Molecular Weight Distribution and Correlation between Chemical Composition and Molecular Weight in a High-Conversion Copolymer of Styrene–Methyl Acrylate

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ABSTRACT: The relationships between the molecular weight (MW) and the chemical composition of components in copolymers and also the molecular weight distributions (MWD) of those copolymers were determined by gel permeation chromatography and compared with the calculations based on the classical theory of copolymerization kinetics. The samples were three low-conversion and one high-conversion copolymers of styrene (St) and methyl acrylate (MA) prepared by radical polymerization in bulk. Agreement between theory and experiments is satisfactory for the low-conversion samples. For the high-conversion copolymer, however, the MWD curve has a long tailing in the higher MW region and is remarkably broader than the curve calculated. Moreover, the MA content of components in the copolymer increases as the MW of the components increases, in contrast to theoretical prediction. The discrepancy between theory and experiments for the high-conversion sample may be due to the gel effect or the diffusion-controlled termination, which was neglected in the theoretical calculation.

The copolymers prepared by radical polymerization generally have dual distributions of molecular weight and chemical composition. If the polymerization is stopped at a low conversion, both the molecular weight distribution (MWD) and chemical composition distribution (CCD) of the copolymer can be theoretically predicted by the classical theory of copolymerization kinetics.[1-3] The polydispersity index, i.e., the ratio of the weight-average molecular weight to the number-average molecular weight ($\bar{M}_w/\bar{M}_n$), is 2 in the case of termination by disproportionation and 1.5 in the case of termination by coupling. And also CCD is Gaussian. These predictions were confirmed by experiments.[4] From those results it can be predicted that in low-conversion copolymers, the chemical composition averaged over all the molecules having the same molecular weight should be constant irrespective of molecular weight. That is, if the copolymer is fractionated with respect to molecular weight, the chemical composition of the fractions should be the same.

If the polymerization is continued to a high conversion, the chemical composition and the molecular weight of the molecules produced vary with conversion. Therefore, a correlation between molecular weight and chemical composition may be observed in high-conversion copolymers. This correlation can also be evaluated by the classical theory of copolymerization kinetics if the so-called gel effect or the diffusion-controlled termination is absent. However, the molecular weight of the polymers produced may be affected by the gel effect, whereas the chemical composition would not be affected. Thus, the dependence of chemical composition on molecular weight observed may deviate from the theoretical prediction from the classical copolymerization theory.

The variation of chemical composition as a function of molecular weight was observed in various kinds of copolymers by using the gel permeation chromatography (GPC) with dual detectors.[5-8] However, the discussion of quantitative comparison of the observed results with the theory of copolymerization kinetics appears to be insufficient. In the present work, the MWD and the chemical composition–molecular weight relationship of styrene (St)–methyl acrylate (MA) random copolymers synthesized by radical copolymerization are studied by GPC equipped with dual detectors.

Experimental Section

Samples. Four samples were prepared by bulk polymerization of St and MA mixtures in the ratios shown in Table I at 60 °C under nitrogen atmosphere using azobis(isobutyronitrile) as initiator. The monomers were washed several times with dilute sodium hydroxide solution, followed by repeated water washing, and then dried over calcium chloride. The monomers were distilled under reduced nitrogen atmosphere just before use.

In the samples of N series, the polymerizations were stopped at low conversions by pouring the reaction mixtures into methanol. Therefore, the samples of N series must have narrow CCD. On the other hand, sample B-60 was polymerized to a high conversion, so that the sample must have a broad CCD. The polymerization conditions for B-60 are the same as those for N-45, except the degree of conversion.

To purify the copolymer samples thus obtained, the samples were dissolved in butanone, precipitated, washed with methanol, and dried in vacuo at about 60 °C. This procedure was repeated twice for each sample.

MA contents of the copolymers were determined by the elemental analysis of carbon and hydrogen. Their $\bar{M}_n$ were determined with a high-speed membrane osmometer of Knauer in butanone at 25 °C. The molecular characteristics of the samples are shown in Table I, together with the initial mixing ratio of two monomers.

GPC Measurements. The GPC apparatus used in the present work is a high-speed liquid-chromatography HLC-802 (Toyo Soda Manufacturing Co., Ltd.) equipped with a differential refractometer (RI) and an ultraviolet detector (254 nm) (UV). In the apparatus, the elution volume (V_e) is measured by a drop counter. The column set used is composed of four columns of TSK-GEL (G3000H6, G4000H6, G5000H8, and G6000H6) packed with polystyrene gels, having length of 2 ft, respectively. All the measurements were carried out at 25 °C, a flow rate of 1.2 mL/min, and a polymer concentration of about 0.1 g/mL. Tetrahydrofuran (THF), used as the eluent, was purified by refluxing and distilling over sodium wire under nitrogen atmosphere and then degassed by ultrasonic wave, just before use.

Conversion of V_e to Molecular Weight. The so-called universal calibration curve was obtained by plotting log ($[\eta]M$) against V_e for standard samples, i.e., monodisperse polystyrene samples obtained from NBS of the U.S.A., Pressure Chemical Co., and Toyo Soda Manufacturing Co. Ltd., and also monodisperse poly(α-methylstyrene) samples from Nagoya University.[9] The molecular weights (M) were the values determined by suppliers. The limiting viscosity index $[\eta]$ was determined in THF at 25.0 °C by using the Ubbelohde type viscometer which was designed

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Table I

	polymerization mixture				copolymer				
	monomer/mol		$[I] \times 10^3$, mol L^{-1}	conversion wt fraction	$\overline{M}_n \times 10^{-4}$		$\overline{M}_w \times 10^{-4}$ GPC	γ^a GPC	MA^b mol fraction
	MA	St			osm	GPC			
N-45	6.00	4.00	9.12	0.134	26.1	24.7	40.7	1.65	0.466
N-60	8.40	2.10	9.59	0.098	27.6	26.4	45.1	1.71	0.573
N-75	10.11	0.761	9.93	0.092	30.2	28.1	64.6	2.30	0.779
B-60	0.600	0.400	9.12	0.920	48.2	47.4	267	5.63	0.602

[a] $\gamma = \overline{M}_w/\overline{M}_n$. [b] Elemental analysis.

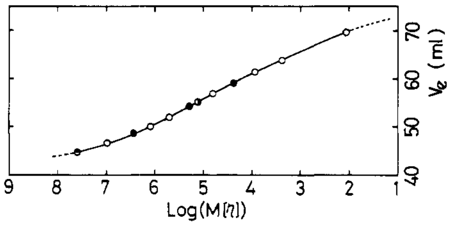

Figure 1. The universal calibration curve of GPC: (○) PSt (Press. Chem.), (◒) PSt (NBS), (◑) PSt (Toyo Soda), (●) P(αMeSt).

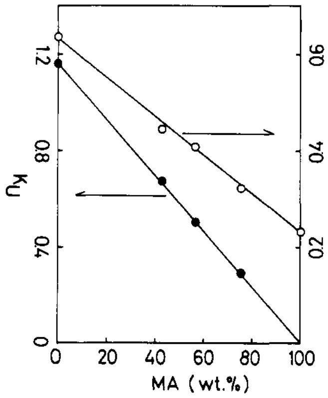

Figure 2. The relationships between MA content and K_R or K_U: (○) K_R, (●) K_U.

so that the kinetic energy correction would be negligible. Using the universal calibration curve shown in Figure 1, the elution volumes in GPC patterns of the copolymer samples were converted to $M[\eta]$ and then the $M[\eta]$ was converted to M by using the $[\eta]$-M relationship determined independently. The elution curve of sample B-60 was spread beyond the maximum molecular weight of the standard samples used for the calibration. The linear extrapolation of the calibration curve shown in Figure 1 was assumed for sample B-60.

Determinations of w_c and F_{MA}. Both detectors of RI and UV were calibrated using the copolymer samples with known chemical compositions. The proportionalities between peak areas obtained by both detectors and polymer concentrations were confirmed by plotting the area against sample concentration. The proportionality constants thus obtained are plotted against the weight fraction of MA in Figure 2. Thus, based on the linear relationships, the heights of peaks from the base lines in GPC patterns, r_{RI} and r_{UV}, are given by

$$r_{RI} = \{(1 - x)K_{RS} + xK_{RM}\}w_c \qquad (1)$$

$$r_{UV} = (1 - x)K_{US}w_c \qquad (2)$$

where x is the weight fraction of MA in the copolymer, w_c is the weight concentration of the copolymer, K_{RS} and K_{US} are the proportional constants for polystyrene in RI and UV patterns, respectively, and K_{RM} is the constant for poly(methyl acrylate) in RI patterns. The values of K_{RS}, K_{RM}, and K_{US} determined are shown in Table II.

From eq 1 and 2, we have

$$x = \frac{K_{US} - K_{RS}(r_{UV}/r_{RI})}{K_{US} - \Delta K_R(r_{UV}/r_{RI})} \qquad (3)$$

$$w_c = \frac{K_{US}r_{RI} - \Delta K_R r_{UV}}{K_{RM}K_{US}} \qquad (4)$$

where $\Delta K_R = K_{RS} - K_{RM}$. The value of x obtained from eq 3 can be converted to mole fraction F_{MA}.

Table II

	PSt	N-45	N-60	N-75	PMA
MA/wt fraction	0	0.428	0.566	0.753	1.0
K_U	1.16_2	0.674	0.503	0.294	0
K_R	0.635	0.443	0.408	0.322	0.232

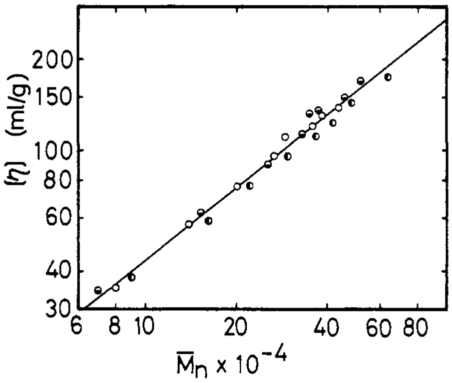

Figure 3. The relationship between $[\eta]$ and $\overline{M}_n$ for the fractions of N-series samples: (○) N-45, (◐) N-60, (◒) N-75.

Determination of the [η]-M Relationship. The copolymer samples used to determine the relationship between $[\eta]$ and M were obtained by fractionation of the samples of N series having narrow CCD. The fractionations were carried out by a successive precipitation method using butanone as solvent and mixture of methanol and water as precipitant at 25.0 °C. The purification of the fractions and the determination of $\overline{M}_n$ of the fractions were carried out by the same methods as in the case of the whole copolymer samples. The measurements of $[\eta]$ were carried out by the same method as in the case of the standard samples.

The double logarithmic plot of $[\eta]$ vs. $\overline{M}_n$ for the fractions is shown in Figure 3. From the data for St-MA copolymers in benzene, Matsuda et al.[10] suggested that the relationship between $[\eta]$ and $\overline{M}_n$ in a common good solvent for both monomer units may be approximated by a common equation, irrespective of chemical composition of the copolymer series. In the present work, too, all the data points fit a common straight line. This implies that the radius of gyration of the present copolymers in THF may be assumed to be, within experimental error, independent of chemical composition. Strictly speaking, the relationship between $[\eta]$ and M cannot be illustrated by a single line if the molecular weights of two monomer units are not equal. In the present copolymer, however, the corrections for the difference between the molecular weights of two monomer units are comparable to the experimental error in determining $\overline{M}_n$. Therefore, the radius of gyration of the present copolymer and then the elution volume in THF may be assumed to be a function of molecular weight, only. The relationship between $[\eta]$ and $\overline{M}_n$ obtained by the least-squares method is

$$[\eta] = 4.40 \times 10^{-5}\overline{M}_n^{0.799} \text{ dL/g} \qquad (5)$$

The present samples are polydisperse with respect to molecular weight. If $\overline{M}_n$ is used in the viscosity equation $[\eta] = K_n\overline{M}_n^a$, the value of K_n must be greatly influenced by MWD of samples. The constant K, which the viscosity equation would have if the samples were monodisperse, can be calculated from K_n using GPC data of the present samples. That is, by assuming the exponential type

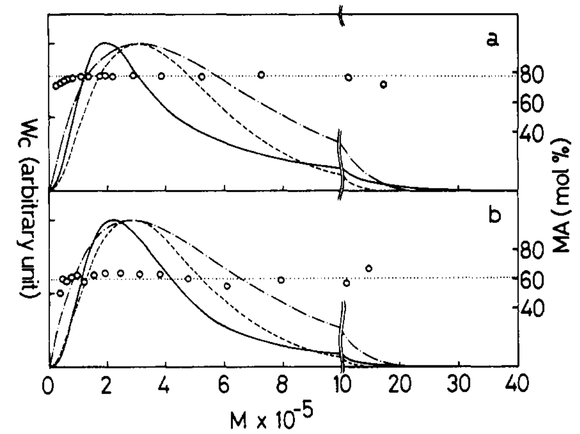

Figure 4. The MWD curves and the chemical composition–molecular weight relationships for N-75 and N-60: (a) N-75; (b) N-60; (—) MWD curve by GPC; (O) MA content by GPC; (---) MWD curve calculated assuming the coupling termination; (- - -) MWD curve calculated assuming the disproportionation; (···) MA content calculated.

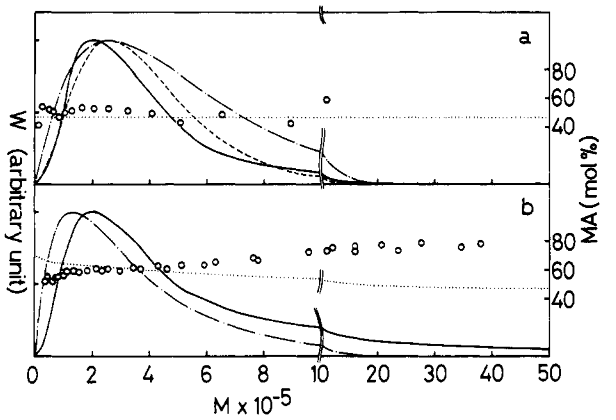

Figure 5. The MWD curves and the chemical composition–molecular weight relationships for N-45 (a) and B-60 (b): (—) MWD curve by GPC; (O) MA content by GPC; (---) MWD curve calculated assuming the coupling termination; (- - -) MWD curve calculated assuming the disproportionation; (···) MA content calculated.

MWD for the samples and also an appropriate value of polydispersity index $\gamma = \bar{M}_w/\bar{M}_n$, the value of K_n/K corresponding to the value of γ can be calculated from the theory of Koningsveld.[11] The value of γ assumed must agree with the values determined by GPC, using the viscosity equation thus calibrated. Assuming γ = 1.50, 1.25, and 1.10 for the present samples, the calculations of K_n/K were carried out. The best consistency between the assumed and the calculated values of γ was obtained at γ = 1.25. The value of K_n/K is 1.18 for this value of γ. Thus, the calibrated viscosity equation for the present copolymers is

$$[\eta] = 3.73 \times 10^{-5} M^{0.799}\ \mathrm{dL/g} \qquad (6)$$

Results

Figures 4 and 5a show MWD curves of N series samples and MA contents of the fractions in GPC. In these samples, the MA content is almost constant irrespective of molecular weight and equal to the average MA content of the whole polymer.

The experimental results for the high-conversion sample B-60 are shown in Figure 5b. Two series of GPC measurements were carried out in this case. The average MWD curve is illustrated by a solid line, and all experimental points for chemical composition are shown by open circles. In Figure 5b, it is clear that there is a correlation between chemical composition and molecular weight. That is, as the molecular weight increases, the MA content increases. Moreover, the MWD curve of sample B-60 is broader than those of N-series samples, extending to the higher molecular weight region.

In Table I, $\bar{M}_n$ determined by the osmometer and calculated from GPC patterns are compared. Fairly good agreement between both values is observed for each sample. The polydispersity index γ calculated from GPC results is also shown in the table. The γ values of N-series samples are near the theoretical values predicted, i.e., they are from 1.5 to 2.0. However, the values of B-60 are clearly larger than the values of N series.

Theoretical Calculations

In copolymerization, the molecular weights are determined by the concentrations of monomers and initiator, while the chemical compositions of the polymers formed are determined by the monomer composition at the instant. Therefore, the chemical composition is a measure of monomer composition which varies with the degree of conversion. The MWD and molecular weight–chemical composition relationship of copolymers can be calculated from the classical theory of copolymerization kinetics, by assuming that the whole copolymer consists of n instantateous copolymers. That is, the entire range of CCD of the whole copolymer is divided into n parts having equal intervals of chemical composition. The chemical composition and MWD of each instantaneous copolymer are calculated, and then those of the whole copolymer are obtained by summing up the values for each instantaneous copolymer. Each instantaneous copolymer is denoted by the subscript l. The calculation was carried out by NEAC 2200 Model 300.

The mole fraction of component 1 in an instantaneous copolymer F_1 is related to monomer composition f_i by the well-known equation

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \qquad (7)$$

where r_1 and r_2 are the monomer reactivity ratios and $f_i = c_i/\sum_i c_i$. c_i is the mole concentration of monomer i (i = 1 or 2). If we assume the steady state for the concentration of the free-radical species and negligible chain transfer reaction, the distribution of polymerization degree $W(P)$ is given by

$$W(P) = \left(1 - \rho + \frac{\rho P}{2\lambda}\right)\frac{P}{\lambda^2}\exp\left\{-\frac{P}{\lambda}\right\} \qquad (8)$$

where ρ is the fraction of the coupling reaction in the termination reaction, and λ is the number average degree of polymerization of polymer radicals. $\lambda = \bar{P}_n$ in the case of disproportionation termination and $\lambda = \bar{P}_n/2$ in the case of coupling termination, if the number average degree of polymerization of the dead polymer is shown by $\bar{P}_n$. The value of $\bar{P}_n$ is given by

$$\bar{P}_n = \frac{r_1 c_1^2 + 2c_1 c_2 + r_2 c_2^2}{(1 - \rho/2) R_I^{1/2}\{\delta_1^2 r_1^2 c_1^2 + 2\phi r_1 r_2 c_1 c_2 + \delta_2^2 r_2^2 c_2^2\}^{1/2}} \qquad (9)$$

where R_I is the rate of initiation, $\delta_i = (2k_{tii}/k_{ii})^{1/2}$, and $\phi = k_{t12}/2(k_{t11}k_{t22})^{1/2}$ if indicating the rate constant of termination reaction between radicals having terminal monomeric units i and j by k_{tij} and the rate constant of propagation reaction between radical i and monomer i by k_{ii}. Moreover, the monomer composition during the copolymerization process can be given as a function of the degree of conversion by [12]

$$(1 - c/c^\circ) = 1 - (f_1/f_1^\circ)^\alpha (f_2/f_2^\circ)^\beta (f_1^\circ - \delta)^\gamma/(f_1 - \delta)^\gamma \qquad (10)$$

Table III

sample	n	range of MA mol fraction (calcd)	MA/mol fraction		γ			$t_{\text{fin.}}$		$f_e \times 10^2$ (calcd)
					calcd					
			calcd	anal.	coup	dispr	GPC	calcd	exptl	
N-45	4	0.459–0.470	0.464	0.466	1.50	2.00	1.65	3.29	3	3.94
N-60	8	0.592–0.611	0.601	0.573	1.50	2.00	1.71	2.34	2	3.91
N-75	15	0.763–0.797	0.779	0.779	1.50	2.00	2.30	2.18	2	3.94
B-60	60	0.459–0.964	0.560	0.602		2.34	5.76	28.8	50	[a]

[a] 3.93×10^{-2} was used in the calculation.

where $c = \sum_i c_i$, $(1 - c/c^\circ)$ is the degree of mole conversion, 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 $\delta = (1 - r_2)/(2 - r_1 - r_2)$. Except R_I, all rate constants in eq 7 and 9 are known in the literature for the copolymerization of styrene and methyl acrylate. The unknown quantity R_I is given by

$$R_I = 2f_e k_d[I]_0 \exp\{-K_d t\} \tag{11}$$

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 regarded as an adjustable parameter. The reaction time t_l can be estimated from copolymerization rate, such as

$$t_l = \sum_l \Delta t_l \tag{12}$$

$$\Delta t_l = -\Delta(c)_l / v_l \tag{13}$$

where $\Delta(c)_l$ is the decrease in monomer concentration $[\Delta(c)_l = c_l - c_{l-1}]$, and v_l is the polymerization rate at the monomer composition, which can be estimated from the data reported by Walling.[3]

$(\bar{P}_n)_l$ and $W_l(P)$ calculated from eq 8, 9, and 11 are converted to $(\bar{M}_n)_l$ and $W_l(M)$, respectively. The $W(M)$ and $\bar{M}_n$ of the whole copolymer are obtained by summing up the $W_l(M)$. The adjustable parameter f_e can be determined, so that the $\bar{M}_n$ thus calculated may be equal to the observed one in the case of N series, since it can be assumed that the value is constant irrespective of the monomer concentrations. Then, the relationship between molecular weight and chemical composition can be obtained from $(F_1)_l$ and $W_l(M)$.

In the actual calculations, the following constants were employed, indicating MA by 1 and St by 2, respectively: $r_1 = 0.18$, $r_2 = 0.75$,[13] $k_{t11} = 9.5 \times 10^6$ (L mol^{-1} 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] $\phi = 40$,[3] $\rho = 1$ or 0, that is, the termination reaction was assumed to be either the coupling or the disproportionation. The calculated results thus obtained for N-series samples and B-60 are shown in Figures 4 and 5 to be compared with experimental results. The polydispersity index γ, width of CCD, average MA content, reaction time, and efficiency of initiation f_e calculated are shown in Table III in comparison with observed values.

Discussion

In Table III, it is observed that f_e determined for N-series samples is constant independent of the initial monomer composition. This justifies the validity of the assumption of f_e. Since the purity of the initiator used was low, the absolute values of f_e determined are not significant. The agreement between the experimental and the calculated MWD curves for N-series samples appears to be fairly good as shown in Figures 4 and 5a, inspite of the several assumptions made in the calculation.

As shown in Figures 4 and 5a, the MA content determined by GPC is approximately constant irrespective of molecular weight in N-series samples. According to the statistical theory of copolymerization,[1] a copolymer formed instantaneously has a symmetrical distribution of chemical composition, whose width is broader as the molecular weight is smaller. However, the average composition must be independent of molecular weight. The present experimental results are in agreement with the theoretical predictions.

The calculated values of the average MA content of the whole polymers are in fair agreement with the analytical values, as shown in Table III. This may imply the validities of eq 7 and 10, and of the values of r_1 and r_2 used in the calculation.

For the high-conversion sample B-60, the calculation was carried out by assuming the average value of f_e for N-series samples, neglecting the gel effect. It was also assumed that the termination is caused only by disproportionation reaction. The MWD curve and MA content–molecular weight relationship thus calculated are illustrated in Figure 5b, together with the experimental results. The difference between both curves is especially remarkable in the region of higher molecular weight. Moreover, polydispersity index γ obtained from the experimental GPC results is remarkably larger than the calculated one. That is, the MWD obtained experimentally are appreciably broader than the calculated one, despite the fact that the disproportionation termination, which gives the broader MWD, was assumed in the calculation. This long tailing in the higher molecular weight region of the experimental MWD may be, at least partially, due to the gel effect, which was neglected in the calculation.

Concerning the correlation between MA content and molecular weight in sample B-60, it is experimentally observed that the MA content increases as the molecular weight increases. Theoretically, on the other hand, the MA content should decrease with molecular weight as shown by a dotted line in Figure 5b. This discrepancy between the calculated and the experimental results may also be due to the gel effect. If there is the gel-effect, the molecular weights of the components produced at higher MA contents, i.e., at higher conversions, are higher than the calculated ones so that the MA content may increase with increasing molecular weight, in disagreement with the theoretical prediction.

It may also be noteworthy that concerning the reaction time of whole polymers t_{fin}, the calculated and the experimental values are different from each other in sample B-60, whereas both values are nearly equal in N-series samples.

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References and Notes

(1) W. H. Stockmayer, *J. Chem. Phys.*, 13, 199 (1945).
(2) H. W. Melville, B. Noble, and W. F. Watson, *J. Polym. Sci.*, 4, 629 (1949).

(3) C. Walling, *J. Am. Chem. Soc.*, **71**, 1930 (1949).
(4) S. Teramachi and Y. Kato, *Macromolecules*, **4**, 54 (1971).
(5) J. R. Runyon, D. E. Barnes, J. F. Rudd, and L. H. Tung, *J. Appl. Polym. Sci.*, **13**, 2359 (1969).
(6) J. E. Adams, "Gel Permeation Chromatography", Marcel Dekker, New York, N.Y., 1971, p 391; *Sep. Sci.*, **6**, 259 (1971).
(7) J. V. Dawkins and M. Hemming, *J. Appl. Polym. Sci.*, **19**, 3107 (1975).
(8) F. M. Mirabella, Jr., et al., *J. Appl. Polym. Sci.*, **19**, 2131 (1975); **20**, 959 (1976).
(9) T. Fujimoto, N. Ozaki, and M. Nagasawa, *J. Polym. Sci., Part A*, **3**, 2259 (1965).
(10) H. Matsuda, K. Yamano, and H. Inagaki, *J. Polym. Sci., Part A-2*, **7**, 609 (1969).
(11) R. Konogsveld and C. A. Tuijnman, *Makromol. Chem.*, **38**, 39, 44 (1960).
(12) V. E. Meyer and G. G. Lowry, *J. Polym. Sci., Part A*, **3**, 2843 (1965).
(13) F. M. Lewis, C. Walling, W. Cummings, Er. Briggs, and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 1519 (1948).
(14) M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, *J. Am. Chem. Soc.*, **73**, 5395, 1700 (1951).
(15) J. P. van Hook and T. V. Tobolsky, *J. Am. Chem. Soc.*, **80**, 779 (1958).

Morphological Studies of Oriented Crystallization of High-Density Polyethylene

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ABSTRACT: Morphological studies of oriented crystallization of a high-density polyethylene were performed by observing small-angle X-ray (SAXS) and light-scattering (SALS) patterns as well as wide-angle X-ray diffraction patterns (WAXS) as a function of molecular orientation in the amorphous phase (melt draw ratio). These patterns were discussed in terms of the change of nucleation parameters in oriented crystallization with draw ratio: (1) the change in bulk free energy of crystallization, the effect of which is identical for all crystals (the "average effect"), and (2) the change in the kinetic factor *H*, i.e., the fraction of the chain segments effectively attached to growing nuclei which is different for crystals having different orientation with respect to the orientation axis of the sample (the "specific effect"). The angular dependences of the SALS, SAXS, and WAXS patterns suggested that the specific effect associated with the kinetic factor *H* is dominant over the average effect for a particular crystallization condition studied in this article.

There is some evidence in the literature that the long spacings measured by small-angle X-ray scattering (SAXS) in polyethylene and other polymers behave with temperature and molecular orientation similarly to the theoretical predictions for the critical cluster (nucleus) thickness, l^*, obtained from the nucleation theory. Peterlin[1] observed an increase of the long spacings with increasing crystallization temperature, T (and reduced undercooling ΔT), an effect resulting from increased critical cluster thickness. Similarly, Kobayashi and Nagasawa[2] observed reduction of the long spacings of oriented crystallized polyethylene films with melt-draw ratio, related to the degree of molecular orientation. The reduction of the long spacing has been correlated to and predicted in terms of a reduction in the critical cluster thickness l^*, due to the average change in the bulk free energy of crystallization Δf.

In this article, we have studied morphology of high-density polyethylene films prepared by oriented crystallization by observing the SAXS, wide-angle X-ray diffraction (WAXS), and small-angle light scattering (SALS) as a function of draw ratio. The results will be interpreted by transmitting the parallelism described above also on the relation between the long spacing and critical cluster thickness l^* for differently oriented crystals. Our primary interest will be focused on the role of orientation dependent "specific" or "kinetic factor" H to be discussed in the following section of this article on the nucleation and growth parameters, and therefore on the resulting morphology of oriented crystallized films.

Table I
Characteristics of the Extruded Films[a]

specimen no.	screw velocity, revolutions/min	take-up velocity, m/min	draw ratio	film thickness, μm
1	20	9.2	20–25	15–25
2	30	9.2	12–13	40 ± 5
3	40	9.2	8–9	55 ± 5
4	40	7.2	6.7	75
5	40	4.1	5	100 ± 10
6	40	4.2	4	130 ± 10

[a] The blow-up ratio = 1, temperature of the extruded melt $T = 160$ °C.

Experimental Section

Material. A high-density polyethylene with viscosity-average molecular weight 7.8×10^4, melt index 0.82 g/10 min, and density 0.963 g/cm^3 (Novatec ET010, Mitsubishi Chemical Industries,

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