

Molecular Weight Distributions in Terpolymerization of α -Methylstyrene/Styrene/Acrylic Acid in Continuous Stirred Tank Reactor

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ABSTRACT: Free-radical terpolymerization of α -methylstyrene/styrene/acrylic acid (AMS/ST/AA) in a continuous stirred tank reactor (CSTR) was studied theoretically and experimentally. A series of reactions were conducted to investigate the effect of the reaction temperature, residence time, solvent contents, initiator concentration, chain-transfer agent level, and different monomer compositions on the molecular weight distribution (MWD). The mathematical model based on “the instantaneous property method (IPM)” and the pseudokinetic rate constant method was introduced and modified to predict the MWD of the bulk terpolymer produced in a CSTR. The effects of process variables were included in the mathematical model. Extensive comparisons were made between the theoretical results and experimental values. The rate of the free-radical terpolymerization of AMS/ST/AA was comparatively slow and it was found that the concentration of α -methylstyrene had a strong influence on the molecular weight and polydispersity of the MWD. This presumably reflected the existence of a normal bimolecular termination rate and a slow propagation rate due to steric hindrances at the doubly substituted vinyl carbon atom or transfer of the allylic hydrogen from the α -methyl group. Good agreement was obtained between calculated MWD and the experimental one by assuming that the disproportionation termination of free radicals was the dominant chain-stoppage mechanism. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 479–487, 2001

Key words: terpolymerization; α -methylstyrene; molecular weight distribution; instantaneous property method; disproportionation

INTRODUCTION

Contemporary industrial standards require that a process to prepare resins suitable for high-solids coating systems has sufficient flexibility to control the molecular weight (MW) of the desired product and its polydispersity index in accordance with

market requirements. The required properties of high-solid polymers are a narrow molecular weight distribution (MWD), low solution viscosity, low volatile contents, good color, and so on. Among the properties, the MWD is considered as the most important property that directly influences the end-use characteristics of a polymer. The MW and the MWD determine the melting point and the flow properties of melted polymer during the processing.^{1–3} Moreover, most of mechanical properties, such as the modulus, strength, and impact resistance, can be influ-

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enced by the MWD. It has been suggested that a continuous bulk polymerization process provides a high-purity yield and low MW polymers suitable for the application of high-solid polymers.⁴ Until recently, the preparation of polymers with very low MW has not been completely successful, since it requires effort to hold down the MW with efficiency. The key to synthesis lies in the capability to control both the propagation rate and the MWD, which can be accomplished by manipulation of the catalysis type and level, reaction temperature control, and chain-transfer agent concentration. The MWD of a polymer depends on a number of factors, including the number of radicals initially produced, the propagation, the termination, and the chain-transfer reaction rate. By choosing a proper initiator level and reaction temperature, one can control the initial radical flux. Also, one can prepare oligomers by selecting an appropriate type and concentration of a chain-transfer agent and keeping the MW of the polymers low.

The α -methylstyrene/styrene/acrylic acid (AMS/ST/AA) terpolymer has been used in ink and coating industries, since it has a number of advantages, for example, high gloss, compatibility, viscosity stability, transfer property and printability, and heat and chemical resistance. For that, the free-radical polymerization of α -methylstyrene has been widely studied, especially in organic solvent. α -Methylstyrene is known to polymerize and copolymerize sluggishly in free-radical reactions and to yield low MW products in such processes. This behavior has been variously ascribed to steric restrictions on the placement of successive monomer units (penultimate effect), the reversibility of AMS polymerization, chain transfer to an AMS monomer, and to kinetic factors.⁵ These kinetic factors include a low propagation rate ($k_p = 26 \text{ mol/L}^{-1} \text{ s}^{-1}$) for AMS homopolymerization.⁶⁻¹¹ In earlier studies of the solution copolymerization of the AMS/ST system, Rudin et al. reported that the observed slow reaction rates and low MW of polymers probably should be ascribed to the stability of the AMS radical.^{12,13} Poly(AMS) is subject to steric hinderance around the α -carbon atom and has a relatively low enthalpy of polymerization. They reported that the ceiling temperature of this polymer is 61°C and it is impossible to produce high MW poly(AMS) from the monomer at a unit or higher concentration above the temperature.¹⁴

In this work, free-radical bulk terpolymerization of AMS/ST/AA was carried out in a continuous stirred tank reactor (CSTR) and the MWD of

the terpolymers over the range of monomer composition and reaction conditions was investigated experimentally and theoretically. Particularly, the effects of AMS on the MWD were studied from an industrial aspect.

MODELING

It is well known that free-radical terpolymerization involves elementary reactions and that as the number of components increases the kinetic expressions become fairly complicated. To avoid such complications, the pseudokinetic rate constant method was developed. For that, the pseudokinetic rate constant method was applied to our free-radical bulk terpolymerization model.^{15,16} Furthermore, it was of great interest to know whether this method could be applicable when the free-radical terpolymerization was carried out in a CSTR. As mentioned above, kinetic modeling was developed using the instantaneous property method (IPM), the pseudokinetic rate constant method, and general CSTR material balances.¹⁷ The model equations were developed based on the following assumptions for simplicity: mixing was perfect; the reactor was operating at the steady state; rate constants were independent of the polymer radical chain length; all radicals had the same reactivity; and no density change occurred during the polymerization.

IPM

The IPM employs both a long-chain hypothesis (LCH) and a quasi-steady-state assumption (QSSA) to derive analytical expressions for the MWD. For homopolymers, it can be shown that the cumulative live radical distribution takes the following form:

$$\overline{w(i)} = (\tau + \beta) \exp[-(\tau + \beta)i] \quad (1)$$

where τ and β are two dimensionless parameters defined as

$$\tau = [(k_{td}R_p)/(k_pM)^2] + [k_t/k_p] + [(k_sS)/(k_pM)] \quad (2)$$

$$\beta = (k_{tc}R_p)/(k_pM)^2 \quad (3)$$

where

$$R_p = k_pMP_0; \quad P_0 = [(2fk_dI)/k_t]^{1/2} \quad (4)$$

On the other hand, the instantaneous chain-length distribution of a dead polymer can be given by the following equation:

$$w(i, x) = (\tau + \beta) \left(\tau + \frac{1}{2} \beta (\tau + \beta) i \right) i \times \exp[-(\tau + \beta) i] \quad (5)$$

where $w(i, x)$ is the fraction of polymer molecules containing i monomer units and produced instantaneously at conversion x . The instantaneous number- and weight-average molecular weights can be obtained from this distribution. They are given by

$$\overline{M}_n = (\text{MW}) \left/ \sum \frac{w(i, x)}{i} \right. \quad (6)$$

$$\overline{M}_w = (\text{MW}) \sum [i w(i, x)] \quad (7)$$

The Pseudokinetic Rate Constant Method

Based on the terminal model for copolymerization, the pseudokinetic rate constants for the propagation reaction, k_p , termination by disproportionation, k_{td} , and termination by combination, k_{tc} , were given by the following equations:

$$k_p = \sum_{i=1}^N \sum_{j=1}^N k_{ij} \phi_i^* f_j \quad (8)$$

$$k_{td} = \sum_{i=1}^N \sum_{j=1}^N k_{td_{ij}} \phi_i^* \phi_j^* \quad (9)$$

$$k_{tc} = \sum_{i=1}^N \sum_{j=1}^N k_{tc_{ij}} \phi_i^* \phi_j^* \quad (10)$$

where N is the number of components, and k_{ij} , the kinetic rate constants for propagation. The subscripts i and j are used to designate the type of polymer radical and monomer, respectively. The kinetic rate constants, $k_{td_{ij}}$ and $k_{tc_{ij}}$, are for termination reactions by disproportionation and combination, respectively. The mol fraction of radical of type i is ϕ_i^* , namely:

$$\phi_i^* = [R_i^*] \left/ \sum_{i=1}^N [R_i^*] \right. = [R_i^*]/[R^*] \quad (11)$$

where $[R_i^*]$ is the polymer radical concentration whose radical center is located on monomer unit i . The mol fraction of monomer j in the monomer mixture, f_j , can be expressed as follows:

$$f_j = [M_j] \left/ \sum_{j=1}^N [M_j] \right. = [M_j]/[M] \quad (12)$$

By application of the pseudokinetic rate constants, the rate expressions for each type of reaction reduce to those of homopolymerization. It has been shown that chain transfer to low MW species plays an important role in controlling the MWs during high-temperature polymerization. Therefore, we could predict that the intermediate products as well as by-products of low MW created during terpolymerization of AMS/ST/AA in a CSTR were responsible for the MWs and MWDs.

EXPERIMENTAL

Materials

Technical-grade monomers were employed without further pretreatment. ST and AA were obtained from Junsei (Tokyo, Japan). AMS, dipropylene glycol monoethyl ether (DPME), *n*-dodecyl mercaptan (*n*-DM), and *t*-butyl perbenzoate (*t*-BPB) were obtained from Aldrich (Milwaukee, WI) and used as received. Double-distilled water (DIW) was used all through the reactions.

Terpolymerization

Free-radical terpolymerization was carried out in the CSTR. A schematic diagram of the CSTR is illustrated in Figure 1. It consists of an SUS vessel equipped with a temperature controller, monomer feed inlet line, and stirrer. The reactor vessel was heated with an oil circulator having a digital PID controller. Premixed monomers and the initiator were fed continuously into the top of the reactor through a preheating tube at a constant temperature, $120 \pm 1^\circ\text{C}$. Before the polymerization, the initial charge was filled to a pre-selected level (0.45 L) and then the volumetric flow rate of the monomer, initiator, and solvent

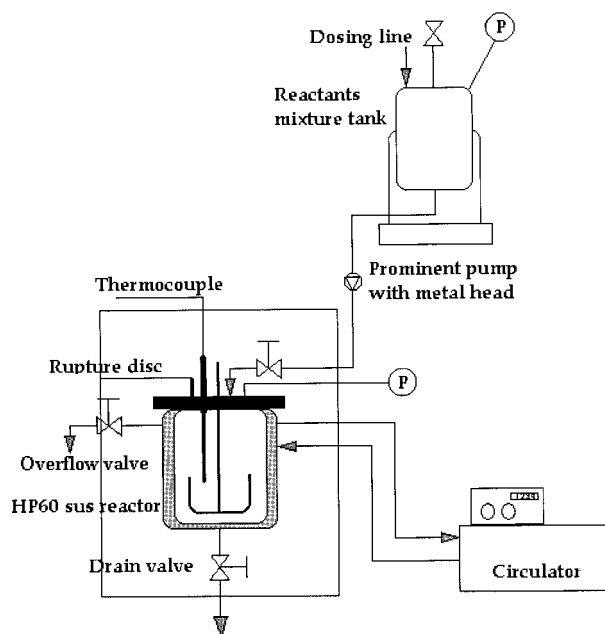


Figure 1 Schematic diagram of CSTR for the terpolymerization of AMS/ST/AA.

mixture were adjusted to maintain the preselected level of the contents in the reactor.

Two different series of polymerization were conducted: The first one was designed to study the effects of the various reaction conditions (e.g.,

reaction temperature, residence time, concentration of the initiator, solvent, and chain-transfer agent) on the MWD. In the first series, the ratio of AMS/ST/AA was fixed at the value of 37/31/32, which is indicated in Table I. The second one was for the effect of the ratio of AMS/ST on the MW and MWD. Experimental conditions of the second series are listed in Table II. The ratio of AMS to ST was varied from 0 to 100% at a fixed AA content. The solvent (DPME) was used to reduce the solution viscosity of the polymer product and to provide a heat sink to prevent a runaway reaction. However, the acid number of the terpolymer may be reduced if the solvent esterifies with the polymer and the MW increases subsequently. *t*-BPB was used as an initiator, which decomposes thermally into radicals in a first-order reaction. Its half-life period in the radical decomposition process is about 1 h at 90°C.

Characterization

The time-conversion was measured by the gravimetric method. A small amount of the samples were withdrawn from the drain line in the CSTR and placed in glass dishes. The weight of the samples and dishes were recorded. A few drops of shortstop (1000 ppm hydroquinone methanol solution) were added and the samples were dried to obtain a constant weight in a vacuum-drying oven

Table I Experimental Conditions and Molecular Weights of Bulk Terpolymers at a Constant Monomer Weight Ratio^a

Sample Code	Reaction Conditions		Ingredients ^b			MW		
	Temperature (°C)	RT ^c (min)	<i>t</i> -BPB ^d (wt %)	DPME ^e (wt %)	<i>n</i> -DM ^f (wt %)	\bar{M}_w (g/mol)	\bar{M}_n (g/mol)	PDI
A1	160	15	5.00	25.0	—	10,800	5700	1.90
A2	170	15	5.00	25.0	—	9 700	5200	1.87
A3	180	15	5.00	25.0	—	8 900	4900	1.82
A4	180	12	5.00	25.0	—	8 200	4600	1.78
A5	180	20	5.00	25.0	—	9 400	5000	1.88
A6	180	15	3.75	25.0	—	10,700	5600	1.91
A7	180	15	6.25	25.0	—	7 900	4400	1.80
A8	180	15	5.00	30.0	—	8 300	4700	1.77
A9	180	15	5.00	37.5	—	7 800	4500	1.73
A10	180	15	5.00	25.0	0.1	8 500	5000	1.70
A11	180	15	5.00	25.0	1.0	7 900	4700	1.69

^a Weight ratio of monomers: AMS/ST/AA = 37/31/32.

^b Weight percents were based on total monomer contents (400 g).

^c Residence time.

^d Initiator.

^e Solvent.

^f Chain-transfer agent.

Table II Experimental Conditions and Results for Investigation of Monomer Weight Ratio Variation (Reaction Temperature = 175°C, Residence Time = 15 min)

Sample Code	Monomer Weight Ratio AMS/ST/AA ^b	Experimental Results			
		Conversion (%)	Pressure (bar)	\bar{M}_w (g/mol)	PDI
B1	0/68/32	72	12	21,500	4.3
B2	7/61/32	76	9	15,300	3.4
B3	14/54/32	77	8	11,900	2.8
B4	20/48/32	84	7	9 800	2.4
B5	27/41/32	82	6	8 600	2.3
B6	34/34/32	85	5	8 000	2.1
B7	41/27/32	82	4	8 700	1.8
B8	48/20/32	80	4	8 200	1.8
B9	54/14/32	73	4	8 000	1.8
B10	61/7/32	68	3	7 800	1.7
B11	68/0/32	61	3	7 200	1.7

Solvent: DPME (150 g); initiator: *t*-BPB (7.5 g); DIW (8 g).

^a Total amount of monomer (AMS/ST/AA): 400 g.

at 120°C. The final steady-state conversion was determined from the dry weight of the polymer. The average MW and MWD were measured using a gel permeation chromatography (GPC, Millipore Waters, Milford, MA) with an RI detector. The GPC columns consisted of a train of μ -Styragel series (10^5 – 10^4 – 10^3 –500 Å pore size, Waters, Milford, MA) columns eluted with tetrahydrofuran (2.0 mL/min). GPC data were calibrated using a narrow standard and a universal calibration method.

RESULTS AND DISCUSSION

Effect of Reaction Condition on MWD

To demonstrate the effect of different reaction conditions on the average MW and the MWD, a series of experiments were carried out at a constant monomer composition (AMS/ST/AA = 37/31/32). Experimental results of the first series are listed in Table I.

To obtain a statistically valid MWD of the terpolymer using the IPM technique in a CSTR, the calculation was reiterated until the value reached the invariant point of the instantaneous MWD. As polymerization progresses, the instantaneous MWD converges on the invariant distribution point. The accumulated distribution was obtained by summing up the instantaneous distributions.

Table III shows the parameters used in the calculation. Other kinetic rate coefficients were quoted from the handbook.²⁰

Effect of Reaction Temperature

Samples A1, A2, and A3 in Table I show that the number-average (\bar{M}_n) and weight-average (\bar{M}_w) MW of the polymers decreased as the reaction temperature increased. It can be explained that the number of generating radicals increased due to the high decomposition rate of the initiator as the reaction temperature increased. Subsequently, many terpolymers with low MW were obtained. Additionally, the polydispersity index (PDI) decreased when a higher reaction temperature was applied, which implied that a narrower MWD can be obtained at higher temperature in this reaction. Figure 2 shows experimental data and simulation results concerning the effect of the reaction temperature on the MWD of the terpolymer. As reaction temperature increased, the MWD was shifted to the low MW range and became narrow. No peak for the oligomers (dimer or trimer whose MW is below 500 g/mol) was detected due to the integration limit (500–4,000,000 g/mol) of the GPC. Simulation results agreed well with the experimental data.

Effect of Residence Time

Residence time was manipulated by controlling the mass flow rate of the total ingredients (see A3,

Table III Kinetic Parameters for the Simulation

Form of the Arrhenius Equation	Reaction Rate Constants ^{5,18-20} :
	$k_p = A_{p0} \exp\left(-\frac{E_p}{RT}\right)$
$\text{eff}_i = 1.0$; $A_i = 4.500 \times 10^{13}$; $A_{caa} = 4.209 \times 10^8$; $A_{cbb} = 1.255 \times 10^9$; $A_{ccc} = 2.700 \times 10^5$; $A_{daa} = 0.000$; $A_{dbb} = 0.000$; $A_{dcc} = 0.000$ $A_{paa} = 3.207 \times 10^4$; $A_{pab} = 1.250 \times 10^6$; $A_{pba} = 2.103 \times 10^4$; $A_{pbb} = 1.751 \times 10^6$; $A_{pcc} = 6.600 \times 10^7$; $A_{pbc} = 6.920 \times 10^7$; $A_{pcb} = 4.900 \times 10^6$; $A_{pca} = 1.233 \times 10^5$; $A_{pac} = 2.103 \times 10^8$	$E_i = 1.25 \times 10^5$; $E_{caa} = 2.69 \times 10^2$; $E_{cbb} = 7.00 \times 10^3$; $E_{ccc} = 1.00 \times 10^2$; $E_{daa} = 0.00$; $E_{dbb} = 0.00$; $E_{dcc} = 0.00$ $E_{paa} = 2.42 \times 10^3$; $E_{pab} = 2.90 \times 10^4$; $E_{pba} = 1.80 \times 10^4$; $E_{pbb} = 2.90 \times 10^4$; $E_{pcc} = 2.00 \times 10^4$; $E_{pbc} = 2.90 \times 10^4$; $E_{pcb} = 2.00 \times 10^4$; $E_{pca} = 2.42 \times 10^4$; $E_{pac} = 1.80 \times 10^4$
Cross-termination rate constants assumed by Reactivity ratios ^{6,20,21}	$k_{tcab} = \sqrt{k_{tcaa}k_{tccb}}$; $k_{tdab} = \sqrt{k_{tdaa}k_{tdbb}}$ $r_{ab} = 0.627$; $r_{ba} = 1.124$; $r_{bc} = 0.380$; $r_{cb} = 0.130$; $r_{ac} = 0.297$; $r_{ca} = 0.193$

Subscripts *a*, *b*, *c*: AMS, ST, and AA monomers; *i*: initiation; *p*: propagation; *t*: termination; *c*, *d*: combination and disproportionation, respectively.

A4, and A5 in Table I). The residence time is inversely proportional to the flow rate. It was found that the residence time had not a signifi-

cant influence on the MWD in Figure 3. However, the number-average and weight-average MW increased as the residence time increased. The

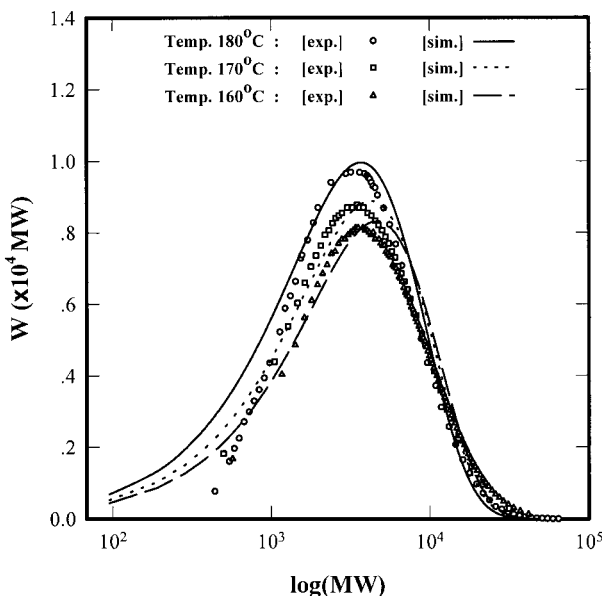


Figure 2 Effect of the reaction temperature on the MWD of terpolymer at constant monomer composition. Residence time = 15 min; initiator concentration = 5 wt % based on total monomer; solvent concentration = 25 wt % based on total monomer; AMS/ST/AA = 37/31/32; [exp.] = experimental data; [sim.] = simulation.

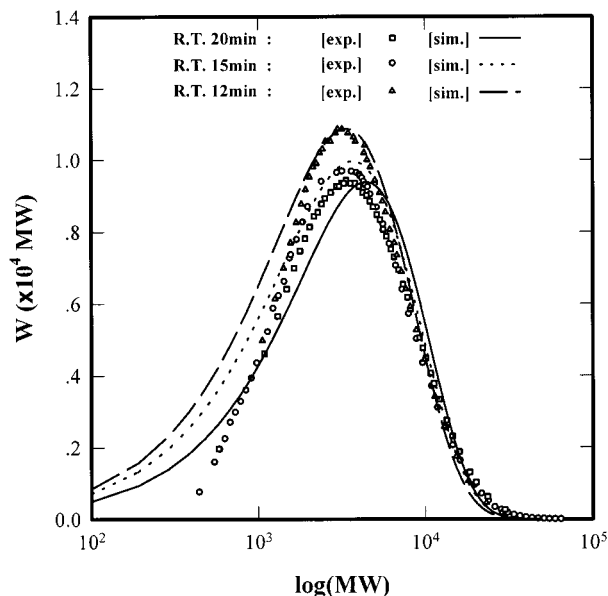


Figure 3 Effect of the residence time on the MWD of the terpolymer at constant monomer composition. Reaction temperature = 180°C; initiator concentration = 5 wt % based on total monomer; solvent concentration = 25 wt % based on total monomer; AMS/ST/AA = 37/31/32; [exp.] = experimental data; [sim.] = simulation.

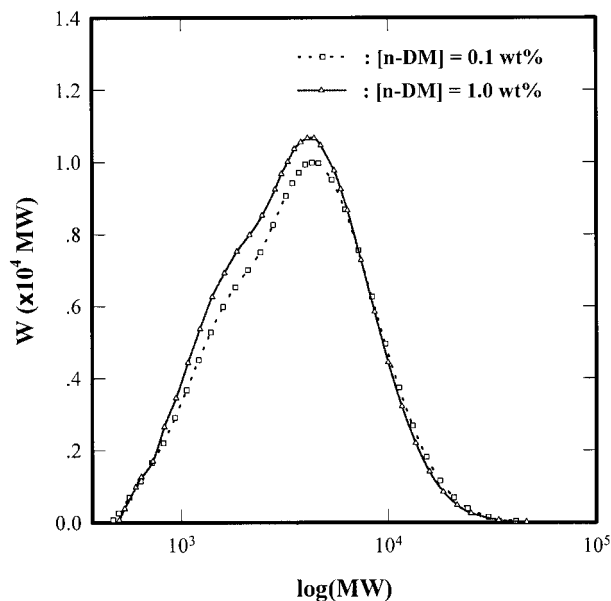


Figure 4 Effect of chain-transfer agent concentration on the MWD of the terpolymer at constant monomer composition. Residence time = 15 min; reaction temperature = 180°C; initiator concentration = 5 wt % based on total monomer; solvent concentration = 25 wt % based on total monomer; AMS/ST/AA = 37/31/32.

MWD was broadened as the residence time increased within the experimental range. From the results, it can be suggested that, if one would get terpolymers with a narrow MWD and low MW, the residence time should be minimized. Additionally, the minimized residence time often has a lower limit, which should be controlled by heat removal during the reaction and steady-state reaction conditions are difficult to achieve.

Effects of Chain-transfer Agent, Initiator, and Solvent Concentration

Figure 4 shows the effect of the chain-transfer agent (*n*-DM) on the MWD. The PDI in the presence of 0.1 and 1.0 wt % *n*-DM was smaller than that in the absence of *n*-DM as given in Table I. Asymmetric peaks appeared in the weight fraction distribution when polymer chains were formed in the presence of *n*-DM. From this result, it can be found that the chain-transfer agent level could be chosen for the MWD control of the AMS/ST/AA terpolymer. For industrial fields, however, the level of the chain-transfer agent often has been limited since it could act as impurities.

In the course of thermal ST/butyl acrylate copolymerization,²² the lowest oligomers (MW

< 500) were generated in much greater quantities than might be expected from the normal distribution of MWs. This result implies that the initial step is analogous to the thermal polymerization of pure ST in the thermal copolymerization of ST/acrylonitrile, that is, a Diels–Alder reaction takes place.²³

Figure 5 illustrates the effect of the initiator concentration on the MWD of the terpolymer. When the concentration of *t*-BPB increased, the number- and weight-average MW decreased and the MWD became narrower. It was concluded that a relatively large amount of radicals might produce polymers having a narrow distribution. This might be due to high levels of radical chain transfer by the monomer itself, which has not been, however, proven yet. Figure 6 illustrates the effect of the solvent concentration on the MWD of the terpolymer. The distribution was relatively broad at the low level of solvent while the distribution became quite narrower at the high level of solvent as listed in Table I. It could be explained that the chain-transfer effects of solvents might contribute to the production of a by-product. However, the solvent concentration might not affect the MW or MWD significantly compared to the effect of the initiator concentration on the MW and MWD.

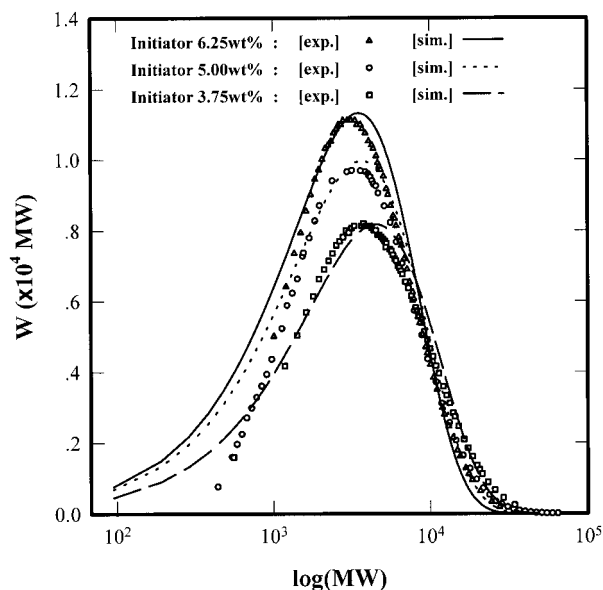


Figure 5 Effect of initiator concentration on the MWD of the terpolymer at constant monomer composition. Residence time = 15 min; reaction temperature = 180°C; solvent concentration = 25 wt % based on total monomer; AMS/ST/AA = 37/31/32; [exp.] = experimental data; [sim.] = simulation.

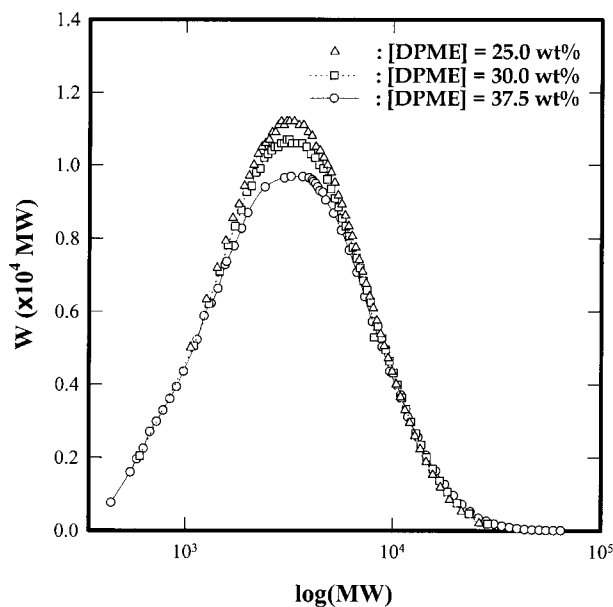


Figure 6 Effect of solvent concentration on the MWD of the terpolymer at constant monomer composition. Residence time = 15 min; reaction temperature = 180°C; initiator concentration = 5 wt % based on total monomer; AMS/ST/AA = 37/31/32.

The MWD of the terpolymer described in the presented graphs might contain large amounts of the oligomer, more than that in the distribution obtained from the GPC analysis. The detailed detection of the oligomeric region is very important; however, GPC might not be a suitable analytical technique to detect such broadening since oligomeric peaks cannot be observed in the elution curve. As shown in the weight fraction distribution that corresponds to the elution curve in GPC, the peaks at the short-chain lengths could not be observed since they possess negligible weight fractions. Especially, extreme care is needed to analyze the distribution when the production of oligomers should not be neglected.

Effects of AMS/ST Ratio in Feeding Compositions on MWD

Experimental results for the effect of the monomer composition on the final conversion, steady-state pressure, average molecular weights, and PDI are listed in Table II. Figures 7 and 8 show the effect of the AMS/ST ratio on the weight-average MW and the PDI, respectively. Both the MW and PDI of these terpolymers decreased significantly with an increasing AMS/ST feed ratio. This effect was pronounced when the AMS/ST

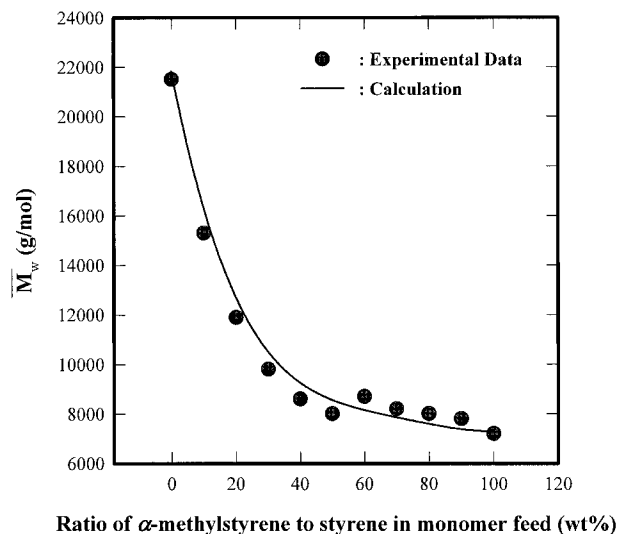


Figure 7 Effect of the ratio of AMS to ST in monomer feed on the weight-average MW of the terpolymer. Reaction temperature = 175°C; residence time = 15 min; (●) experimental data; (—) simulation.

ratio was smaller than 50/50. Decrease in the MW of the polymers is attributed to the depolymerization of AMS units or penultimate group effects due to the steric restrictions on the placement of successive AMS units in the terpolymer. These effects would be more prevalent in these reactions which contained large proportions of AMS in the

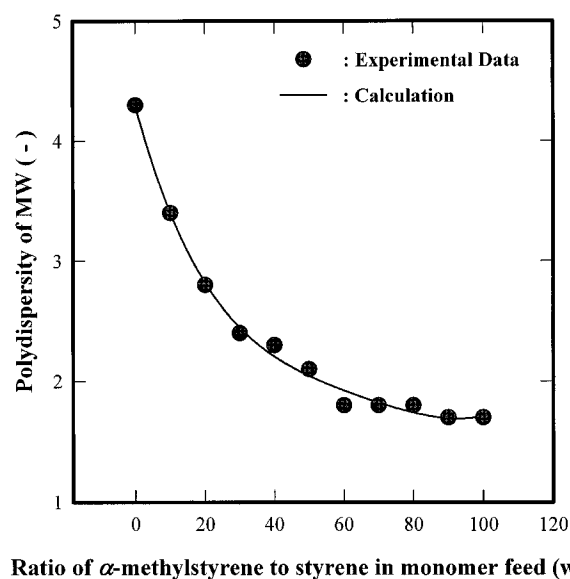


Figure 8 Effect of the ratio of AMS to ST in monomer feed on PDI of the terpolymer. Reaction temperature = 175°C; residence time = 15 min; (●) experimental data; (—) simulation.

feeding. However, there exists a limitation of the AMS effect on the MW and PDI. In other words, when the AMS/ST ratio is higher than 50/50, the MW and PDI were constant though the content of AMS increased. These results show that the depolymerization rate of AMS did not increase, that is, there was an optimum point of yield.

CONCLUSIONS

Free-radical bulk terpolymerizations using a CSTR were carried out successfully to investigate the effects of the various reaction conditions, the ingredient contents, and the AMS contents. In the case of a fixed-feed composition, the reaction temperature, concentrations of the initiator, and the chain-transfer agent were found to be useful variables for controlling the MW and MWD. The rate of the free-radical terpolymerization of AMS/ST/AA tended to be comparatively slow. This presumably reflected the existence of a normal bimolecular termination rate and a slow propagation rate due to steric hindrances at the doubly substituted vinyl carbon atom or transfer of the allylic hydrogen from the α -methyl group. It was shown that the manipulation of the AMS contents could be used to control the MW more effectively than that of the other ingredients such as the initiator, solvent, and chain-transfer agent. In the terpolymerization of AMS/ST/AA, it was concluded that the observed low MWs and narrow MWDs of the products probably resulted from the stability of the AMS radical.

The terpolymer of AMS/ST/AA with a small amount of AMS (less than 50 wt % of AMS) was of obvious practical interest as a mean for controlling the MW and MWD. In this case, depolymerization and chain transfer to the monomer of AMS affected the properties of the bulk terpolymer more critically than in the case where the large amount of AMS was used.

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