Characterization of Styrene–Methyl Methacrylate–*n*-Butyl Acrylate Terpolymers. I. Average Diad Concentration Determined by ¹H-NMR

MINORU KOBAYASHI, *Nippon Shokubai Kagaku Kogyo Company Ltd., Kogin Bldg. 5-1, Koraibashi, Higashiku, Osaka 541, Japan*

Synopsis

The average diad concentrations of methyl methacrylate (MMA) unit, $\bar{P}_2\{M_iM_j\}$, of the title terpolymer prepared by radical polymerization with various conversions were studied by ¹H-NMR measurements. Several methoxy proton peaks of MMA resolved by the diamagnetic shielding effects of styrene were assigned to the individual microstructures of MMA-centered triads. The $\bar{P}_2\{M_iM_j\}$ were determined from these peak ratios according to the terminal copolymerization model and the Ham's assumption of statistical simplification for a multicomponent copolymer ($P_2\{M_iM_j\} = P_2\{M_jM_i\}$). The observed values, $\bar{P}_2\{M_iM_j\}$, agreed with the values calculated from the monomer reactivity ratios for each conversions, and agreement with the copolymerization theory was evident.

INTRODUCTION

The determination of the sequence distribution of copolymers is an important characterization in relation to the fundamental properties such as glass transition temperature. Although many measurements, such as those by NMR, have been carried out on the sequence distribution of binary copolymers, there are only a few reports on terpolymers owing to the difficulty in making spectral assignments. Acrylic resins for industrial paints are usually multicomponent copolymers composed of monomers such as acrylate, methacrylate, and styrene. For the determination of sequence distribution of these multicomponent copolymers, ¹H-NMR results were examined using, as a model polymer, the terpolymer of styrene (St)–methyl methacrylate (MMA)–*n*-butyl acrylate (BA) obtained by the radical polymerization with various conversions.

Previously, St–MMA copolymer has been studied in detail by Kato et al.,[1] Bovey,[2] and Ito and Yamashita[3] by ¹H-NMR (utilizing the diamagnetic shielding effect of St in the vicinity of MMA). In the present work, the same analytical methods were used to examine the St–MMA–BA terpolymer. From the data on polymer composition and the microstructure obtained from NMR spectra, the average diad concentration related to the MMA unit was obtained using several assumptions related to the copolymerization. These average diad concentrations were compared with values calculated from monomer reactivity ratios based on the copolymerization theory.

Terpolymers	Monomer feed composition (mol)			Polymerization times (h)	Conversions (%)
	St	MMA	BA		
R1-1				0.5	8.4
R1-2				2.0	36.2
R1-3	0.38	0.40	0.22	4.0	52.2
R1-4				7.0	74.7
R1-5				16.0	98.1
R2	0.42	0.44	0.14	16.0	98.0
R3	0.58	0.20	0.22	17.5	99.0
R4	0.19	0.60	0.21	15.0	99.6

EXPERIMENTAL

Synthesis of Terpolymers

A 0.5-L four-necked flask was equipped with a stirrer, a thermometer, and a tube for introducing nitrogen gas. Into the flask were charged 140 g of toluene, 60 g of n-butyl acetate, 2 g of azobisisobutyronitrile, and 200 g of a mixture of specific amounts of each monomer. The polymerization was conducted at 75°C until the conversion was 98% or more. The monomer feed compositions are shown in Table I.

For the conversion measurement, the sample was weighed in an aluminium pan and diluted with ethyl acetate containing a slight amount of hydroquinone. A film was prepared from the solution and dried at 50°C under reduced pressure to a constant weight.

Measurement of ^{1}H-NMR Spectra

The film was dissolved in o-dichlorobenzene to prepare a 10–15 wt % solution, and tetramethylsilane (TMS) was added as the internal standard. A Hitachi Perkin-Elmer, Type R-20B (60 MHz) NMR was used. Spectra were measured at 140°C. The relative intensity of each peak in the spectra was obtained by weighing the paper cut from the spectra.

Analysis of Polymer Composition

For the determination of St level, IR spectra were measured. The intensity of δ_{CH} 699 cm^{-1} in St to $\nu_{C=O}$ 1725 cm^{-1} in MMA and BA was taken. The molar ratio of St was obtained from a calibration curve which was prepared by measuring those intensity ratios for many kinds of St–MMA–BA terpolymers synthesized with 98% or more conversions (for examples, R1-5, R2, R3, and R4 in Table I).

The relative amounts of MMA and BA were calculated using the intensity ratio of methoxy proton of MMA to —OCH$_2$— proton of BA (peak: 3.8–3.9 ppm) obtained from the ^{1}H-NMR spectra.
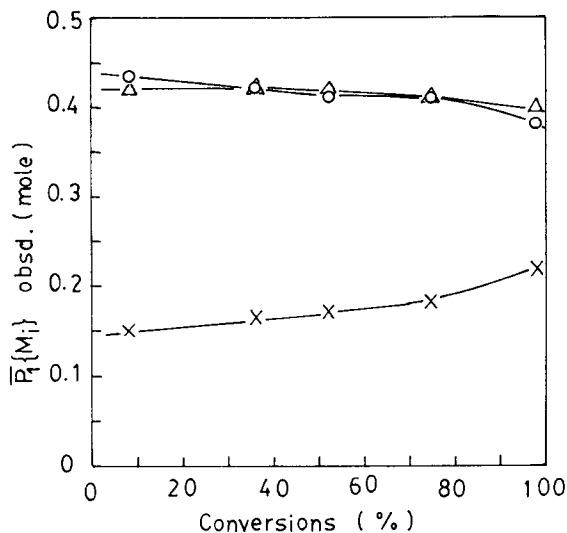
Fig. 1. Plots of polymer compositions, $\bar{P}_1\{M_i\}$ obs vs. conversions: $\bar{P}_1\{M_i\}$ obsd.: (○) $\bar{P}_1\{S\}$; (△) $\bar{P}_1\{M\}$; (×) $\bar{P}_1\{B\}$ (S = St, M = MMA, B = BA).

RESULTS AND DISCUSSION

Polymer Composition

The results of polymerization for various monomer compositions are shown in Table I. For samples with conversions less than 98%, the average polymer compositions ($\bar{P}_1\{M_i\}$) were measured, since the polymer compositions may differ from monomer feed concentrations because of differential reactivities between the comonomers. The results are shown in Table II and Figure 1. For samples with conversions of 98% or more, the monomer feed compositions were represented as $\bar{P}_1\{M_i\}$.

Peak Resolution of Methoxy Proton

Figure 2 shows an example of the NMR spectra of St–MMA copolymer (St/MMA = 49/51 mol). There is a total of three peaks for the methoxy proton of MMA: X (3.3 ppm), Y (2.9 ppm), and Z (2.4 ppm). This is because of the diamagnetic shielding effect of St in the vicinity of MMA.[1-3] These peaks
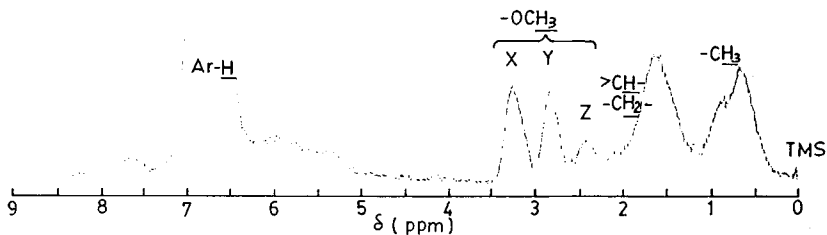

Fig. 2. ^{1}H-NMR spectra of St–MMA copolymer. Copolymer: Polymerization conditions are same as in St–MMA–BA terpolymers; St/MMA ratios (mol) 49/51; Conversions 98.3%. NMR: Measured at 140°C in o-dichlorobenzene.
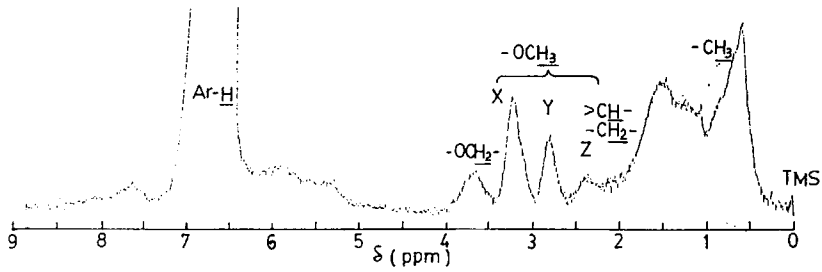
Fig. 3. ^{1}H-NMR spectra of St–MMA–BA terpolymer (R1–5). NMR: Measured at 140°C in o-dichlorobenzene.

have been assigned to the MMA-centered triad, and the sequence distribution could be determined from their relative intensities.[1-3]

A similar diamagnetic shielding effect was observed for a St–MMA–BA terpolymer. An example of the spectra of a terpolymer (R1–5) is shown in Figure 3. The spectral feature for the methoxy proton is similar to that of the St–MMA copolymer, and the same diamagnetic shielding effect was observed. R1-5 and the binary copolymer in Figure 2 were made under the same polymerization conditions and with the same St–MMA ratio. However, when
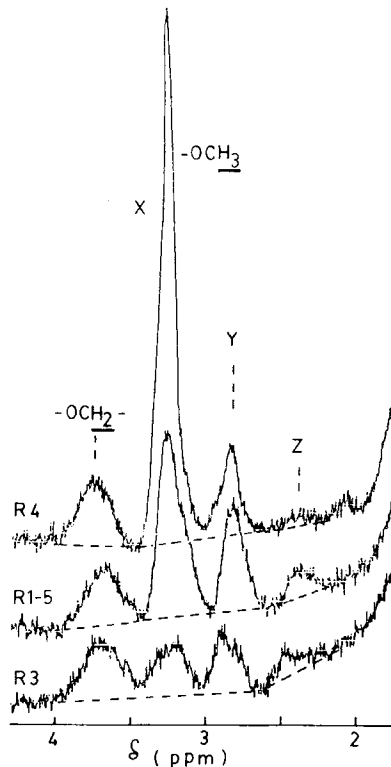

Fig. 4. Peak resolution of methoxy proton in NMR spectra: (- - -) baselines for methoxy proton peaks.

TABLE II
Analysis of Polymer Compositions

| Terpolymers | Spectra analysis | | Polymer compositions $\bar{P}_1\{M_i\}$ (mol)[a] | | |
	$\delta_{CH}/\nu_{C=O}$ in IR	$-OCH_3/-OCH_2-$ in NMR	$\bar{P}_1\{S\}$	$\bar{P}_1\{M\}$	$\bar{P}_1\{B\}$
R1-1	0.613	4.21	0.43	0.42	0.15
R1-2	0.699	3.92	0.42	0.42	0.16
R1-3	0.785	3.70	0.41	0.42	0.17
R1-4	0.805	3.42	0.41	0.41	0.18
R1-5	0.825	2.73	0.38	0.40	0.22

[a] S = St, M = MMA, B = BA.

the relative intensities of the triad peaks of both are compared, the ratios of peaks Y and Z to peak X in the terpolymer are smaller than those in the binary copolymer. This suggests that the concentration of St–MMA sequence decreases in the terpolymer by "intrusion" of a BA unit, the third component. The other examples of methoxy proton spectra are shown in Figure 4. The same spectral features are observed for all samples.

The relative intensities of the methoxy triads were determined for each sample. As shown in Figures 3 and 4, the signal of the methoxy proton partly overlaps the signals of methine and methylene proton from the main chains of each monomer. Accordingly, the baseline for methoxy proton was set up so that the ratio of the methoxy proton amount to the total proton amount (except phenyl proton) agreed with the theoretical value. For the actual setting up the baseline, several types of baselines were drawn on the spectra, and the most reasonable baseline for the theoretical value was used (see Fig. 4). The results are shown in Table III, where R1-5, R3, and R4 have the same amount of BA, but different St–MMA ratios. The X values decrease with an increase in the amount of St. Furthermore, R1-5 and R2 have the same St–MMA ratio, but different amounts of BA. The X values decrease with a decrease in the amount of BA. Both these observations arise from the fact that the amount of St neighboring on MMA increases relatively and the methoxy proton incurs diamagnetic shielding due to St.

TABLE III
Relative Intensities of Methoxy Proton Peaks X, Y, and Z

Terpolymers	X	Y	Z
R1-1	0.520	0.354	0.126
R1-2	0.521	0.354	0.125
R1-3	0.541	0.338	0.122
R1-4	0.560	0.306	0.134
R1-5	0.592	0.306	0.102
R2	0.530	0.340	0.130
R3	0.445	0.372	0.175
R4	0.760	0.207	0.033

The dependence of the relative intensity of the resolved peak on conversion (Table III) may reflect $\bar{P}_1\{M_i\}$ (Fig. 1) at each corresponding conversion. That is, in relation to $\bar{P}_1\{M_i\}$, the amount of BA increases with conversion keeping the same St–MMA ratio, and the increase in X value with conversion may result from the fact that the amount of St neighboring on MMA decreases and, in contrast, the amount of BA neighboring on MMA increases relatively.

Determination of Average Diad Concentration

The scheme in Figure 5 shows all MMA-centered triads in terpolymers divided into the assignments of X, Y, and Z peaks (essentially based on the tacticity of St to MMA). In accordance with this scheme, the intensities of $\{X\}$, $\{Y\}$, and $\{Z\}$ ($\{X\} + \{Y\} + \{Z\} = \bar{P}_1\{M\}$, M = MMA) are represented by eq. (1) using MMA-centered triad concentrations ($\bar{P}_3\{M_iM_jM_k\}$), where σ is a "coisotactic parameter" proposed by Ito and Yamashita[3] in St–MMA copolymer, and represents the probability that St is coisotactic to MMA. It was assumed that σ is constant regardless of the order of addition of MMA and St and the presence of BA units:

$$\{X\} = \bar{P}_3\{MMM\} + 2\bar{P}_3\{MMB\} + \bar{P}_3\{BMB\}$$

$$+ 2(1 - \sigma)\bar{P}_3\{MMS\} + 2(1 - \sigma)\bar{P}_3\{SMB\}$$

$$+ (1 - \sigma)^2 \bar{P}_3\{SMS\}$$

$$\{Y\} = 2\sigma\bar{P}_3\{MMS\} + 2\sigma P_3\{SMB\}$$

$$+ 2\sigma(1 - \sigma)\bar{P}_3\{SMS\}$$

$$\{Z\} = \sigma^2\bar{P}_3\{SMS\} \tag{1}$$

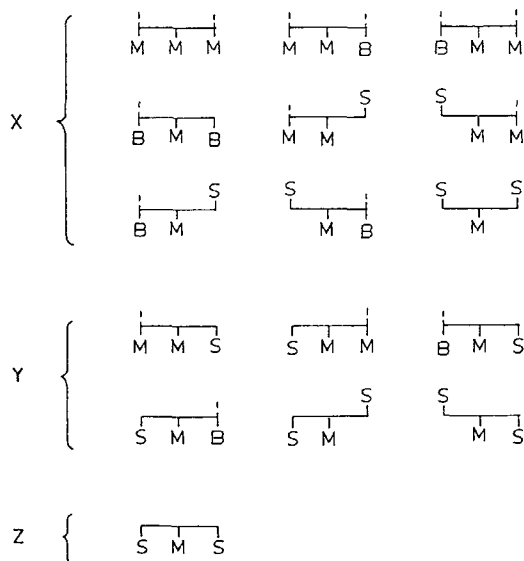where S = St, M = MMA, and B = BA.

Fig. 5.   Assignments of X, Y, and Z peaks to MMA-centered triads: S = St, M = MMA, B = BA.

When a terminal copolymerization model is assumed for the terpolymer, eq. (1) can be represented by eq. (2) below, using conditional probability P_{ij} (the probability that monomer j adds to monomer i). In eq. (2), Ham's[4] assumption of statistical simplification for a multicomponent copolymer ($P_2\{M_iM_j\} = P_2\{M_jM_i\}$) is introduced.

$$X = \{X\}/\bar{P}_1\{M\}$$

$$= P_{MM}^2 + 2P_{MM}P_{MB} + P_{MB}^2$$

$$+ 2(1 - \sigma)P_{MM}P_{MS} + 2(1 - \sigma)P_{MB}P_{MS} + \{(1 - \sigma)P_{MS}\}^2$$

$$= (1 - \sigma P_{MS})^2$$

$$Y = \{Y\}/\bar{P}_1\{M\}$$

$$= 2\sigma P_{MM}P_{MS} + 2\sigma P_{MB}P_{MS} + 2\sigma(1 - \sigma)P_{MS}^2$$

$$= 2\sigma P_{MS}(1 - \sigma P_{MS})$$

$$Z = \{Z\}/\bar{P}_1\{M\} = (\sigma P_{MS})^2 \tag{2}$$

where $P_{MS} + P_{MM} + P_{MB} = 1$.
$\bar{P}_2\{M_iM_j\}$ related to the MMA unit was obtained from eqs. (2) and (3). For the actual calculation of P_{ij}, P_{MS} was first obtained from eq. (4) as derived from equations of X and Y in eq. (2). P_{MM} and P_{MB} were obtained by substituting the obtained value for P_{MS} in eq. (2). The σ value in the literature[3] ($\sigma = 0.48$, polymerization temperature = 60°C) was used. The calculated results are shown in Table IV.

$$\bar{P}_2\{MS\} = \bar{P}_1\{M\}P_{MS}$$

$$\bar{P}_2\{MM\} = \bar{P}_1\{M\}P_{MM}$$

$$\bar{P}_2\{MB\} = \bar{P}_1\{M\}P_{MB} \tag{3}$$

$$1/P_{MS} = \sigma(2X/Y + 1) \tag{4}$$

TABLE IV
Observed Conditional Probabilities P_{ij} and Average Diad Concentrations $\bar{P}_2\{M_iM_j\}$

Terpolymers	Conversions (%)	P_{ij} obs			$\bar{P}_2\{M_iM_j\}$ obs (mol)		
		P_{MS}	P_{MM}	P_{MB}	$\bar{P}_2\{MS\}$	$\bar{P}_2\{MM\}$	$\bar{P}_2\{MB\}$
R1-1	8.4	0.556	0.253	0.190	0.234	0.106	0.081
R1-2	36.2	0.556	0.250	0.193	0.234	0.105	0.081
R1-3	52.2	0.523	0.277	0.199	0.214	0.114	0.082
R1-4	74.7	0.482	0.278	0.240	0.197	0.114	0.099
R1-5	98.1	0.452	0.341	0.207	0.181	0.136	0.083
R2	98.0	0.537	0.255	0.208	0.236	0.112	0.092
R3	99.0	0.662	0.112	0.226	0.132	0.022	0.045
R4	99.6	0.255	0.619	0.126	0.153	0.371	0.076

Comparison of the Value Calculated from the Monomer Reactivity Ratios and Measured Value

The diad concentration ($P_2\{M_iM_j\}$) of a terpolymer can be represented by eq. (5) using P_{ij}. P_{ij} is reaction kinetically given by eq. (6)[5] using the monomer reactivity ratio (r_{ij}) and monomer concentration ($[M_i]$), assuming the first order Markov chain (terminal model). The polymer composition ($P_1\{M_i\}$) can be obtained from eq. (7):

$$P_2\{M_iM_j\} = P_1\{M_i\}P_{ij} \tag{5}$$

$$P_{ij} = \frac{[M_j]/r_{ij}}{\sum\limits_{h=1}^{3}[M_h]/r_{ih}} \tag{6}$$

$$\frac{P_1\{M_1\}}{P_1\{M_2\}} = \frac{P_{21}P_{31} + P_{32}P_{21} + P_{23}P_{31}}{P_{31}P_{12} + P_{12}P_{32} + P_{13}P_{32}}$$

$$\frac{P_1\{M_2\}}{P_1\{M_3\}} = \frac{P_{31}P_{12} + P_{12}P_{32} + P_{13}P_{32}}{P_{12}P_{23} + P_{21}P_{13} + P_{13}P_{23}} \tag{7}$$

TABLE V
Monomer Reactivity Ratios r_{ij}[6]

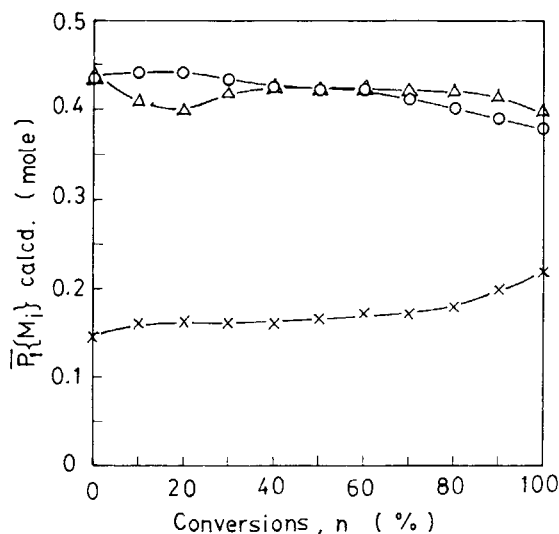| r_{SM}	0.50	r_{SB}	0.66	r_{MB}	1.74
r_{MS}	0.50	r_{BS}	0.19	r_{BM}	0.20

Fig. 6. Plots of polymer compositions, $\bar{P}_1\{M_i\}$ calcd, vs. conversions. Initial monomer compositions used in calculation (mol): St 0.38; MMA 0.40; BA 0.22. $\bar{P}_1\{M_i\}$ calcd: (○) $\bar{P}_1\{S\}$; (△) $\bar{P}_1\{M\}$; (×) $\bar{P}_1\{B\}$.

TABLE VI

Calculated Average Diad Concentrations $\bar{P}_2\{M_iM_j\}$ (mol)

Terpolymers	Conversions n (%)	$\bar{P}_2\{M,S\}$ calcd			$\bar{P}_2\{M,B\}$ calcd			$\bar{P}_2\{MM\}$ calcd
		$\bar{P}_2\{MS\}$	$\bar{P}_2\{SM\}$	$\bar{P}_2\{M,S\}^a$	$\bar{P}_2\{MB\}$	$\bar{P}_2\{BM\}$	$\bar{P}_2\{M,B\}^b$	
R1-1	8	0.222	0.200	0.211	0.056	0.078	0.067	0.156
R1-2	36	0.246	0.219	0.233	0.046	0.073	0.060	0.132
R1-3	52	0.243	0.215	0.229	0.047	0.075	0.061	0.130
R1-4	75	0.235	0.205	0.220	0.053	0.083	0.068	0.129
R1-5	98	0.216	0.185	0.201	0.066	0.097	0.082	0.124
R2	98	0.259	0.234	0.247	0.041	0.066	0.054	0.143
R3	99	0.160	0.140	0.150	0.020	0.039	0.030	0.020
R4	100	0.147	0.127	0.137	0.114	0.134	0.124	0.335

$^a \bar{P}_2\{M,S\} = \frac{1}{2}[P_2\{MS\} + \bar{P}_2\{SM\}]$.
$^b \bar{P}_2\{M,B\} = \frac{1}{2}[\bar{P}_2\{MB\} + \bar{P}_2\{BM\}]$.

$P_2\{M_iM_j\}$ in the initial stage of polymerization can be calculated using the monomer feed composition. However, for the increase in conversion, it is necessary to consider the variation in residual monomer composition. Here, when 1% of the initial monomer is consumed to produce a terpolymer having the composition of $P_1\{M_i\}_k$ [eq. (8)], the average diad concentration at each conversion $(\bar{P}_2\{M_iM_j\})$ is obtained by repeating the calculation for each conversion at an interval of 1%, using eqs. (5)–(7) [eq. (9)]. The values of $r_{ij}{}^6$ used for this are shown in Table V.

$$[M_i] = [M_i]_0 - (1/100)P_1\{M_i\}_k \qquad (8)$$

$$\bar{P}_2\{M_iM_j\} = \frac{1}{n} \sum_{n=1}^{n} P_2\{M_iM_j\}_k \qquad (9)$$

where $[M_i]_0$ = concentration of initial monomer and n = conversion (%).

Figure 6 shows $P_1\{M_i\}$ at each conversion calculated for the monomer feed composition of R1. The results are in satisfactory agreement with the measured values (Fig. 1), and the polymer composition distribution is in accordance with the copolymerization theory.

Table VI shows the calculation results of $\bar{P}_2\{M_iM_j\}$ for all the samples. For a comparison with the measured values, in the case of $\bar{P}_2\{M_iM_j\}$ for diads composed of different monomers $(i \neq j)$, the average values of two kinds of diad concentrations $(\bar{P}_2\{M_i, M_j\})$ are shown together.

The measured values of $\bar{P}_2\{M_iM_j\}$ (Table IV) and corresponding calculated values were compared. Errors in setting up the baseline and measurements of peak ratios for methoxy proton peaks are included in the table. The error from that in the measurement of peak ratio to $\bar{P}_2\{M_iM_j\}$ ranged from ± 4–8%. By taking such error into consideration, measured values may be regarded as essentially in agreement with the calculated values for all samples. In the present case, as the "coisotactic parameter" (σ), the value observed for St–MMA copolymer was used, and it was assumed that the presence of a BA unit has no effect on it. In calculating $\bar{P}_2\{M_iM_j\}$, the terminal copolymerization model and Ham's[4] assumption for multicomponent copolymer were introduced. Our measured results agree essentially with the theoretical values, which demonstrates that these assumptions are reasonable.

SUMMARY

For St–MMA–BA terpolymers of various compositions, the average diad concentrations of MMA units were studied by ^{1}H-NMR. The results agreed with the values calculated from monomer reactivity ratios for each conversion, and agreement with the copolymerization theory was evident. In the case of any other St–methacrylate–acrylate terpolymers, our results indicate that their average diad concentrations can be estimated by the copolymerization theory, based on the analogy of each monomer to other monomers in copolymerization reactivities.

References

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