temperature for 2 h. The pale yellow solid was filtered, washed with cold CCl_4, and dried under vacuum to give 0.40 g (82%) of product. Recrystallization twice from methanol gave colorless crystals: mp 178.0–179.0 °C; IR (KBr) 3140 (s, br), 2992 (w), 2940 (w), 1765 (s), 1680 (s), 1495 (w), 1470 (s), 1450 (s), 1435 (s), 1388 (m), 1380 (m), 1370 (m), 1338 (w), 1280 (w), 1252 (m), 1232 (m), 1218 (m), 1200 (w), 1150 (m), 1080 (m), 1070 (w), 1050 (w), 1030 (w), 1010 (w), 1005 (w), 950 (w), 930 (m), 800 (m), 790 (m), 760 (s), 725 (m), 700 (s), 688 (m), 648 (m) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 1.76 (d, 3 H, J = 7.5 Hz); 3.84 (dd, 2 H, J = 4.5 Hz), 4.00 (m, 2 H), 4.62 (m, 1 H), 5.20 (q, 1 H, J = 7.5), 7.31 (m, 5 H), 10.52 (s, 1 H); ^{13}C NMR (Me_2SO-d_6) 17.20, 35.47, 49.45, 49.73, 50.62, 126.48, 127.32, 128.25, 140.30, 153.40, 153.53 ppm; $[\alpha]^{25}{}_D$ −23.0° (c 9.9 Me_2SO); mass spectrum calcd for $M^+ - HBr$ 323.0264, obsd 323.0267.

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Registry No. **4**, 2627-86-3; **5**, 17279-30-0; **6**, 14649-03-7; **7**, 75600-65-6; **8**, 75600-66-7; **9**, 75600-67-8; **10**, 94427-70-0; **11**, 94427-71-1; ethyl carbazate, 4114-31-2; propylene, 115-07-1.

Supplementary Material Available: Tables of the hydrogen atom positions, the thermal parameters for the non-hydrogen atoms, and observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Thiele, J.; Strange, O. *Justus Liebigs Ann. Chem.* **1894**, *283*, 1.

(2) Middleton, W. J.; Heckert, R. E.; Little, E. L. *J. Am. Chem. Soc.* **1958**, *80*, 2783.

(3) Pirkle, W. H.; Stickler, J. C. *Chem. Commun.* **1967**, 760.

(4) Turner, S. R.; Guilbault, L. J.; Butler, G. B. *J. Org. Chem.* **1971**, *36*, 2838.

(5) Wagener, K. B.; Turner, S. R.; Butler, G. B. *J. Polym. Sci., Part B* **1972**, *10*, 805.

(6) (a) Wagener, K. B.; Turner, S. R.; Butler, G. B. *J. Org. Chem.* **1972**, *37*, 1454. (b) Wagener, K. B.; Butler, G. B. *J. Org. Chem.* **1973**, *38*, 3070.

(7) Williams, A. G.; Butler, G. B. *J. Org. Chem.* **1980**, *45*, 1232.

(8) Ohashi, S.; Butler, G. B. *J. Org. Chem.* **1980**, *45*, 3472.

(9) Ohashi, S.; Ruch, W. E.; Butler, G. B. *J. Org. Chem.* **1981**, *46*, 614.

(10) Butler, G. B.; Williams, A. G. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 1117.

(11) Leong, K.-W.; Butler, G. B. *J. Macromol. Sci., Chem.* **1980**, *A14*, 287.

(12) Ohasi, S.; Leong, K.-W.; Matyjaszewski, K.; Butler, G. B. *J. Org. Chem.* **1980**, *45*, 3467.

(13) Butler, G. B., unpublished results.

(14) (a) Gardlik, J. M.; Paquette, L. A. *Tetrahedron Lett.* **1979**, 3597. (b) Paquette, L. A.; Doehner, R. F., Jr. *J. Org. Chem.* **1980**, *45*, 5105. (c) Klobucar, W. D.; Paquette, L. A.; Blount, J. F. *J. Org. Chem.* **1981**, *46*, 4021.

(15) Fuchs, B. "Topics in Stereochemistry"; Ehel, E. L., Allinger, M. L., Eds.; Wiley: New York, 1978; Vol. 10.

(16) Naik, D. V.; Palenik, G. J. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2396.

(17) Merck & Co., Inc. "Deuterated NMR Solvents—Handy Reference Data"; Merck & Co., Inc.: Quebec, 1978.

(18) Kolomiets, V. F.; Gracheva, R. A.; Potapov, V. M.; Samusenko, A. L. *J. Org. Chem. USSR* **1980**, 854.

(19) Gillis, B. T.; Hagarty, J. D. *J. Org. Chem.* **1967**, *32*, 330. Cookson, R. C.; Gilani, S. S. H.; Stevens, I. D. R.; Watts, C. T. *Org. Synth.* **1971**, *51*, 121.

Molecular Weight Distribution and Relationship between Chemical Composition and Molecular Weight in High-Conversion Samples of Copoly(styrene–methyl acrylate) Prepared in Solution by Adding Initiator

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ABSTRACT: The molecular weight distributions and the relationships between chemical composition and molecular weight for the samples of statistical copolymer of styrene and methyl acrylate prepared by radical copolymerization in solution were determined by gel permeation chromatography with dual detectors and compared with those calculated by using simple copolymerization kinetics (negligible penultimate effects). Results obtained both experimentally and theoretically are in good agreement. The agreement between theory and experiment confirms the validity of simple copolymerization kinetics when the gel effect is negligible.

Introduction

Statistical copolymers prepared by radical copolymerization have distributions with respect to chemical composition (CC) and molecular weight. Along with these distributions, the relationship between molecular weight and CC is also important for practical uses of copolymers. These two distributions and also the relationship between CC and molecular weight can be experimentally determined and also calculated by using simple copolymerization kinetics. Chemical composition distributions (CCD) of copolymers determined experimentally were found to be in good agreement with those calculated by using simple copolymerization kinetics in all cases.[1–6] However, molecular weight distribution (MWD) and also the relationship between CC and molecular weight are not always in satisfactory agreement with theoretical calculations.

In our previous work,[7] MWD and the relationship between CC and molecular weight in several samples of styrene (S)–methyl acrylate (MA) statistical copolymer prepared by radical copolymerization *in bulk* were determined by gel permeation chromatography (GPC) equipped with dual detectors, and the data were compared with the theoretical calculations by using simple copolymerization kinetics. Agreement between the theoretical and experimental results was satisfactory for low-

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Table I

				$10^{-4}M_n$			$10^{-4}M_w$			M_w/M_n			MA content, mol %	
	conversion, wt	time, h		exptl				calcd			calcd			
sample	fr	exptl	calcd	osm	GPC	calcd[a]	exptl[b]	$\rho = 0$	$\rho = 1$	exptl[b]	$\rho = 0$	$\rho = 1$	anal.	calcd
1	0.372	70	57.2	12.1	12.3	12.1[c]	20.4	24.9	18.7	1.66	2.06	1.55	50.5	49.9
2	0.594	140	106.0	8.4	11.0	9.58	18.7	20.7	15.5	1.70	2.16	1.62	52.5	51.9
3	0.727	215	147.1	7.5	10.1	8.07	17.7	18.6	14.0	1.75	2.30	1.73	54.5	53.9
4	0.784	290	197.7	6.7	8.9	8.03	15.9	18.5	13.8	1.79	2.30	1.72	55.7	55.1

[a] $\rho = 0, 1$. [b] By GPC. [c] This value was adjusted to the data obtained by osmometry.

conversion samples, whereas for a high-conversion sample, the MWD curve had a remarkably longer high molecular weight tail than the theoretical curve and the MA content increased with increasing molecular weight in opposition to the theoretical prediction. It was suggested that the discrepancy between theory and experiment for the high-conversion sample was a consequence of the gel effect, which was neglected in the copolymerization calculations.

In addition, the three-dimensional distribution diagram of molecular weight and CC of the same high-conversion sample was determined by a combination of preparative GPC and thin-layer chromatography.[8] It became clear from the result that the gel effect does not affect CCD but does affect MWD.

The purpose of this work is to confirm the previous conclusions by comparing theoretical predictions with data for samples prepared *in solution*, in which the gel effect is negligible.

Experimental Section

Materials. The monomers, styrene and methyl acrylate, were washed several times with dilute aqueous solution of sodium hydroxide, followed by repeated water washing, and then dried over calcium chloride. The monomers were distilled under reduced nitrogen atmosphere just before use. Benzene was purified by washing with sulfuric acid and water several times, drying with calcium chloride, and distilling fractionally. Azobis(isobutyronitrile), AIBN, was purified by recrystallization from methanol solution.

Copolymerization. Copolymerization of S and MA was carried out in benzene, at 60 °C, under nitrogen, using AIBN as initiator. For determination of MWD by GPC, we required copolymer samples with fairly high molecular weight. To achieve this, small amounts of initiator, in comparison with monomers, were used in the copolymerizations. To force the copolymerizations to high conversion, we therefore added the initiator during polymerization. That is, $[S]_0 = 0.747$ mol·dm^{-3}, $[MA]_0 = 1.299$ mol·dm^{-3}, and $[AIBN]_0 = 9.61 \times 10^{-4}$ mol·dm^{-3} in the start solution. This total monomer concentration corresponds to about 20 vol %. Sample 1 was obtained by separating a part of the reaction mixture after 70 h from the start of the copolymerization. The separated reaction mixture was poured into methanol. Immediately after the separation, an amount of AIBN was added to the residual part of the reaction mixture, and the polymerization continued. By repeating the same procedure, we obtained four copolymer samples at different conversions as shown in Table I. The amounts of AIBN added in the course of polymerization were 8.84×10^{-4} mol·dm^{-3} after the separation of sample 1 and 8.80×10^{-4} mol·dm^{-3} after sample 2. After sample 3, the initiator was not added. These amounts of initiator were chosen so that the initiator concentration may be almost equal at three stages of copolymerization, excepting the last stage (sample 4).

To purify the copolymer samples, the precipitated samples were washed several times with fresh methanol by decantation and dried in vacuo. Then, the samples were dissolved in 2-butanone, precipitated and washed with methanol, and dried in vacuo at 40 °C until they reached constant weights (about 3 days).

MA contents of the copolymer samples were determined by the elemental analysis of carbon and hydrogen. Their number-average molecular weights (M_n) were determined by using a Wescan Model 231 high-speed membrane osmometer (Wescan Instruments, Inc.) in toluene at 25 °C.

GPC Measurements. The GPC instrument used in the present work is an HLC-802 UR of Toyo Soda Manufacturing Co., Ltd. (Tokyo, Japan) equipped with an ultraviolet detector (UV) and a high-sensitivity differential refractometer RI-8 (RI). Three commercial columns of TSK-GEL, GMH6 (Toyo Soda Manufacturing Co., Ltd., 60 cm in length and 0.75 cm in inner diameter) packed with a mixture of polystyrene gel particles with different porosities, were used. The total number of theoretical plates of the column set was 2×10^4, when determined with benzene.

All measurements were carried out at 25 °C, flow rate 1.00 cm^3·min^{-1}, copolymer concentration ca. 2.0 g·dm^{-3}, and injection volume 0.5 cm^3. The eluent was tetrahydrofuran (THF) purified by reflux and distillation over sodium wire under nitrogen atmosphere and then degassed by ultrasonic wave, just before use.

The so-called universal calibration curve was determined by plotting log ($M[\eta]$) against elution volume (V_e) for monodisperse polystyrene samples supplied from Toyo Soda Manufacturing Co., Ltd., Pressure Chemical Co., and NBS (U.S.A.). The molecular weights (M) were values determined by the suppliers. The limiting viscosity index, $[\eta]$, was determined in THF at 25 °C by using an Ubbelohde type viscometer which was designed so that the kinetic energy correction would be negligible. Using the universal calibration curve, we converted V_e in the GPC chromatogram of the copolymer samples to $M[\eta]$ and then $M[\eta]$ was converted to M by using the viscosity equation

$$[\eta] = (3.7 \times 10^{-3})M^{0.799} \quad (\text{cm}^3\text{·g}^{-1}) \tag{1}$$

which was previously obtained for the present copolymer with calibration for polydispersity.[7] Equation 1 is independent of chemical composition of the copolymer.

As in the previous work,[7] the weight concentration of the copolymer, w_c, and the weight fraction of MA in the copolymer, x, were calculated from the heights of peaks in GPC chromatograms obtained with both UV and RI detectors, by using the equations

$$x = \frac{K_{US} - K_{RS}(r_{UV}/r_{RI})}{K_{US} - \Delta K_R(r_{UV}/r_{RI})} \tag{2}$$

$$w_c = \frac{K_{US}r_{RI} - \Delta K_R r_{UV}}{K_{RM}K_{US}} \tag{3}$$

where r_{UV} and r_{RI} are UV and RI chromatogram heights at the same V_e, K_{RS} and K_{US} are peak area response factors for polystyrene for RI and UV detectors with respect to polymer concentration, K_{RM} is the corresponding response factor for poly(MA), and $\Delta K_R = K_{RS} - K_{RM}$. These response factors were previously determined by using homopolymers, since it was confirmed in the previous work[7] that the response factors of copolymers with different compositions are linear with respect to the copolymer composition (weight fraction). The value of x was converted to mole fraction of MA, F_{MA}.

The correction for zone spreading was neglected in the present work, since the MWD's of these samples were broad and the theoretical plate number of the present column set was sufficiently high.

Experimental Results

In Table I, the values of conversion, reaction time, M_n by osmometry, M_n calculated from MWD, weight-average molecular weight (M_w) by GPC, M_w/M_n by GPC, and average MA content obtained for all four samples are sum-

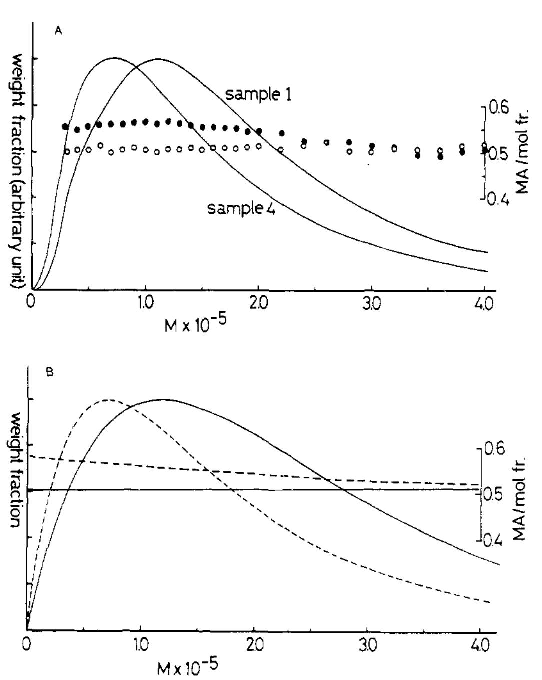

Figure 1. (A) Experimental results of MWD curves (—) and the relationships between MA content and molecular weight (○: sample 1; ●: sample 4). (B) Calculated results for the case of $\rho = 0$ (—: sample 1; ---: sample 4).

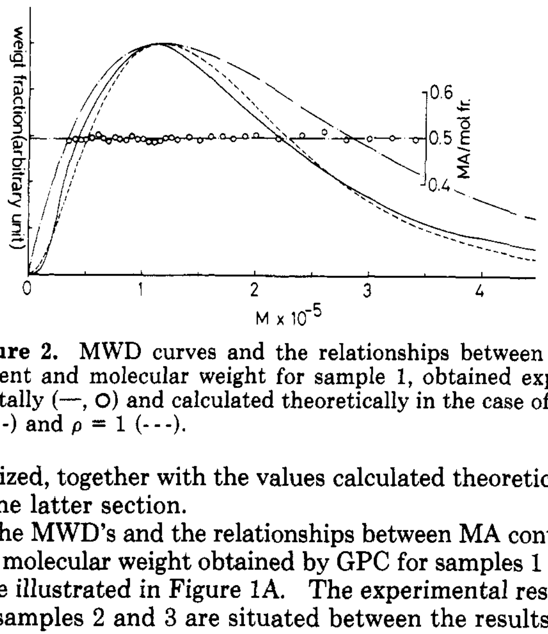

Figure 2. MWD curves and the relationships between MA content and molecular weight for sample 1, obtained experimentally (—, ○) and calculated theoretically in the case of $\rho = 0$ (···) and $\rho = 1$ (---).

marized, together with the values calculated theoretically in the latter section.

The MWD's and the relationships between MA content and molecular weight obtained by GPC for samples 1 and 4 are illustrated in Figure 1A. The experimental results for samples 2 and 3 are situated between the results for samples 1 and 4, in the order of the sample number. In Figures 2 and 3, MWD's and MA content-molecular weight relationships for samples 1 and 4, respectively, are replotted for comparison with theoretical calculations.

Theoretical Calculations

In order to compare with the experimental results, MWD, M_n, M_w, and the relationship between MA content and molecular weight were calculated theoretically. Although there are many papers on theoretical calculation of copolymerization,[9] which should be consulted, we used the simplest model of copolymerization kinetics.[10] The terminal model (neglecting the penultimate effect) of copolymerization and the chemical-controlled termination (neglecting the gel effect) were applied in the calculations. The chain transfers to monomers, solvent, and initiator were neglected, since the effects of the chain transfers are orders of 10^{-5}–10^{-6} comparing to the rate of the propagation reaction.[11] The induction period was neglected for simplicity, since the reaction components (monomers, solvent, initiator) were carefully purified and the sure knowledge about the induction period in this system is short.

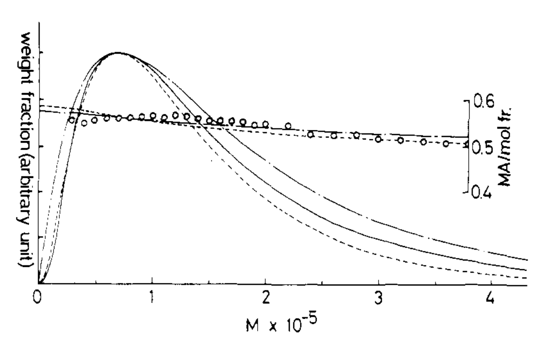

Figure 3. MWD curves and the relationships between MA content and molecular weight for sample 4, obtained experimentally (—, ○) and calculated theoretically in the cases of $\rho = 0$ (···) and $\rho = 1$ (---).

The calculations were carried out in the same manner as in the previous paper.[7] Only the outline of the calculation is shown as follows.

The integral CCD of whole copolymer can be calculated from the initial monomer composition and the conversion, as the relationship between the instantaneous composition of copolymer (F_1) and the weight conversion $(1 - W/W^0)$, using the equations

$$1 - W/W^0 = 1 - \frac{C[(M_1 - M_2)f_1 + M_2]}{C^0[(M_1 - M_2)f_1^0 + M_2]} \tag{4}$$

$$\frac{C}{C^0} = \left(\frac{f_1}{f_1^0}\right)^{\alpha}\left(\frac{1 - f_1}{1 - f_1^0}\right)^{\beta}\left(\frac{\delta - f_1^0}{\delta - f_1}\right)^{\gamma} \tag{5}$$

$$F_1 = \frac{(r_1 - 1)f_1^2 + f_1}{(r_1 + r_2 - 2)f_1^2 + 2(1 - r_2)f_1 + r_2} \tag{6}$$

where C is the total mole concentration of monomers, f_1 is the mole fraction of monomer 1 in the monomer mixture, M_1 and M_2 are the molecular weights of monomers 1 and 2, r_1 and r_2 are the monomer reactivity ratios, the superscript zero shows the initial values, $\alpha = r_2/(1 - r_2)$, $\beta = r_1/(1 - r_1)$, $\gamma = (1 - r_1 - r_2)/(1 - r_1)(1 - r_2)$, and $\delta = (1 - r_2)/(2 - r_1 - r_2)$. The whole copolymer was assumed to be a mixture of n instantaneous copolymers; that is, the entire range of the CCD calculated was divided into n parts having equal intervals of CC. The average CC, $(F_1)_i$, and the weight fraction, ω_i, of the part i were calculated. The instantaneous statistical CCD's of the respective parts were neglected for simplicity.

The distributions of polymerization degree, $W(P)$, of the respective instantaneous copolymers were calculated by the equation

$$W_i(P) = (1 - \rho + \rho P/2\lambda_i)(P/\lambda_i^2)\exp(-P/\lambda_i) \tag{7}$$

where ρ is the fraction of the coupling termination and λ is the number-average polymerization degree of polymer radicals. $\lambda = P_n$ in the case of $\rho = 0$ and $\lambda = P_n/2$ in the case of $\rho = 1$, if P_n is the number-average polymerization degree of the dead polymer. The values of P_n can be calculated by

$$(P_n)_i = \{r_1(C_1)_i^2 + 2(C_1)_i(C_2)_i + r_2(C_2)_i^2\}/\{(1 - \rho/2) \times (R_I)_i^{1/2}[\epsilon_1^2 r_1^2 (C_1)_i^2 + 2\phi r_1 r_2 (C_1)_i(C_2)_i + \epsilon_2^2 r_2^2 (C_2)_i^2]^{1/2}\} \tag{8}$$

where $(C_1)_i$ and $(C_2)_i$ are the monomer concentrations at the stage where the copolymer component i is produced,

$\epsilon_p = (2k_{tpp}/k_{pp})^{1/2}$ and $\phi = k_{t12}/2(k_{11}/k_{t22})^{1/2}$, indicating the rate constant of termination reaction between radicals with terminal monomeric units p and q by k_{tpq} and the rate constant of propagation reaction between radical with terminal unit p and monomer p by k_{pp}. R_I is the rate of initiation and is given by

$$(R_I)_i = 2f_e k_d [I]_0 \exp(-k_d t_i) \qquad (9)$$

where k_d is the rate constant of initiator decomposition, $[I]_0$ is the initial concentration of initiator, and f_e is the efficiency factor of initiation and is regarded as an adjustable parameter in the present calculation. The reaction time, t_i, can be estimated by the equations

$$t_i = \sum_i \Delta t_i \qquad (10)$$

$$\Delta t_i = -\Delta C_i/(R_P)_i \qquad (11)$$

where $\Delta C_i = C_i - C_{i-1}$ and $(R_P)_i$ is the copolymerization rate at the monomer composition $(f_1)_i$ which can be estimated from the data of Walling[12] and the value of $[I]_i = [I]_0 \exp(-k_d t_i)$. In the present calculation procedure, however, the circle of $t_i \rightarrow [I]_i \rightarrow (R_P)_i \rightarrow \Delta t_i \rightarrow t_i$ cannot be avoided. In order to cut the circle off, t_i was approximated by t_{i-1} in the calculation of $[I]_i$. Since the number of parts, n, is large, this may be a good approximation.

$(P_n)_i$ and $W_i(P)$ thus calculated were converted to $(M_n)_i$ and MWD of the component i, $W_i(M)$, respectively. The MWD, M_n, and M_w for the whole copolymer were calculated from the $W_i(M)$ and ω_i. The adjustable parameter, f_e, was determined so that the M_n thus calculated may be equal to the observed value by osmometry. Then, the relationship between molecular weight and the average CC of the components having a molecular weight of X, $(F_1)_x$, can be obtained from $W_i(M)$, $(F_1)_i$, and ω_i.

In the actual calculations, the following constants were used, indicating MA by 1 and S by 2, respectively: $r_1 = 0.18$ and $r_2 = 0.75$,[13] $k_{t11} = 9.5 \times 10^6$ ($dm^3 \cdot mol^{-1} \cdot s^{-1}$), $k_{t22} = 7.2 \times 10^7$, $k_{11} = 2.09 \times 10^3$, $k_{22} = 1.76 \times 10^2$,[14] $k_d = 9.86 \times 10^{-6}$,[15] $\phi = 40$.[12] The values of f_e were obtained to be 0.1148 for the case of $\rho = 0$ and 0.4591 for the case of $\rho = 1$, respectively, by adjusting the calculated M_n of sample 1 to the observed value by osmometry, 1.21×10^5. Since the value of f_e was found to be constant irrespective of monomer composition in our previous paper,[7] the same values of f_e were used for the other samples 2–4. As a matter of course, the addition of initiator was taken into consideration in the course of calculations for samples 2 and 3. The values of n were determined by dividng the entire ranges of CCD of the respective samples by an equal interval of CC, 0.237 mol %. The values of n used in the calculations were 20, 46, 81, and 110 for samples 1–4, respectively.

The MWD's and MA content–molecular weight relationships of samples 1 and 4 in the case of $\rho = 0$ thus calculated are shown in Figure 1B for comparison with the experimental results in Figure 1A. Although the calculated results for samples 2 and 3 are not shown in Figure 1B, those are also situated between the curves of samples 1 and 4, in the order of the sample number, in agreement with experimental results. In Figures 2 and 3, too, the calculated results for samples 1 and 4 in both cases of $\rho = 0$ and $\rho = 1$ are compared with the experimental results, respectively. The MA content–molecular weight relationship for sample 1 in the cases of $\rho = 0$ and $\rho = 1$ cannot be distinguished in Figure 2.

Discussion

It can be concluded from Table I and Figures 1–3 that M_n, M_w, M_w/M_n, MWD, average MA content, and the MA content–molecular weight relationship calculated from simple copolymerization kinetics are in satisfactory agreement with experimental data for the present experiments where the gel effect is negligible. In more detail, the experimental data are between those calculated ones for $\rho = 0$ and $\rho = 1$, but closer to the data for $\rho = 1$. The same is true for samples 2 and 3.

In the lower molecular weight region of Figures 2 and 3, the experimental curves are lower than the theoretical curves calculated for $\rho = 1$. However, the experimental curves may be underestimated in the lower molecular weight region, since MWD was determined by GPC using the universal calibration method. The viscosity equation such as eq 1 becomes unreliable; that is, the exponent in the equation may become smaller, if the molecular weight is too low. This may also be the reason for the higher values of M_n obtained by GPC than those by osmometry in Table I.

The gel effect becomes often noticeable at a conversion of about 30% in bulk polymerization,[16] while in the present experiments, polymer concentrations were less than 16%. Thus, it may be concluded that simple copolymerization kinetics satisfactorily describe the copolymerization of styrene and methyl acrylate when the gel effect is negligible.

As was reported in the previous paper,[7] it is probable that the discrepancy between theory and experiments concerning MWD and the MA content–molecular weight relationship of high-conversion samples prepared in bulk was due to the neglect of the gel effect.

Finally, we would like to mention that the calculated values of M_n are always somewhat higher than the measured values by osmometry and the reaction times used in the course of the calculations are always shorter than the actual ones. This disagreement may be improved if a rate constant of initiator decomposition, k_d, a little smaller than the value used in the present calculations is used.

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References and Notes

(1) Inagaki, H.; Matsuda, H.; Kamiyama, F. *Macromolecules* **1968**, *1*, 520.

(2) Teramachi, S.; Kato, Y. *Macromolecules* **1971**, *4*, 54.

(3) Walchili, J.; Miyamoto, T.; Inagaki, H. *Bull. Inst. Chem. Res., Kyoto Univ.* **1978**, *56*, 80.

(4) Teramachi, S.; Hasegawa, A.; Hasegawa, S.; Ishibe, T. *Polym. J.* **1981**, *13*, 319.

(5) Teramachi, S.; Hasegawa, A.; Yoshida, S. *Polym. J.* **1982**, *14*, 161.

(6) Teramachi, S.; Hasegawa, A.; Uchiyama, N. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 71.

(7) Teramachi, S.; Hasegawa, A.; Akatsuka, M.; Yamashita, A.; Takemoto, N. *Macromolecules* **1978**, *11*, 1206.

(8) Teramachi, S.; Hasegawa, A.; Yoshida, S. *Macromolecules* **1983**, *16*, 542.

(9) For example, see: Ray, W. H., *J. Macromol. Sci., Rev. Macromol. Chem.* **1972**, *C8*, 1.

(10) Odian, G. "Principles of Polymerization", 2nd ed.; Wiley-Interscience: New York, 1981.

(11) Young, L. J. "Polymer Handbook", 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1975; p II-57.

(12) Walling, C. *J. Am. Chem. Soc.* **1949**, *71*, 1930.

(13) Lewis, F. M.; Walling, C.; Cummings, W.; Briggs, Er.; Mayo, F. R. *J. Am. Chem. Soc.* **1948**, *70*, 1519.

(14) Matheson, M. S.; Auer, E. E.; Bevilacqua, E. B.; Hart, E. J. *J. Am. Chem. Soc.* **1951**, *73*, 1700.

(15) van Hook, J. P.; Tobolsky, T. V. *J. Am. Chem. Soc.* **1958**, *80*, 779.

(16) For example: Cardenas, J. N.; O'Driscoll, K. F. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 883; **1977**, *15*, 1883. Johnson, M.; Karmo, T. S.; Smith, R. R. *Eur. Polym. J.* **1977**, *14*, 409.