already been described in the preceding paper.[1] The infrared spectra were observed with a Hitachi EPI-2 infrared spectrometer. In order to improve the reproducibility of the results, the sample films were made on glass plates from a benzene solution by evaporating the solvent. So far as we know, benzene is the best solvent to use to obtain sample films uniform in thickness. Two pairs of bands of the infrared spectra, i. e., the 1063 cm^{-1} and 1393 cm^{-1} and the 749 cm^{-1} and 757 cm^{-1} bands, were used to estimate the fractions of the S- and I-parts of the sample respectively.[2,3] The rest was taken to be the D-part. The estimations were based on a quantitative curve which had been obtained through the analysis of mixtures of two samples. The infrared spectrum of a "stereoblock polymer" is exactly the same as that of a mixture of isotactic and syndiotactic polymers if the proportions of their quantities are appropriately chosen. Therefore, two standard samples were employed to fix the quantitative curve; one was a polymethyl methacrylate prepared with benzoyl peroxide at −35°C, and the other was a sample obtained with phenylmagnesium bromide at 20°C. The stereochemical configurations of these samples were determined by the NMR method. For the former, s=0.85 and h=0.13, while for the latter almost all of the monomer placements in the molecular chains were recognized as isotactic. Taking account of these findings, the samples were mixed in various proportions to

TABLE I. COMPARISON OF THE TACTICITY MEASUREMENTS OF POLYMETHYL METHACRYLATE BY TWO METHODS

Polymerization temp., °C	NMR method		IR method	
	h	s	h	s
−35*	0.13	0.85	0.13	0.85
−25	0.14	0.84	0.15	0.83
−15	0.14	0.83	0.17	0.81
0	0.18	0.77	0.19	0.78
20	0.19	0.77	0.23	0.74
40	0.21	0.75	0.26	0.70
70	0.26	0.68	0.29	0.65
100	0.28	0.67	0.30	0.62
150	0.41	0.54	0.37	0.55
—**	0.14	0.40	0.14	0.38

* One of the two standard samples employed to calibrate the IR method.

** Polymer prepared with Grignard's reagent as a catalyst; other samples were made in a free radical polymerization.

* Part of this paper was presented at the Annual Meeting of the Physical Society of Japan, Matsumoto, May, 1961. This paper was also read at the 1st Symposium on "The Application of High Resolution Nuclear Magnetic Resonance Spectroscopy to Chemistry," Tokyo, November, 1961.

1) Y. Kato and A. Nishioka, This Bulletin, 37, 1614 (1964).

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

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

obtain the infrared spectra. Once the quantitative curve is fixed, the estimation of the degree of stereoregularity for any polymethyl methacrylate becomes possible. Part of the results, together with those obtained by the NMR method, are given for ready comparison in Table I. There is practical agreement between these two sets of results. Therefore, they will be used without distinction throughout the rest of this paper.

The extraction of the sample with acetone was carried out at room temperature in order to measure the stereoregularities of both the extract and the residue. If any difference is found between them, the process of polymerization will consist of more than one mechanism.

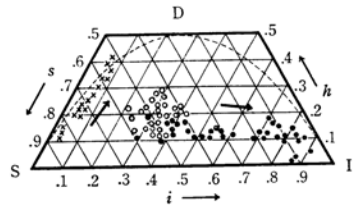

Fig. 1. Ternary diagram representing the stereoregularities of polymethyl methacrylates prepared with free radical initiators (×), and anionic initiators: R_2Mg (○), and RMgBr (●). Two bold arrows indicate how the stereoregularities vary as the polymerization temperature increases.

Results

To examine the habit of distribution in the ternary diagram, many samples, prepared with different catalysts at various polymerization temperatures, were used. The results are shown in Fig. 1. Most of them were obtained by the infrared method described above. The types of catalyst for our anionic polymerization of methyl methacrylate may be represented as RMgBr and R_2Mg, where R indicates an alkyl group, and so on. For our experiments, ethyl, *n*-butyl, *n*-propyl, *n*-amyl, *n*-heptyl and phenyl groups have been taken as R in RMgBr, and, again, ethyl, *n*-butyl, isobutyl, phenyl and cyclohexyl groups as R in R_2Mg.

From Fig. 1 it may be seen that the polymer prepared with an R_2Mg-type catalyst, especially at 0°C and below, seems to have a rather constant stereochemical configuration regardless of the polymerization temperature and the species of R. As compared with the above polymer, the stereochemical configuration of the polymer with RMgBr as a catalyst is more isotactic and varies to a considerable degree with the polymerization temperature. The bold horizontal arrow in Fig. 1 indicates how the configuration changes as the polymerization temperature increases from −78°C to 20°C.

It is not correct to base discussions of the mechanism of polymerization upon the apparent stereochemical configuration of the polymer chains if the apparent configuration is not homogeneous. In fact, the extraction of the samples with acetone frequently resulted in two components with different stereoregularities. For polymers made with R_2Mg as the catalyst, the extracted components include more *D*-units than the residues. On the other hand, samples with RMgBr as the catalyst seem to contain both isotactic (the extracts) and stereoblock (the residues) components. In Fig. 2 are collected the results of the extraction with acetone. As has been mentioned previously, a mixture of two components of different stereoregularities exhibits an average stereochemical configuration. This configuration can be represented, in terms of our ternary diagram, by the point which divides the distance between the two plots corresponding to the two components in the inverse ratio of each weight. Therefore, in order to discuss the mechanism of the polymerization, it is necessary to weigh both the extract and the residue separately. Otherwise we can not say which mechanism is more important in the course of polymerization. These average configurations are also shown in Fig. 2.

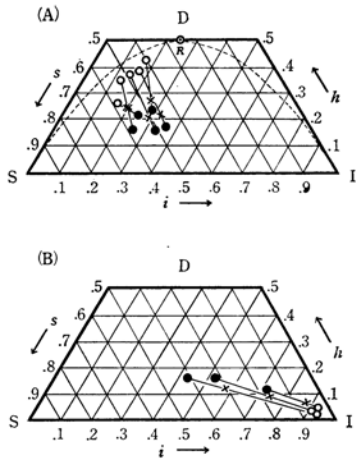

Fig. 2. Ternary representation of the stereoregularities of the acetone-extract (○) and the residue (●) of the samples: (A) with R_2Mg, at −50°C; (B) with ethylmagnesiumbromide; at −40, −20 and −10°C. The average configurations of unseparated samples are represented by the crosses, ×.

Statistical Treatment. — In the preceding paper, a simple statistical method was applied to some cases.

Here we will initially consider the concept of the Ising model, which has been used in formulating the statistical mechanics of the

linear chain.[4] In has also been applied in an extended way to a problem of the polymer chain by Chûjô and Miyake.[5] Since the proportions of *I*-, *D*- and *S*-units in the polymer chains are given through the analysis of the NMR spectrum, the statistical method can be applied to interpret any locus in the ternary diagram which corresponds to the change in stereoregularity of polymers with the polymerization temperature under the conditions of a definite type of catalyst. For free radical polymers, however, the situation is so simple that, on the basis of the statistics, we can discuss the mechanism of the polymerization itself.[1]

In order to cover all the distributions of the plots in the ternary diagram, two parameters must be introduced, because the degree of freedom of our data obtained from NMR measurements is two by nature; that is the proportions of stereoregularity of the three components, *i*, *h* and *s*, always satisfy the relationship;

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

and, therefore, only two of them are independent.

We define a transition matrix as:

$$A=\begin{array}{c} \\ 0 \\ 1 \end{array}\begin{array}{c} \begin{array}{cc} 0 & 1 \end{array} \\ \begin{pmatrix} BC & B^{1/2} \\ B^{1/2} & 1 \end{pmatrix} \end{array} \tag{2}$$

where B and C are the parameters whose physical meanings are to be clarified in connection with the polymerization reaction. The notations of rows and columns are the same as those defined with the sequence $\oplus\{A\}$, which represents the states of bonds. Let us denote the product of the matrix as:

$$A^n=\overbrace{A\times A\times\cdots\cdots\times A}^{n} \tag{3}$$

Then it can easily be shown that the element of A^n, for example, in the upper row and the right column represents the possible transitions which begin with the state "0" and end in the state "1". The number of ways of transition equals 2^{n-1}, the same as the number of terms contained in the matrix element. The correspondence between the element expressed by B and C and the binary sequence of 0's and 1's, that is, the sequence $\oplus\{A\}$, is illustrated (for $n=10$) in the following example:

$$\begin{array}{cccccccc} 0 & 0 & 1 & 0 & 0 & 1 & 0 & \\ BC\times & B^{1/2}\times & B^{1/2}\times & BC\times & B^{1/2}\times & B^{1/2}\times & B^{1/2}\times & \\ 1 & 0 & 1 & 1 & : & \oplus\{A\} & & \\ \times B^{1/2}\times & B^{1/2}\times & 1 & = & B^{11/2}C^2 & & & \end{array}$$

From this, we may say that the matrix element increases by the factor of B when any 0 occurs in the sequence $\oplus\{A\}$, and by the factor of C only when a 0-0 pair is formed in it. The square root of B in Eq. 2 was taken so as to prevent the double counting of 0's. Since the above-mentioned 0-0 pair represents two isotactic placements among three consecutive monomer units, we may say that C in Eq. 2 has been introduced to denote a kind of longer-range effect which will occur within the three consecutive monomer units. As is always the case with very long chains,[6] we can close the sequence $\oplus\{A\}$ on the assumption that the first digit is equal to the last one. On this assumption, the off-diagonal elements of the matrix A^n vanish for the large integer, N. Our next problem is to calculate only the sum of the diagonal elements which will contain, on our assumption, all the possible sequences of $\oplus\{A\}$. In practice, however, the sequences are represented by two parameters, B and C, in the sum instead of by 0 and 1. We designate the sum by Z. Then, for instance, the number of 0's in a possible sequence of $\oplus\{A\}$ equals the weighted mean of all the terms in Z, each weighted by the power of B. Therefore, it can be obtained as the partial derivative of $\ln Z$ with respect to $\ln B$.

It is clear that:

$$Z=\text{Trace}\,(A^n) \tag{4}$$

If we transform A into a diagonal matrix:

$$S^{-1}AS=\begin{pmatrix}\lambda_1 & 0\\ 0 & \lambda_2\end{pmatrix} \tag{5}$$

then from Eq. 4 we get:

$$\begin{aligned} Z&=\text{Trace}\,((S^{-1}AS)^n)\\ &=\text{Trace}\begin{pmatrix}\lambda_1{}^n & 0\\ 0 & \lambda_2{}^n\end{pmatrix}=\lambda_1{}^n+\lambda_2{}^n \end{aligned} \tag{6}$$

Without the loss of generality, we may assume here that $\lambda_1>\lambda_2$.

Finally, if the length, n, of the sequence $\oplus\{A\}$ tends to infinity, the smaller root, λ_2, may be neglected. That is:

$$Z\cong\lambda_1{}^n \tag{7}$$

The larger eigenvalue, λ_1, can be given from the secular equation:

$$\begin{vmatrix} BC-\lambda & B^{1/2}\\ B^{1/2} & 1-\lambda\end{vmatrix}=0 \tag{8}$$

4) H. A. Kramers and G. H. Wannier, *Phys. Rev.*, **60**, 252 (1941).

5) R. Chûjô and A. Miyake, *Busseiron-Kenkyu*, [2], **3**, 754 (1958), (in Japanese); A. Miyake, ibid., [2], **4**, 671 (1958); A. Miyake and R. Chûjô, *J. Polymer Sci.*, **46**, 163 (1960).

6) E. W. Montroll, *J. Chem. Phys.*, **9**, 26 (1941).

and the results is:

$$\lambda_1=\frac{BC+1+\sqrt{(BC-1)^2+4B}}{2} \tag{9}$$

From this equation, the probability of the occurrence of 0's in a possible sequences of $\oplus\{A\}$ is given by:

$$P_0=\frac{1}{n}\cdot\frac{\partial \ln Z}{\partial \ln B}=\frac{\partial \ln \lambda_1}{\partial \ln B}$$

$$=\frac{BC\sqrt{(BC-1)^2+4B}+BC(BC-1)+2B}{(BC+1)\sqrt{(BC-1)^2+4B}+(BC-1)^2+4B} \tag{10}$$

and that of 1's is found to be:

$$P_1=1-P_0$$

$$=\frac{\sqrt{(BC-1)^2+4B}-(BC-1)+2B}{(BC+1)\sqrt{(BC-1)^2+4B}+(BC-1)^2+4B} \tag{11}$$

In the sequence $\ominus\oplus\{A\}$, the relationships:

$$P_0=i+h/2 \tag{12}$$

and

$$P_1=s+h/2 \tag{13}$$

must hold, where i, h and s represent the probabilities of the occurrence of I-, D- and S-units respectively in the sequence $\ominus\oplus\{A\}$. Since

$$i=\frac{\partial \ln \lambda_1}{\partial \ln C}$$

$$=\frac{BC\sqrt{(BC-1)^2+4B}+BC(BC-1)}{(BC+1)\sqrt{(BC-1)^2+4B}+(BC-1)^2+4B} \tag{14}$$

therefore, from Eq. 10 to Eq. 13, it is found that:

$$s=\frac{\sqrt{(BC-1)^2+4B}-(BC-1)}{(BC+1)\sqrt{(BC-1)^2+4B}+(BC-1)^2+4B} \tag{15}$$

$$h=\frac{4B}{(BC+1)\sqrt{(BC-1)^2+4B}+(BC-1)^2+4B} \tag{16}$$

Here we notice that when the parameter C tends to unity, these results must become as follows:[7]

$$i=B^2/(B+1)^2 \tag{14'}$$

$$s=1/(B+1)^2 \tag{15'}$$

$$h=2B/(B+1)^2 \tag{16'}$$

Equations 14' to 16' correspond to Eqs. 16 to 18 in the previous paper,[1] where only the single parameter p was introduced into our discussion. The equivalent to Eq. 19 in the paper may be obtained from Eqs. 14 to 16 as:

$$4i\cdot s/h^2=C \tag{17}$$

This means that the parameter C is a measure of the deviation from the single parameter case. When C is given, the locus in the ternary diagram will be fixed by using Eqs. 1 and 17.

Using h and s, BC and B may be represented as:

$$BC=1+\left(\frac{h}{s}\right)\left(\frac{1-2s-h}{2-2s-h}\right) \tag{18}$$

$$B=\frac{1}{4}\left(\frac{h}{s}\right)^2\left\{\frac{1}{2-2s-h}\right\} \tag{19}$$

Further, we define the following matrix to calculate the average sequence lengths in the sequence $\ominus\oplus\{A\}$:

$$\boldsymbol{G}=\begin{array}{c} \\ 0\,0 \\ 0\,1 \\ 1\,0 \\ 1\,1 \end{array}\begin{array}{c} \begin{array}{cccc} 0\,0 & 0\,1 & 1\,0 & 1\,1 \end{array} \\ \begin{pmatrix} BC & B^{2/3}C^{1/2}E & 0 & 0 \\ 0 & 0 & B^{2/3} & B^{1/3}F \\ B^{2/3}C^{1/2}E & B^{1/3} & 0 & 0 \\ 0 & 0 & B^{1/3}F & 1 \end{pmatrix} \end{array} \tag{20}$$

The derivation of the matrix element in the 00th row and the 01th column, which corresponds to an ID pair, is illustrated in the following sequence of $\oplus\{A\}$:

$$\cdots\cdots\ 1\quad 0\quad 0\quad 0\quad 1\ \cdots\cdots$$
$$1\quad B^{1/3}\quad \underbrace{B^{1/3}\ B^{1/3}}\quad 1$$
$$1\quad C\quad \underbrace{C\quad 1}$$
$$E\quad 1\quad E$$

Two temporary parameters, E and F, have been introduced into Eq. 20 to specify the pairs, ID (or DI) and SD (or DS) respectively. The secular equation of this problem is:

$$\begin{vmatrix} BC-\lambda & B^{2/3}C^{1/2}E & 0 & 0 \\ 0 & -\lambda & B^{2/3} & B^{1/3}F \\ B^{2/3}C^{1/2}E & B^{1/3} & -\lambda & 0 \\ 0 & 0 & B^{1/3}F & 1-\lambda \end{vmatrix}=0 \tag{21}$$

which is equivalent to the equation:

$$\lambda^4-(1+BC)\lambda^3+B(C-1)\lambda^2$$
$$+B(1+BC-F-BCE^2)\lambda$$
$$+B^2C(E^2+F^2-1-E^2F^2)=0 \tag{22}$$

Let us denote the largest eigenvalue by λ_2. If we replace both E and F by unity, λ_2 becomes equal to λ_1. Therefore, in our previous notation[1] we obtain:

$$[\{I\}]=\frac{n}{2}\lim_{E,F\to 1}\frac{\partial \ln \lambda_2}{\partial \ln E}$$

$$=\frac{nB^2C}{4\lambda_1^3-3(1+BC)\lambda_1^2+2B(C-1)\lambda_1} \tag{23}$$

7) A. Miyake, Private communication.

Finally, from Eqs. 9 and 23 we get:

$$\langle I\rangle = [I]/[\{I\}] = \lambda_1(\lambda_1-1)/B$$
$$= \frac{BC^2-C+2+C\sqrt{(BC-1)^2+4B}}{2} \quad (24)$$

Similarly,

$$\langle S\rangle = \frac{\lambda_1-B(C-1)}{B}$$
$$= \frac{1-BC+2B+\sqrt{(BC-1)^2+4B}}{2B} \quad (25)$$

and

$$\langle D\rangle = \frac{2\lambda_1}{BC+1} = \frac{BC+1+\sqrt{(BC-1)^2+4B}}{BC+1} \quad (26)$$

are obtained by noticing that

$$[\{I\}] + [\{S\}] = [\{D\}] \quad (27)$$

Using measurable values, these average lengths may be written in this form;

$$\langle I\rangle = 1+2i/h \quad (28)$$

$$\langle S\rangle = 1+2s/h \quad (29)$$

$$\langle D\rangle = 1+h/\{1-h-(i-s)^2\} \quad (30)$$

The same procedure has been independently developed by Miyake and Sakakibara.[8] In spite of our different interpretation of the parameters, the two sets of obtained results are easily interchangeable by replacing our BC and B parameters with their B and C^2 parameters respectively.

Discussion

Table II lists the observed results of the samples prepared in anionic polymerization. They are also shown in Fig. 2.

Since the product of the parameters B and C corresponds to the probability of forming a 0-0 pair in the sequence $\oplus\{A\}$, the polymer characterized by $BC=1$ has the same values of i and s. It is easily shown that when $BC>1$, the value of i is larger than that of s, while when $BC<1$, that of i is smaller. The average sequence lengths can be calculated from Eqs. 28 to 30; they are given in Table III.

The extraction with acetone has been made in expectation of separating the contributions from several different mechanisms which coexist in our anionic polymerization.

As for the sample prepared with an R_2Mg-type catalyst, the stereochemical configuration depends little upon the polymerization temperature, especially between $-30°C$ and $-60°C$. Therefore, the extraction was carried out only with the samples obtained at $-50°C$. It must be noticed that, in the ternary diagram, the plots for the soluble parts are located comparatively near the point, R, which corresponds to the random polymer. This implies that the configuration of these parts resembles that of the polymer made in free radical polymerization. Unfortunately, because of the narrow range of the polymerization temperature, we can not conclude at present whether or not the mechanism yielding these soluble parts may be interpreted by the single parameter p.

Assuming, however, the uniformity of stereochemical configuration in each polymer chain, it is certain that two mechanisms of polymerization take place with an R_2Mg-type catalyst. They may be ascribed to two states of the catalyst, such as the monomer state and the associated state.[9] If this is the case probably the catalyst in the former state would produce polymer chains with a configuration similar to those obtained in free radical polymerization. On the other hand, the catalyst in the latter state would have a strong influence on the addition of the monomer and yield more stereoregular polymer chains. In

TABLE II. STEREOCHEMICAL CONFIGURATIONS OF SEPARATED COMPONENTS OF THE SAMPLES PREPARED WITH ANIONIC INITIATORS

Sample No.	Polymerization temp., °C	Catalyst	Extraction with acetone	Configuration h	Configuration s
1	−40	Ethylmagnesium-bromide		0.04	0.06
2	−20		Soluble	0.04	0.03
3	−10			0.04	0.04
4	−40			0.18	0.41
5	−20		Insoluble	0.15	0.33
6	−10			0.11	0.18
7	−50	Phenylmagnesium-bromide		0.08	0.09
8	−40			0.04	0.07
9	−30		Soluble	0.04	0.05
10	−20			0.03	0.05
11	−10			0	0
12	−50			0.19	0.35
13	−40			0.15	0.35
14	−30		Insoluble	0.15	0.34
15	−20			0.16	0.22
16	−10			0.10	0.15
17	−50	Diethylmagnesium	Soluble	0.26	0.58
18			Insoluble	0.21	0.53
19	−50	Di-*n*-butylmagnesium	Soluble	0.39	0.45
20			Insoluble	0.16	0.46
21	−50	Diisobutylmagnesium	Soluble	0.36	0.53
22			Insoluble	0.16	0.59
23	−50	Diphenylmagnesium	Soluble	0.44	0.40
24			Insoluble	0.21	0.50
25	−50	Dicyclohexylmagnesium	Soluble	0.38	0.49
26			Insoluble	0.15	0.51

8) A. Miyake, and M. Sakakibara, *Rep. Progress Polymer Phys. Japan*, **5**, 257 (1962).

9) J. Furukawa, *Kagaku-no-ryoiki*, **12**, 85 (1958), (in Japanese).

Table III. Calculated parameters and average sequence lengths

Sample No.	Parameter			Average sequence length		
	BC	$B^{1/2}$	C	I	S	D
1	1.31	0.10	13.7	47.6	3.95	1.16
2	1.63	0.15	71.0	47.9	2.49	1.27
3	1.47	0.13	91.8	47.5	2.99	1.22
4	1.00	0.22	20.7	5.55	5.55	1.22
5	1.07	0.19	30.4	7.93	5.39	1.18
6	1.21	0.17	42.0	13.8	4.27	1.18
7	1.38	0.17	46.7	21.8	3.25	1.22
8	1.26	0.09	160	45.5	4.50	1.14
9	1.37	0.11	114	46.5	3.50	1.18
10	1.28	0.08	203	62.3	4.33	1.14
11	~1	—	—	—	—	—
12	1.05	0.24	17.9	5.85	4.68	1.24
13	1.06	0.18	31.0	7.66	5.66	1.18
14	1.06	0.19	30.8	7.80	5.53	1.18
15	1.21	0.24	21.4	8.75	3.75	1.24
16	1.25	0.17	45.1	16.0	4.00	1.19
17	0.68	0.35	5.50	2.23	5.45	1.46
18	0.85	0.26	12.5	3.48	6.06	1.29
19	0.65	0.59	1.89	1.82	3.30	1.74
20	0.97	0.19	27.3	5.76	6.76	1.19
21	0.51	0.53	1.80	1.61	3.94	1.77
22	0.86	0.19	23.1	4.13	8.37	1.22
23	0.65	0.70	1.32	1.73	2.82	1.88
24	0.89	0.26	13.2	3.76	5.76	1.28
25	0.56	0.57	1.76	1.68	3.58	1.78
26	0.94	0.18	30.8	5.53	7.82	1.18

fact, the results shown in Fig. 2 demonstrate that the insoluble part of the sample made with an R_2Mg catalyst has nearly the same stereochemical configuration as that of the polymer prepared with RMgBr as a catalyst. These facts may be also found from the values of the parameters $B^{1/2}$ and C collected in Table II. For each sample prepared with various R_2Mg-type catalysts, a comparison of the parameters of the insoluble part with those of the soluble one clearly shows that the value of B decreases, while that of C conspicuously increases. For the sake of simplicity, let us assume here that no essential change will occur in the S-blocks of both parts. Then, following the notations defined with the sequence $\ominus \oplus\{A\}$, the above-mentioned change of parameters indicates the possibility of forming subsequences which contain even D's between I-blocks, such as:

$$\cdots\cdots SIIIDDIIDDDDIS\cdots\cdots$$

Of course, we have no evidence to support the assumption concerning the S-blocks, so it is impossible to discuss the formation of such polymer chains. However, as has been mentioned already, from the unique locus of the plots in the ternary diagram, it seems quite reasonable to conclude that two mechanisms take place in the course of the polymerization using an R_2Mg catalyst and that they yield both atactic and stereoblock polymer chains separately.

Next, let us consider the polymers made with an RMgBr catalyst. In this case, the results of the viscosity measurement strongly suggest that the apparent difference in the configuration parameters between the soluble and the insoluble parts can not be attributed to the polymerization mechanisms alone. This point has been examined in detail using the polymer prepared at $-78°C$. The typical value of η_{sp}/C ($C=0.20$ g./100 cc.) for the soluble part in acetone is about 0.2, while that for the insoluble part is about 0.6. In spite of these broad molecular weight distributions, the average stereochemical configurations did not change with the values of conversion. On this basis, we may conclude that a single mechanism takes place in the polymerization catalyzed by RMgBr.

It has been shown that the statistical treatment of the polymer chain is a convenient method for the analysis of the polymerization mechanism. However, there is a limitation in this treatment. Since the NMR spectra of polymethyl methacrylate can only give the proportions of I-, D- and S-units in the polymer chains, any longer-range effect needs another parameter whose interpretation is not always unique. Recently several workers[8,10-12] have dealt with the data obtained from the NMR spectra, and very recently the applicability of the statistics based on these data has been discussed in detail from the viewpoint of statistical stationarity.[13]

Summary

In the preceding paper[1] it was reported that the degree of the stereoregularity of polymethyl methacrylate could be determined from the NMR spectrum through the analysis of three peaks due to the α-methyl groups. It has been found that the infrared spectrum can also give an equivalent result if it is once calibrated by the NMR method.

We have considered a statistical method to interpret any locus in the ternary diagram which corresponds to the change in the stereoregularity of polymers with the polymerization temperature and with the type of catalyst. By

10) U. Johnsen, *Kolloid Z.*, **178**, 161 (1961).
11) R. L. Miller, *J. Polymer Sci.*, **56**, 375 (1962).
12) F. P. Price, *J. Chem. Phys.*, **36**, 209 (1962).
13) B. D. Coleman and T. G. Fox, *J. Polymer Sci.*, **A1**, 3183 (1963).

introducing two parameters, the average sequence lengths of *I*-, *D*- and *S*-blocks have been calculated.

On the other hand, the acetone-extraction of the samples prepared in anionic polymerization has been carried out in order to determine the degree of stereoregularity of both the extract and the residue. From the plots in the ternary diagram, we have discussed some mechanisms of the anionic polymerization. We may conclude that two different mechanisms take place in the course of the polymerization using an R_2Mg catalyst in contrast with the polymerization catalyzed by RMgBr.

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