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Copolymerization Characteristics of Methyl Acrylate and Methyl Methacrylate. II. Analysis of Methyl Acrylate - Methyl Methacrylate Copolymers by Infrared Spectroscopy

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The infrared absorption spectra of polymers and copolymers of methyl acrylate and methyl methacrylate have been measured, and then used as the basis of a spectrophotometric method for the analysis of the copolymers. The 6.73 μ band, which may be due to methyl ($-C-CH_3$) vibration, was selected as the key band for measuring the methyl methacrylate component, while the 6.89 μ band was used as the standard. The monomer reactivity ratios for copolymerization of methyl acrylate - methyl methacrylate system have been determined to be $r_1=0.5\pm0.1$, and $r_2=2.3\pm0.4$ (M_1; methyl acrylate, M_2; methyl methacrylate) at 130°C. These values are in good agreement with those previously obtained by the deuterium tracer method. It has also been shown that the procedure used in this study is appropriate for the analyses of methyl acrylate - methyl methacrylate copolymers.

In a preceeding paper,[1] we have investigated the copolymerization kinetics of the methyl acrylate-methyl methacrylate system by using monomers containing deuterium as a tracer. As we mentioned in that paper, it is difficult to determine the composition of the copolymers of methyl acrylate and methyl methacrylate by using the conventional combustion analysis because of the similarity of the component monomers in chemical composition. In such a case, the spectrophotometric method may be useful.

When the infrared absorption spectra of the polymers and the copolymers of methyl acrylate and methyl methacrylate were measured, it was found that the ratio of the optical density of the absorption band at 6.73μ, which may be due to methyl ($-C-CH_3$) vibration, to that of the band at 6.89μ, which is probably due to methylene ($-CH_2-$) vibration, changes linearly with the change in the composition of copolymers. By using these two bands as the key bands for the analysis of the copolymer, the composition of the copolymers were determined; we also attempted to determine the monomer reactivity ratios for the copolymerization of this system.

Experimental

Copolymerization.—The methyl acrylate and methyl methacrylate monomers used in these experiments were supplied by the Mitsubishi Rayon Company. They were distilled twice under a reduced nitrogen atmosphere; the b. p.'s were 28°C/110 mmHg and 35.5°C/70 mmHg respectively. The polymerizations were carried out thermally in sealed pyrex tubes, each of which contained about 0.2 mol. of the monomer mixture and no catalyst. The tubes were kept in an oil-bath at 130°C and removed when the desired degree of conversion ($\leq 10\%$) had been reached. The polymers were precipitated from a benzene solution into methanol and dried in a high vacuum to a constant weight.

Measurements of Infrared Absorption Spectra.—The infrared spectra of the samples were measured by using a Nippon Bunko, Model SD101, double-beam spectrometer with a NaCl prism. All the samples were in the form of a solid film approximately 0.01 mm. thick; these films were prepared on a surface of mercury from the chloroform solution. The infrared spectra of polymethyl acrylate, polymethyl methacrylate, and copolymers are shown in Figs. 1—3.

In the 6—7 μ region, the spectra of polymethyl methacrylate and the copolymer show two absorption bands. The absorption band at 6.73 μ, which may be due to a methyl ($-C-CH_3$) deformation vibration,[2] decreases as the methyl methacrylate component in the copolymer decreases, and disappears in polymethyl acrylate. On the other hand, the intense band at 6.89 μ, which is probably due to a methylene ($-CH_2-$) vibration,[3] doesn't change appreciably with the change in the composition of the copolymers.

These two bands were used as a measure of methyl ($-C-CH_3$) groups and methylene ($-CH_2-$) groups respectively. The optical density at 6.73 μ, D_1 is, expressed as follows from the Beer-Lambert law:[4]

$$D_1=\log\frac{I_0{}^1}{I_1}=k_1{}^1c_1t+k_1{}^2c_2t \qquad (1)$$

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[1] M. Shima and A. Kotera, *J. Polymer Sci.*, Part A, **1**, 1115 (1963).

[2] U. Baumann, H. Schreiber and K. Tessmar, *Makromol. Chem.*, **36**, 81 (1959).

[3] W. Fuchs and D. Louis, ibid., **22**, 1 (1957).

[4] E. J. Slowinski, Jr., H. Walter and R. L. Miller, *J. Polymer Sci.*, **19**, 353 (1956).

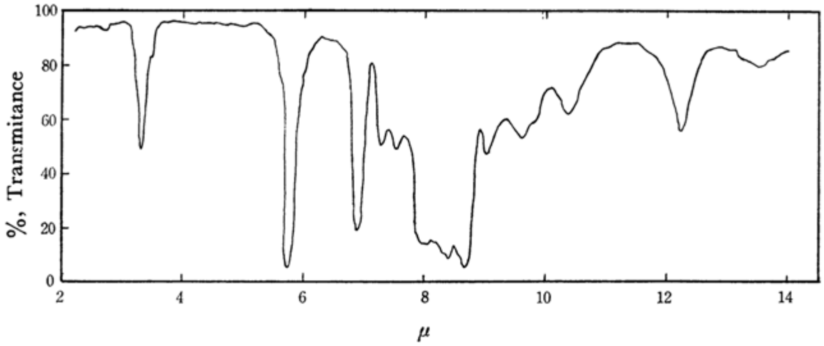


Fig. 1. Infrared spectra of polymethyl acrylate for ca. 0.01 mm. solid film.

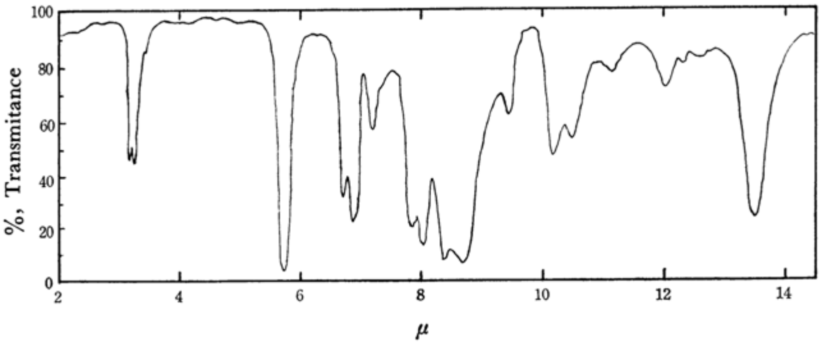


Fig. 2. Infrared spectra of polymethyl methacrylate for ca. 0.01 mm. solid film.

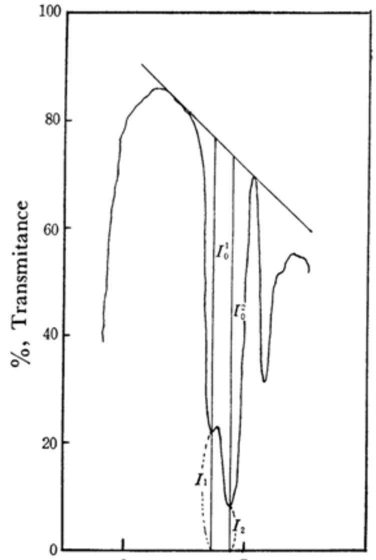


Fig. 3. The 6 to 7 μ region of a typical copolymer of methyl acrylate and methyl methacrylate.

where I is the transmission measured by the height of the absorption peak; k_1^1 and k_1^2 are the extinction coefficients of the 6.73 μ band and of the 6.89 μ band at 6.73 μ respectively; c_1 and c_2 are the number of methyl (-C-CH_3) groups and methylene (-CH_2-) groups per gram respectively, and t is the thickness of the film. The optical density at 6.89 μ, D_2, is given as:

$$D_2=\log\frac{I_0^2}{I_2}=k_2^2c_2t \tag{2}$$

where k_2^2 is the extinction coefficient of the 6.89 μ band at 6.89 μ. In order to eliminate the necessity of making an accurate measurement of the thickness of each sample, the ratio of the optical density of the 6.73 μ band, D_1, to that of the 6.89 μ band, D_2, was employed:

$$\frac{D_1}{D_2}=\frac{k_1^1\,c_1}{k_2^2\,c_2}+\frac{k_1^2}{k_2^2} \tag{3}$$

Therefore, if it is assumed that the Beer-Lambert law is valid in these samples and that the effect of methyl groups at chain ends can be neglected, a linear relationship should exist between D_1/D_2 and the mole fraction of methyl methacrylate in the copolymer, $f_2(=c_1/c_2)$.

The calibration curve was obtained from the measurements of the samples of a mixture of polymethyl acrylate and polymethyl methacrylate. All the samples were optically-uniform films which had been prepared from the chloroform solution of polymethyl acrylate and polymethyl methacrylate. The measurements for D_1/D_2 were repeated three to five times on each sample; the mean values of the measurements are shown in Table I. The data in this table are plotted in Fig. 4, where they prove the linear relation between D_1/D_2 and f_2. A least-square treatment of the points gives the following equation:

$$\frac{D_1}{D_2}=0.744(\pm 0.0018)\,f_2+0.053(\pm 0.012) \tag{4}$$

Using this equation, the composition of the copolymers in Table III was calculated.

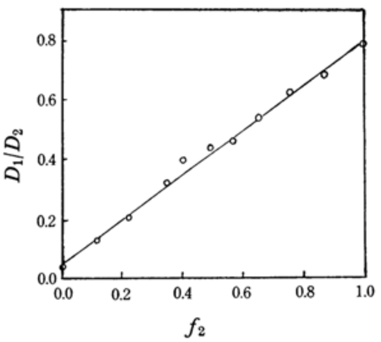


Fig. 4. Calibration curve for the composition of copolymers.

TABLE I. DATA FOR CALIBRATION CURVE

Sample	f_2	D_1/D_2
PMA	0.0000	0.0297
1	0.1133	0.129
2	0.2190	0.198
3	0.3531	0.319
4	0.3965	0.407
5	0.4886	0.445
6	0.5687	0.460
7	0.6487	0.540
8	0.7542	0.626
9	0.8736	0.678
PMMA	1.0000	0.783

f_2 is the mole fraction of methyl methacrylate in the sample. D_1 and D_2 are the optical densities of the absorption band at 6.73 μ and of the absorption band at 6.89 μ, respectively. The measurements for D_1/D_2 were repeated three to five times on each sample, and the mean values of the measurements are shown.

Results

The results of the experiments are summarized in Table II and Table III. The monomer reactivity ratios were determined by the method of Fineman and Ross.[5] The ratio of the molar concentrations of two monomers in the copolymer formed may be given by the following relation,[6] provided the conversion is low;

$$\frac{m_1}{m_2}=\frac{M_1}{M_2}\cdot\frac{r_1M_1+M_2}{r_2M_2+M_1}$$

where M_1 and M_2 represent the molar concentrations of the respective monomers in the initial monomer mixture, and where r_1 and r_2 are the monomer reactivity ratios. Fineman and Ross made the $F=M_1/M_2$ and $f=m_1/m_2$ substitutions in the above equation, and so obtained the following equations:

$$\frac{f-1}{F}=\frac{-r_2f}{F^2}+r_1 \tag{5}$$

$$\frac{F(f-1)}{f}=\frac{r_1F^2}{f}-r_2 \tag{6}$$

Thus, a plot of $(f-1)/F$ against f/F^2 yields a straight line with a slope of r_2 and an intercept of r_1, while the latter equation yields r_1 as the slope and r_2 as the intercept. The data of Table III are plotted in Fig. 5 using both Eqs. 5 and 6.

A least-square treatment of the points yields:

TABLE II. COPOLYMERIZATION CONDITION

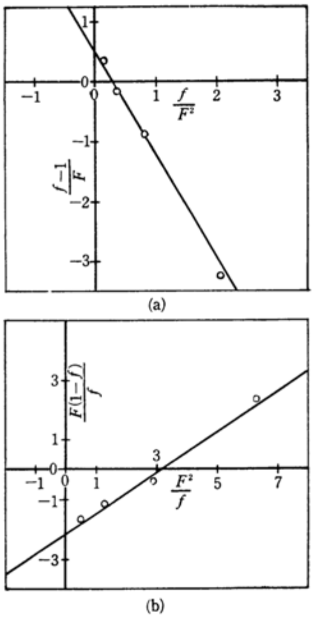
Expt. No.	F_2	Monomer g.	Polymer g.	Time min.	Conversion %
C1	1.0000	20.05	0.8066	60	4.02
C2	0.7915	19.557	0.8605	50	4.40
C3	0.5912	19.272	1.2256	55	6.36
C4	0.3971	18.392	0.9242	45	5.03
C5	0.1998	17.867	1.1491	45	6.43
C6	0.0000	29.758	16.1247	50	54.19

F_2 is the mole fraction of methyl methacrylate in the initial monomer mixture.

TABLE III. COMPOSITIONS OF COPOLYMERS

Sample	F_2	D_1/D_2	f_2
C2	0.7915	0.7047	0.876
C3	0.5912	0.5913	0.724
C4	0.3971	0.4732	0.565
C5	0.1998	0.2619	0.281

F_2 is the mole fraction of methyl methacrylate in the initial monomer mixture, and f_2 is the mole fraction of methyl methacrylate in the copolymer.



(a)

(b)

Fig. 5. Treatment of copolymer composition data by the method of Fineman and Ross. (a) using Eq. (5), (b) using Eq. (6).

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[5] M. Fineman and S. D. Ross, *J. Polymer Sci.*, **5**, 259 (1950).

[6] T. Alfrey, Jr., J. J. Boher and H. Mark, "Copolymerization," Interscience Publishers, New York (1952), p. 10.

$r_1=0.5\pm0.1$ using Eq. 5

$r_2=2.3\pm0.4$ using Eq. 6

(M_1: methyl acrylate; M_2: methyl methacrylate)

These values agree with those previously obtained by the deuterium tracer method, $r_1=0.47\pm0.09$ and $r_2=2.3\pm0.5$. This means that the procedure used in these experiments is quite appropriate for the analysis of methyl acrylate - methyl methacrylate copolymers.