The expressions for the remaining sets of independent variables are easily derived by using the relations for the set T, V, and L together with the following relations

$$\mathrm{d}L = L(\alpha_{P,f} - \gamma_{V,f}\chi_{T,f})\mathrm{d}T + (L\chi_{T,f}/V\kappa_{T,f})\mathrm{d}V + (\mu_{T,P}{}^{-1} - L^2\chi_{T,f}{}^2/V\kappa_{T,f})\mathrm{d}f \quad \text{(A-1.9)}$$

$$\mathrm{d}V = V\beta_{P,f}\mathrm{d}T - V\kappa_{T,f}\mathrm{d}P + L\chi_{T,f}\mathrm{d}f \quad \text{(A-1.10)}$$

$$\mathrm{d}V = V\beta_{P,L}\mathrm{d}T - V\kappa_{T,L}\mathrm{d}P + \phi_{T,L}\mathrm{d}L \quad \text{(A-1.11)}$$

$$c_{V,L} = c_{P,L} - TV\beta_{P,L}\gamma_{V,L} \quad \text{(A-1.12)}$$

$$c_{V,f} = c_{P,f} - TV\beta_{P,f}\gamma_{V,f} \quad \text{(A-1.13)}$$

$$c_{P,L} = c_{P,f} + TL\alpha_{P,f}\psi_{P,L} \quad \text{(A-1.14)}$$

$$\beta_{P,L} = \beta_{P,f} + L\chi_{T,f}\psi_{P,f}/V \quad \text{(A-1.15)}$$

$$\kappa_{T,L} = \kappa_{T,f} - L\chi_{T,f}\phi_{T,L}/V \quad \text{(A-1.16)}$$

For example, to obtain an expression for the potential D in terms of independent variables T, P, and f, we substitute eq A-1.9 and A-1.10 into eq A-1.7 and simplify using eq A-1.14, A-1.15, and A-1.16.

Appendix II

This appendix lists the useful Maxwell relations according to the potential function from which they are derived.

$$U{:}\quad \left.\frac{\partial T}{\partial V}\right|_{S,L} = -\left.\frac{\partial P}{\partial S}\right|_{V,L} \qquad \left.\frac{\partial T}{\partial L}\right|_{S,V} = \left.\frac{\partial f}{\partial S}\right|_{V,L} \qquad -\left.\frac{\partial P}{\partial L}\right|_{S,V} = \left.\frac{\partial f}{\partial V}\right|_{S,L}$$

$$A{:}\quad \left.\frac{\partial S}{\partial V}\right|_{T,L} = \left.\frac{\partial P}{\partial T}\right|_{V,L} \qquad -\left.\frac{\partial S}{\partial L}\right|_{T,V} = \left.\frac{\partial f}{\partial T}\right|_{V,L} \qquad -\left.\frac{\partial P}{\partial L}\right|_{T,V} = \left.\frac{\partial f}{\partial V}\right|_{T,L}$$

$$H{:}\quad \left.\frac{\partial T}{\partial P}\right|_{S,L} = \left.\frac{\partial V}{\partial S}\right|_{P,L} \qquad \left.\frac{\partial T}{\partial L}\right|_{S,P} = \left.\frac{\partial f}{\partial S}\right|_{P,L} \qquad \left.\frac{\partial V}{\partial L}\right|_{S,P} = \left.\frac{\partial f}{\partial P}\right|_{S,L}$$

$$G{:}\ -\left.\frac{\partial S}{\partial P}\right|_{T,L} = \left.\frac{\partial V}{\partial T}\right|_{P,L} \qquad -\left.\frac{\partial S}{\partial L}\right|_{T,P} = \left.\frac{\partial f}{\partial T}\right|_{P,L} \qquad \left.\frac{\partial V}{\partial L}\right|_{T,P} = \left.\frac{\partial f}{\partial P}\right|_{T,L}$$

$$D{:}\quad \left.\frac{\partial T}{\partial V}\right|_{S,f} = -\left.\frac{\partial P}{\partial S}\right|_{V,f} \qquad \left.\frac{\partial T}{\partial f}\right|_{S,V} = -\left.\frac{\partial L}{\partial S}\right|_{V,f} \qquad \left.\frac{\partial P}{\partial f}\right|_{S,V} = \left.\frac{\partial L}{\partial V}\right|_{S,f}$$

$$B{:}\quad \left.\frac{\partial S}{\partial V}\right|_{T,f} = \left.\frac{\partial P}{\partial T}\right|_{V,f} \qquad \left.\frac{\partial S}{\partial f}\right|_{T,V} = \left.\frac{\partial L}{\partial T}\right|_{V,f} \qquad \left.\frac{\partial P}{\partial f}\right|_{T,V} = \left.\frac{\partial L}{\partial V}\right|_{T,f}$$

$$M{:}\quad \left.\frac{\partial T}{\partial P}\right|_{S,f} = \left.\frac{\partial V}{\partial S}\right|_{P,f} \qquad \left.\frac{\partial T}{\partial f}\right|_{S,P} = -\left.\frac{\partial L}{\partial S}\right|_{P,f} \qquad \left.\frac{\partial V}{\partial f}\right|_{S,P} = -\left.\frac{\partial L}{\partial P}\right|_{S,f}$$

$$Z{:}\quad \left.\frac{\partial V}{\partial T}\right|_{P,f} = -\left.\frac{\partial S}{\partial P}\right|_{T,f} \qquad \left.\frac{\partial S}{\partial f}\right|_{T,P} = \left.\frac{\partial L}{\partial T}\right|_{P,f} \qquad \left.\frac{\partial L}{\partial P}\right|_{T,f} = -\left.\frac{\partial V}{\partial f}\right|_{T,P}$$

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Copolymerization with Depropagation. IX. Molecular Weights in Copolymerization with Depropagation

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ABSTRACT: A method is described for calculating number and weight average molecular weights of copolymers polymerizing under conditions where reversibility of the propagation reaction must be considered. Generating functions combined with our diad model were used for derivation of equations which yielded leading moments of macromolecular weight distribution. The resulting equations were tested experimentally by using the copolymerizing system, styrene-α-methylstyrene. Rapid decrease of molecular weight with increasing α-methylstyrene feed concentration can be explained by relating the molecular weight decrease to a progressive increase of the apparent termination rate constant.

Molecular weight distribution (MWD) in copolymers was previously discussed by Simha and Branson[1a] and Stockmayer[1b] for irreversible polymerization at zero conversion. Zeman and Amundson[2] applied the continuous variable technique to copolymerization in batch reactors. The effect of the depropagation reaction was also discussed, but the penultimate unit effect on the depropagation steps of copolymerization was neglected.

In the fourth paper of this series[3] the use of the Monte Carlo method for calculating composition and chain length distribution was demonstrated. Recently, the theory of linear kinetics has been used by Horn and Klein[4] to derive asymptotic expressions for the dynamic behavior of the molecular weight distribution moments for living copolymerization systems. Ray, *et al.*,[5] have applied generating functions to determine the moments of the MWD in irreversible copolymerization in various reactors.

In the eighth paper of this series[6] a general solution for composition behavior was presented for multicomponent reversible polymerization using a probability approach for a diad model. By combining Ray's generating function technique for calculating moments of the MWD of irreversible copolymerization and our diad model for reversible copolymerization, we show in this paper that the moments of the MWD of reversible copolymerization can be calculated.

In this paper numerical calculations of average molecular weights from the resulting equations are compared with data obtained experimentally using the free radical copolymerization system of styrene (ST) and α-methylstyrene (AMS) at 60 and 100°. Molecular weights were experimentally found to decrease very rapidly as AMS feed concentration increases. We attribute this phenomenon to a progressive decrease of the apparent termination constant as AMS feed concentration increases. Therefore, we propose that the effect of depropagation reactions on both the copolymer molecular weight and the copolymerization rate is due to an increasing termination rate rather than a decrease of the net propagation rate.

Theoretical

We shall attempt to check the effect of ST–AMS copolymerization reversibility on molecular weight by calculating leading moments by the generating function technique and then comparing these with molecular weight averages experimentally obtained by gel permeation chromatography or membrane osmometry.

We introduce the following simplifications: (1) the long chain hypothesis is applied; (2) the pseudo-steady-state assumption is made; (3) interchain compositional heterogeneity is neglected, and the composition of the copolymer is calculated from our diad model.[6]

Kinetic Mechanism. Interchain compositional heterogeneity is neglected because of the difficulty of an experimental approach. Therefore, no attempt is made to describe separately the number of units of monomer A and B inside the polymer chain.

We shall assume that the copolymerization of ST with AMS can be represented by the following mechanism

Initiation

$$\mathrm{I} \xrightarrow{k_i} 2\mathrm{R}\cdot \qquad \text{rate} = 2fk_i[I] \tag{1}$$

$$\mathrm{R}\cdot + \mathrm{A} \longrightarrow \mathrm{P}_1 \qquad = I_{\mathrm{A}} \tag{2}$$

$$\mathrm{R}\cdot + B \longrightarrow \mathrm{Q}_1 \qquad = I_{\mathrm{B}} \tag{3}$$

Propagation–depropagation

$$\mathrm{P}_n + \mathrm{A} \underset{r_{11}}{\overset{f_{11}}{\rightleftharpoons}} \mathrm{P}_{n+1} \tag{4}$$

$$\mathrm{P}_n + B \underset{r_{12}}{\overset{f_{12}}{\rightleftharpoons}} \mathrm{Q}_{n+1} \tag{5}$$

$$\mathrm{Q}_n + \mathrm{A} \underset{r_{21}}{\overset{f_{21}}{\rightleftharpoons}} \mathrm{P}_{n+1} \tag{6}$$

$$\mathrm{Q}_n + B \underset{r_{22}}{\overset{f_{22}}{\rightleftharpoons}} \mathrm{Q}_{n+1} \tag{7}$$

Termination by combination

$$\mathrm{P}_n + \mathrm{P}_m \xrightarrow{k_t} \mathrm{M}_{n+m} \tag{8}$$

$$\mathrm{P}_n + \mathrm{Q}_m \xrightarrow{k_t} \mathrm{M}_{n+m} \tag{9}$$

$$\mathrm{Q}_n + \mathrm{Q}_m \xrightarrow{k_t} \mathrm{M}_{n+m} \tag{10}$$

(The significance of k_t is treated in the discussion.)

Chain transfer to monomer

$$\mathrm{P}_n + \mathrm{A} \xrightarrow{k_{f11}} \mathrm{M}_n + \mathrm{P}_1 \tag{11}$$

$$\mathrm{P}_n + \mathrm{B} \xrightarrow{k_{f12}} \mathrm{M}_n + \mathrm{Q}_1 \tag{12}$$

$$\mathrm{Q}_n + \mathrm{A} \xrightarrow{k_{f21}} \mathrm{M}_n + \mathrm{P}_1 \tag{13}$$

$$\mathrm{Q}_n + \mathrm{B} \xrightarrow{k_{f22}} \mathrm{M}_n + \mathrm{Q}_1 \tag{14}$$

Description of Reversible Copolymerization by Irreversible Copolymerization Equations. As shown in the kinetic mechanism, copolymerization reversibility is considered only in the propagation–depropagation steps. In an earlier paper,[6] we have shown that composition behavior of reversible copolymerization can be described by a hypothetical irreversible copolymerization.

If the apparent propagation rate constants of the hypothetical irreversible copolymerization are denoted by $f_{ij}{}^{\mathrm{a}}$, propagation–depropagation reactions (eq 4, 5, 6, and 7) may be expressed

$$\begin{aligned} \mathrm{P}_n + \mathrm{A} &\xrightarrow{f_{11}{}^{\mathrm{a}}} \mathrm{P}_{n+1} \\ \mathrm{P}_n + \mathrm{B} &\xrightarrow{f_{12}{}^{\mathrm{a}}} \mathrm{Q}_{n+1} \\ \mathrm{Q}_n + \mathrm{A} &\xrightarrow{f_{21}{}^{\mathrm{a}}} \mathrm{P}_{n+1} \\ \mathrm{Q}_n + \mathrm{B} &\xrightarrow{f_{22}{}^{\mathrm{a}}} \mathrm{Q}_{n+1} \end{aligned} \tag{15}$$

The apparent propagation rate constant includes a contribution from the depropagation rate constant, r_{ij}, as well as the true propagation rate constant, f_{ij}.

$$f_{ij}{}^{\mathrm{a}} = f_{ij}/(1 + r_{ij}x_j) \tag{16}$$

The parameter x_i in eq 16 may be determined as the solution of the set of equations

$$1/x_1 = f_{11}A/(1 + r_{11}x_1) + f_{12}B/(1 + r_{12}x_2) \tag{17}$$

$$1/x_2 = f_{21}A/(1 + r_{21}x_1) + f_{22}B/(1 + r_{22}x_2) \tag{18}$$

where A and B denote feed concentrations of monomer A and B, respectively.

The parameter x_i also has an explicit physical meaning in that it is defined as

$$x_i = \alpha_i\tau/a_i \tag{19}$$

where α_i and a_i respectively define chain end monad probability and chain interior monad probability, while τ defines the average time to add one monomer unit.

With this approach, problems of reversible copolymerization may be treated in exactly the same way as those of irreversible copolymerization. Copolymer compositions a_1 and a_2 of monomer A and B, respectively, can be found from the Mayo–Lewis equation

$$a_1/a_2 = (1 + R_{12}{}^{\mathrm{a}}A/B)/(1 + R_{21}{}^{\mathrm{a}}B/A) \tag{20}$$

where $R_{ij}{}^{\mathrm{a}}$ are the apparent reactivity ratios

$$R_{ij}{}^{\mathrm{a}} = f_{ii}{}^{\mathrm{a}}/f_{ij}{}^{\mathrm{a}} \tag{21}$$

Reactivity ratios reported in the literature are usually found by modifying eq 20. Therefore, reported reactivity ratios for ST–AMS copolymerization which have ignored depropagation are apparent reactivity ratios. If the apparent reactivity ratios are known, $f_{ij}{}^{\mathrm{a}}$ may be found as follows. Equations 16 and 17 can be rewritten as

$$1/f_{11}{}^{\mathrm{a}} = 1/f_{11} + x_1/K_{11} \tag{22}$$

$$1/x_1 = f_{11}{}^{\mathrm{a}}(A + (B/R_{12}{}^{\mathrm{a}}) \tag{23}$$

where the equilibrium constant for the propagation–depropagation equilibrium is $K_{ij} = f_{ij}/r_{ij}$. Substituting eq 23 into 22 and solving for $f_{11}{}^{\mathrm{a}}$

$$f_{11}{}^{\mathrm{a}} = f_{11}\left[1 - \frac{1}{K_{11}(A + B/R_{12}{}^{\mathrm{a}})}\right] \tag{24}$$

Similarly

$$f_{22}{}^{\mathrm{a}} = f_{22}\left[1 - \frac{1}{K_{22}(B + A/R_{21}{}^{\mathrm{a}})}\right] \tag{25}$$

$f_{12}{}^{\mathrm{a}}$ and $f_{21}{}^{\mathrm{a}}$ are found from eq 21. Therefore, $f_{ij}{}^{\mathrm{a}}$ can be calculated if the apparent reactivity ratios, equilibrium constants, and propagation rate constants for homopolymerization are known.

Table I
Polystyrene Standard Samples

	Standard values				Recovered values		
Standard no.	$M_W \times 10^{-3}$	$M_N \times 10^{-3}$	$M_{peak} \times 10^{-3}$	M_W/M_N	$M_W \times 10^{-3}$	$M_N \times 10^{-3}$	M_W/M_N
25167	867	773	830	1.12			
25166	498	404	451	1.23			
41984	200	193	196	1.04			
41995	111	111	111	1.00	111.6	104.2	1.07
7a[a]			51	1.06	51.7	48.4	1.07
25170	36	33	34.5	1.09	36.6	43.2	1.07
2a[a]			19.8	1.06	19.9	17.9	1.10
8a[a]			10.3	1.06	10.4	9.29	1.12
25169	4.0	3.1	3.55	1.29			
25971	2.1	1.95	2.03	1.08			
15a[a]			0.9	1.10			

[a] Pressure Chemical Co. (Pittsburgh, Pa.). Others from Waters Associates Inc. (Framingham, Mass.).

Calculations of MWD Moments. The procedure to calculate the MWD moments of dead polymer is that given by Ray, *et al.*,[5] except that the generating functions are defined in a simpler way, as follows

$$G(u) = \sum_{n=1}^{\infty} u^n \mathrm{P}_n \tag{26}$$

$$\phi(u) = \sum_{n=1}^{\infty} u^n Q_n \tag{27}$$

$$H(u) = \sum_{n=1}^{\infty} u^n M_n \tag{28}$$

For typographical simplicity, the following are defined

$$P = \sum_{n=1}^{\infty} P_n = G(1)$$

(the total amounts of active polymers)

$$Q = \sum_{n=1}^{\infty} Q_n = \phi(1)$$

$$c_1 = f_{11}{}^{\mathrm{a}}A/[(f_{11}{}^{\mathrm{a}} + k_{f11})A + (f_{12}{}^{\mathrm{a}} + k_{f12})B + k_t(P + Q)]$$

(the probability of a P chain adding another A monomer)

$$c_3 = f_{22}{}^{\mathrm{a}}B/[(f_{22}{}^{\mathrm{a}} + k_{f22})B + (f_{21}{}^{\mathrm{a}} + k_{f21})A + k_t(P + Q)]$$

(the probability of a Q chain adding another B monomer)

$$c_2 = c_1 f_{21}{}^{\mathrm{a}}/f_{11}{}^{\mathrm{a}}$$

$$c_4 = c_3 f_{12}{}^{\mathrm{a}}/f_{22}{}^{\mathrm{a}}$$

P and Q can be found by applying the long-chain hypothesis

$$P = [(I_A + I_B)/k_t(1 + \beta)^2]^{1/2} \tag{29}$$

$$Q = \beta P \tag{30}$$

where β can be found from the chain end monad probabilities, α_1 and α_2, of our diad model using eq 19.

$$\beta = \alpha_2/\alpha_1 = x_2 a_2/x_1 a_1 \tag{31}$$

Applying the pseudo-steady-state assumption to the active polymer rate equations gives

$$P_n = c_1 P_{n-1} + c_2 Q_{n-1} \tag{32}$$

$$Q_n = c_3 Q_{n-1} + c_4 P_{n-1} \tag{33}$$

and

$$P_1 = (I_A/A + k_{f11}P + k_{f21}Q)c_1/f_{11}{}^{\mathrm{a}} \tag{34}$$

$$Q_1 = (I_B/B + k_{f22}Q + k_{f12}P)c_3/f_{22}{}^{\mathrm{a}} \tag{35}$$

By multiplying eq 32 and 33 by u^n and summing, we get

$$(c_1 u - 1)G(u) + c_2 u\phi(u) = -P_1 u \tag{36}$$

$$(c_3 u - 1)\phi(u) + c_4 u G(u) = -Q_1 u \tag{37}$$

First and second moments of the MWD of active polymers can be obtained by differentiating eq 36 and 37 with respect to u and substituting 1 for u. (Details are given in B. K. Kang, Ph.D. Thesis, University of Waterloo, 1973, pp 106 ff.)

Suppose that M_n is the amount of dead polymer produced per unit volume of reaction mixture during a very short time, Δt; then

$$M_N = \Delta t\left[k_t\left(1/2 \sum_{r=1}^{n-1} P_r P_{n-r} + \sum_{r=1}^{n-1} P_r Q_{n-r} + 1/2 \sum_{r=1}^{n-1} Q_r Q_{n-r}\right) + (k_{f11} + k_{f12})P_n + (k_{f22}B + k_{f21}A)Q_n\right] \tag{38}$$

By multiplying eq 38 by u^n and summing, we get

$$H(u) = \Delta t[k_t(1/2G(u)^2 + G(u)\phi(u) + 1/2\phi(u)^2) + (k_{f11}A + k_{f12}B)G(u) + (k_{f22}B + k_{f21}A)\phi(u)] \tag{39}$$

Number and weight average molecular weights are obtained by differentiating eq 39 with respect to u and substituting 1 for u

$$\bar{M}_N = W[\mathrm{d}H(1)/\mathrm{d}u]/H(1) \tag{40}$$

$$\bar{M}_W = W[(\mathrm{d}^2H(1)/\mathrm{d}u^2)/(\mathrm{d}H(1)/\mathrm{d}u) + 1] \tag{41}$$

where W is the average molecular weight of the monomer unit in the copolymer. If the copolymer compositions (mole fraction) are denoted by a_1 and a_2 for monomer units A and B, respectively, and the molecular weights of monomers A and B are denoted W_1 and W_2, respectively.

$$W = a_1 W_1 + a_2 W_2 \tag{42}$$

Experimental Section

(A) Materials. Commercial styrene (ST) and α-methylstyrene (AMS) (Baker grade) were washed with aqueous solutions of 5% sodium hydroxide and 20% sodium chloride to remove the inhibitor, washed with distilled water, dried over anhydrous calcium chloride, and vacuum distilled twice under a nitrogen atmosphere. Monomers were kept at −20° and used within 2 days after preparation. Monomer purity was checked by gas chromatography and confirmed to be more than 99% pure.

2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from a 50% solution of acetone in water, and *tert*-butyl perbenzoate (TBPB, Lucidol) was used as received.

(B) Polymerization Procedure. All polymerizations were carried out in freeze–thaw degassing ampoules containing 10 ml of

Table II
Feed Conditions of ST-AMS Copolymerizations at 60 and 100°

Sample no.	ST	AMS	Total feed Concn, mol/l.
Monomer Feed Composition (mol % in bulk)			
1	91.0	9.0	8.63
2	81.8	18.2	8.53
3	72.4	27.6	8.43
4	52.9	47.1	8.24
5	10.1	89.9	7.84
Initiator Feed Concentration (mol/l.)			
AIBN	0.053	(at 60°)	
TBPB	0.040	(at 100°)	

monomer. Bulk copolymerizations of styrene and α-methylstyrene were carried out at 60 and 100° in a constant temperature paraffin oil bath which was controlled to ±0.05°. The ampoules were shaken vigorously for 3 min and left for the required time. At 60° AIBN (0.053 mol/l.) was used as initiator and at 100° TBPB (0.040 mol/l.) was used. Conversions of monomer to polymer were always kept under 5%. The reaction mixture was poured into 10 to 20 times its volume of rapidly stirred methanol, filtered, washed, and dried in a vacuum oven overnight.

(C) Characterization of the Polymer. GPC Analysis. Gel permeation chromatography was carried out with the GPC Model ALC/GPC-301 produced by Waters Associates, with the digital translation system (Hewlett-Packard 3480A Digital Voltmeter, 5055A Digital Recorder, home-made programmed timer) and chart recorder (Honeywell Electronik 194). The millivolt output from GPC (maximum 100 mV) was digitalized through the digital voltmeter and was printed out every 30 sec.

All work was done using tetrahydrofuran (THF) as the solvent at room temperature. Solvent flow rates of *ca.* 1 ml/min were used throughout. All of the samples chromatographed were 0.2% solutions in THF, and injection times were 2 min (sample size of about 4 mg). The columns were one 3 ft section of 1×10^6 Å styragel, one 3 ft section of 1×10^3 Å styragel, one 3 ft section of 1×10^4 Å styragel, one 3 ft section of 3×10^3 Å styragel, and one 3 ft section of 1×10 Å styragel. The siphon has a volume of 5 ml. Typical copolymer samples were spread over about 6–7 counts of elution volume from the onset to completion of sample elution.

GPC Calibration. Calibration of the GPC was carried out using 11 well-characterized polystyrenes of narrow molecular weight distribution, obtained from Waters Associates and Pressure Chemical Co. A smooth curve was drawn through the 11 points on a plot of log of the molecular weight at the peak *vs.* elution volume, and the molecular weights at every 0.1 elution volume counts were read from this curve and smoothed again by using the seven-point cubic method[7] and punched out for further use. Using these punched out data for the calibration curve, average molecular weights of the standard polystyrenes were recovered by using Chang and Huang's[7] computer program. Imperfect resolution due to longitudinal diffusion of the polymer samples in the GPC columns was not serious within the experimental range of interest. Recovered average molecular weights and polydispersity ratios of standard samples calculated by Chang and Huang's method using the resolution factor $h = 4.0$ were in good agreement with the standard values.

A summary of calculated values and standard values of average molecular weights of standard polystyrene samples is given in Table I.

All samples were run through the GPC within a period of 1 week; the calibration standards were each run two times through the GPC and interspersed among the polystyrene samples. The calibration curve remained constant during the week, and since good results were obtained for the calculated standards, the molecular weight distributions for the experimental samples were considered to be valid. Repeated passage (two times) of the same polymer sample through the GPC gave less than 5% deviation of calculated molecular weights.

Calibration Line for Styrene-α-Methylstyrene Copolymer. The GPC calibration lines for polystyrene, poly-AMS, and some other polymers were extensively studied by Coll and Gilding.[8] The GPC calibration curve obtained by means of fractionated poly-AMS samples using 1,2,4-trichlorobenzene as column solvent almost coincided with the polystyrene calibration curve. There is also very little difference in the intrinsic viscosity–molecular weight relationship for polystyrene compared with that of poly-AMS.

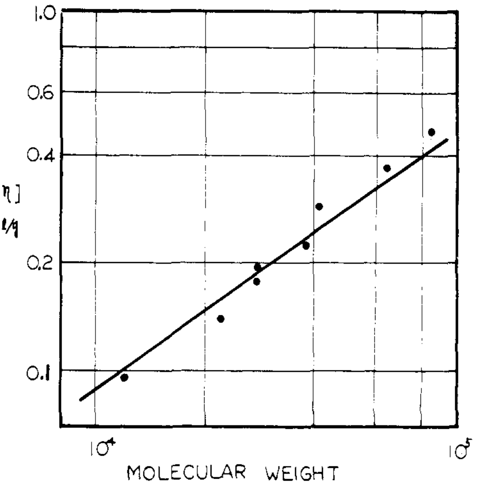

Figure 1. Plots of intrinsic viscosity *vs.* number average molecular weight of ST–AMS copolymers polymerized in bulk at 60 and 100°. Intrinsic viscosities are measured in toluene at 30° and number average molecular weights are measured in toluene at 25° by using membrane osmometer. The solid line is the plot of the Mark–Houwink equation for polystyrene: $[\eta] = 1.10 \times 10^{-4} M^{0.725}$ (ref 9).

In order to confirm the intrinsic viscosity–molecular weight relationship for ST–AMS copolymers, intrinsic viscosities and number average molecular weights of ST–AMS copolymers of various compositions were measured in toluene by viscometry and membrane osmometry. These results are plotted in Figure 1 together with the plots of the Mark–Houwink equation for polystyrene from the literature: $[\eta] = 1.10 \times 10^{-4} M^{0.725}$.[9] The plots of the copolymers were again very close to the polystyrene curve. Therefore, it was considered safe to use the calibration line of polystyrene for ST–AMS copolymers.

Intrinsic Viscosity Measurements. Intrinsic viscosities were measured in toluene with an Ubbelohde viscometer (Cannon 50 K914) in a water bath controlled at 30 ± 0.05°, and all samples and solvent flow times were measured to 0.1 sec. The size of the viscometer capillary was so chosen that the efflux time for the solvent was around 200 sec, thus eliminating the effect of shear rate. The readings were repeated until three successive flow times varying by less than ±0.1 sec from the mean were obtained.

Membrane Osmometry. The number-average molecular weight, M_N, of each sample was determined at 25° with a Model 502 Hewlett-Packard high speed membrane osmometer, using degassed toluene as solvent.

The osmometer membrane, ArRo type 600-D, was originally supplied in a solution of 20% 2-propanol in water and kept in a refrigerator. This membrane can be operated at a quite low average molecular weight (10,000 and up).

The membrane as received was conditioned for toluene operation by several successive steps. These steps involved soaking the membrane for each 5-hr period (minimum) in the following solvents: 50–50% solution of water and 2-propanol, 100% 2-propanol, 75–25% solution of 2-propanol and toluene, 50–50% solution of 2-propanol and toluene, 25–75% solution of 2-propanol and toluene, 100% toluene.

To confirm the accuracy of the membrane osmometer measurement, two standard narrow distribution polystyrene samples (M_N = 19,800 and 111,000) provided by Waters Associates were run and good agreement was noted (M_N = 19,600 and 110,000). It should be emphasized that a copolymer with broad MWD and a sample number-average molecular weight around 10,000 will give higher than the true value with a 600-D type membrane.

Results

Experimental results for bulk copolymerization of styrene and α-methylstyrene at various monomer feed compositions and temperatures, together with predictions, are shown in Tables II, III, and IV and Figure 2. Predicted

Table III
Parameters Used for Prediction of ST-AMS Copolymerization at 60 and 100°

Thermodynamic parameters for K_{ii}		ST	AMS
$-\Delta H_{ss}°$	(kcal/mol)	16.7[9]	9.0[6]
$-\Delta S_{ss}°$	(eu)	25.0[9]	28.8[6]
Propagation rate constants			
f_{ii}	(60°)	176[9]	26[6]
E_a	(kcal/mol)	6.9	6.9[6]
Apparent copolymerization reactivity ratios			
R_{1j}[a]	(1 = ST)		1.3[11]
R_{2j}[a]	(2 = AMS)	0.3[11]	

Initiation Rate Constants ($2fk_i \times 10^5$, sec^{-1})

AIBN	1.33[b]	(at 60°)
TBPB	2.14[9]	(at 100°)

Apparent Termination Rate Constants,[a] 1./mol/sec

$k_{t_{11}} = 4.5 \times 10^7$ (at 60°), $k_{t_{11}} = 6.0 \times 10^7$ (at 100°)

Transfer constants[a] ($C_{ij} = kf_{ij}/f_{ii}$)	60°	100°
$C_{f11} \times 10^4$	0.6[9]	1.8[9]
$C_{f12} \times 10^4$	2.1[12]	7.1[12]

[a] See Discussion. [b] G. E. Ham, "Kinetics and Mechanisms of Polymerization, Vinyl Polymerization," Vol. 1, Marcel Dekker, New York, N. Y., 1967, pp 1, 160.

Table IV
Average Molecular Weights and Intrinsic Viscosities η of ST-AMS Copolymers for Free Radical Copolymerization in Bulk at 100 and 60° with Monomer and Initiator Feed Concentrations given in Table II

Sample no.	Prediction $\bar{M}_N$	$\bar{M}_W$	$\bar{M}_W/\bar{M}_N$	GPC $\bar{M}_N$	$\bar{M}_W$	M_{peak}	$M_W/\bar{M}_N$	Osmometer $\bar{M}_N$	η, dl/g
				100°					
100-1	7.4	12.0	1.60	7.4	11.3	11.1	1.54	8.2	0.478
100-2	5.1	8.3	1.62	5.1	7.8	8.4	1.54	6.0	0.378
100-3	3.6	5.7	1.62	3.8	5.9	6.1	1.56	4.1	0.282
100-4	1.6	2.6	1.58	1.9	2.9	3.0	1.48	2.7	0.192
100-5	0.15	0.24	1.57			0.55	(0.27)		
				60°					
60-1	3.9	5.8	1.51	3.2	5.1	4.7	1.58	3.8	0.225
60-2	2.7	4.0	1.51	2.2	3.4	3.1	1.52	2.8	0.178
60-3	1.8	2.7	1.51	1.6	2.4	2.4	1.54	2.0	0.138
60-4	0.81	1.2	1.51	0.91	1.3	1.3	1.48	1.2	0.095

[a] Parameters used for predictions are given in Table III. Average molecular weights × 10^{-4}.

values were calculated by using the parameters given in Table III.

Discussion

As shown in Figure 2, ST-AMS copolymer molecular weights decreased rapidly as the AMS feed composition increased. If the AMS feed compositions were over 50%, resulting polymer molecular weights were too low for analysis by GPC or membrane osmometry. One sample (100-5) was polymerized at 90 mol % AMS feed composition for 156 hr at 100°, and the reaction mixture was directly injected into GPC after being diluted 20 times with THF. As shown in Table IV, the values of M_{peak} were very close to $\bar{M}_W$ for all other samples and thus the value of M_{peak} of this sample was considered to be the same as $\bar{M}_W$. This value was adjusted down by a factor of 1.95, calculated to account for the greatly reduced rate of initiation due to the polymerization time extending over many half-lives of the initiator (18 hr).

In order to mask the effect of thermal initiation, initiator concentrations were kept above 0.04 mol/l. and the polymerization temperatures at 100° or below. (It should be mentioned that the long chain assumption which was used for prediction may fail in the low molecular weight region.)

In the second paper of this series,[10] it was shown that the rate of termination of the ST-AMS bulk copolymerization system cannot be described by termination rate constants which are independent of monomer feed compositions because the termination reaction is diffusion controlled. The rate of termination of ST-AMS system can be effectively described by defining an *apparent* termination rate constant, k_t

$$R_t = \tfrac{1}{2}k_t(P + Q)^2 \qquad (43)$$

This apparent termination rate constant was experimentally determined by measuring the rate of copolymerization at various monomer feed compositions. O'Driscoll and Dickson[10] showed that k_t can be expressed as an exponential function of AMS feed mole fraction, m_2

$$\log\,(k_t/k_{t11}) = Sm_2 \qquad (44)$$

where k_{t11} denotes the termination rate constant of styrene homopolymerization, m_2 is the AMS feed mole fraction, and the constant S was reported to be approximately 3.0 for bulk copolymerization at 60° with 2.4 × 10^{-3} mol/l. of benzoyl peroxide.

The implication of this is that attempted initiation of copolymerization above the low ceiling temperature of the co-

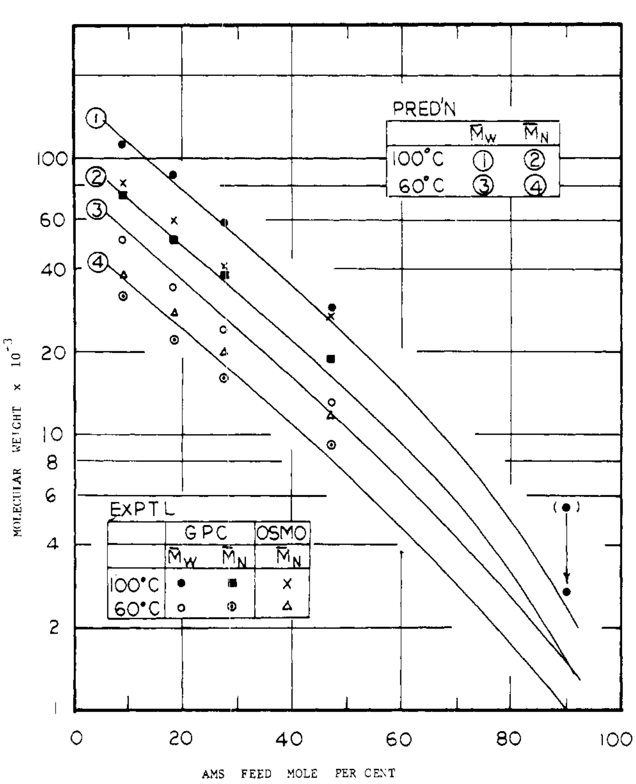

Figure 2. Variation of average molecular weights of ST–AMS copolymer with AMS feed mole per cent in the bulk copolymerization at 60° with AIBN and at 100° with TBPB. Predicted curves using moment generating technique and parameters of Table III (solid lines) and experimental results (symbols).

Prediction Curves

Curve no.	$\bar{M}_W$ or $\bar{M}_N$	Polymerization temp, °C
1	$\bar{M}_W$	100
2	$\bar{M}_N$	100
3	$\bar{M}_W$	60
4	$\bar{M}_N$	60

Experimental

Symbol	$\bar{M}_W$ or $\bar{M}_N$	Polymerization temp, °C	Instrument
●	$\bar{M}_W$	100	GPC
■	$\bar{M}_N$	100	GPC
×	$\bar{M}_N$	100	Osmometer
○	$\bar{M}_W$	60	GPC
⊙	$\bar{M}_N$	60	GPC
△	$\bar{M}_N$	60	Osmometer

monomer AMS probably produces a considerable concentration of low molecular weight free radicals which rapidly diffuse to other radicals and terminate them, resulting in an increase of the termination rate and retardation of the rate of copolymerization. Consequently, the rate of termination is expected to be a function of the concentration of the low ceiling temperature monomer.

It is well known that AMS has an apparent "retarding effect" [10–14] on the rate of copolymerization with styrene. Smets, *et al.*,[14] and Baldwin, *et al.*,[13] attempted to explain this retarding effect on the basis of degradative chain transfer. Smets, *et al.*, obtained a large value for the transfer constant of a polystyryl radical to AMS, but Baldwin, *et al.*, could obtain no evidence of degradative chain transfer in this system. We prefer to use our earlier interpretation.[10]

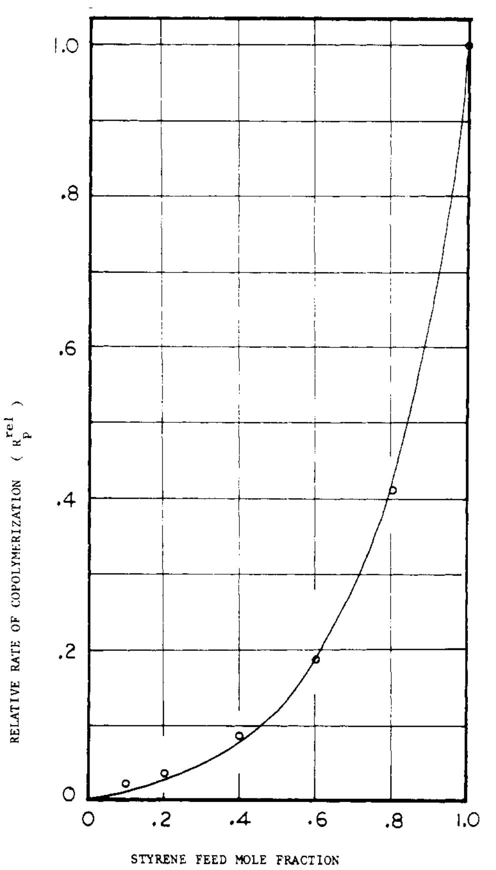

Figure 3. Rate of copolymerization of ST–AMS relative to rate of homopolymerization of ST. Circles are experimental results of copolymerization of ST with AMS at 60° using 2.4 × 10^{-3} mol/l. of benzoyl peroxide as initiator (raw data from ref 10). The solid line is calculated from eq 45 using S = 2.5 and k_{t11} = 4.5 × 10^7.

We believe that the decrease in the rate of polymerization may be caused (1) by the participation of the depropagation reaction in the course of formation of the polymer chain or (2) by the presence of a considerable concentration of low molecular weight free radicals which increases the rate of termination. These are different phenomena, although both occur because of the presence of a low ceiling temperature comonomer. The latter shall be called the *"indirect effect"* of depropagation and the former the *"direct effect"* of deprogagation. As shown below, the existing data indicate that the indirect effect is most important; neither the direct effect nor reasonable chain transfer constants can account for the lower molecular weights found at higher AMS feed concentrations.

The value S = 3.0 of eq 44 was obtained on the basis of a model which used Lowry's case II[15] and O'Driscoll and Gasparro's[11] experimental data, but a slightly different value results if the experimental results are fitted to the present model. Figure 3 shows O'Driscoll and Gasparro's experimental results, together with the results calculated from the present model using S = 2.5. The solid curve is the result of calculations of the relative rate of copolymerization, R_p^{rel}, the ratio of the rate of copolymerization to that of styrene homopolymerization from the following equation.

$$R_p^{rel} = \frac{[(f_{11}^a + k_{f11})P + (f_{21}^a + k_{f21})Q]A + [(f_{22}^a + k_{f22})Q + (f_{12}^a + k_{f12})P]B}{\text{rate of ST homopolymerization}} \qquad (45)$$

The value of S is the only adjustable parameter, and S = 2.5 gave the best fit of the calculated curve to the experi-

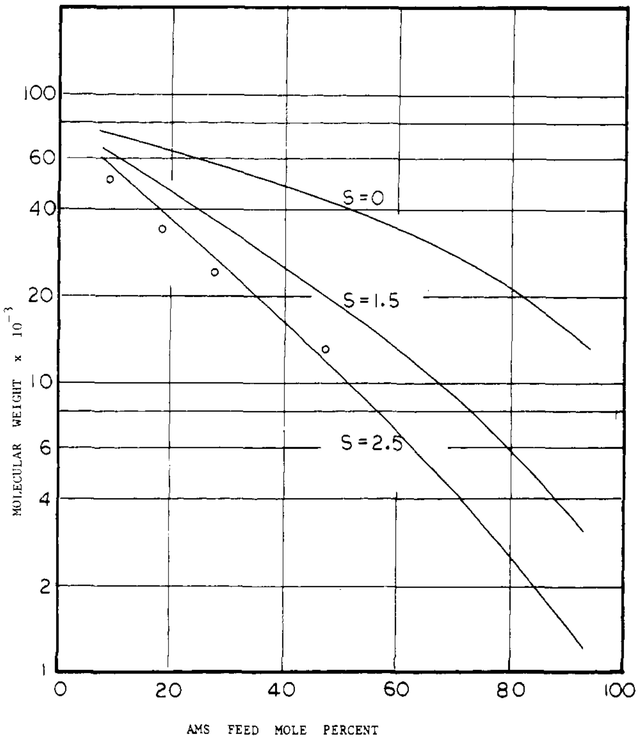

Figure 4. Results of the calculation of variation of weight average molecular weight with AMS feed mole per cent at various values of *S*, in the bulk copolymerization of styrene with AMS at 60° using 0.053 mol/l. of AIBN as initiator. Parameters used for the calculations are given in Table III. Circles are experimental results from GPC.

mental results. This value was used throughout for predictions of average molecular weights.

Perhaps the parameter whose value is most uncertain is k_{t11}, *i.e.*, the termination rate constant of styrene homopolymerization. Existing experimental values of the activation energy of the termination reaction and termination rate constants of styrene have been tabulated.[9] The average value of the activation energy was 1.89 kcal/mol. A least-squares fit of literature values (k_{t11} *vs.* $1/T$), using this activation energy and giving a weighting factor of 3 to the values obtained by the rotating sector method, yielded

$$\begin{aligned} k_{t11} &= 7.72 \times 10^8 \exp(1890/RT) \\ &= 4.5 \times 10^7 \text{ l./mol/sec (at } 60°) \\ &= 6.0 \times 10^7 \text{ l./mol/sec (at } 100°) \end{aligned}$$

To investigate the "indirect effect" of depropagation on the molecular weights, weight average molecular weights of ST–AMS copolymers, polymerized at 60 and 100°, were calculated at various values of *S*, as functions of the feed composition. Figure 4 shows the results of these calculations together with experimental results. It is clearly shown that the "indirect effect" on the molecular weight is quite large.

The retarding effect may be considered from another point of view. In order to observe the "direct effect" on the molecular weight, average molecular weights predicted by the irreversible copolymerization model (all the depropagation rate constants, r_{ij}, were set to zero) and those predicted by the reversible copolymerization model were compared. As shown in Figure 5 (upper set), a small effect was observed only at high AMS feed concentrations.

The direct effect ought to be enhanced by diluting the polymerization mixture. Calculated results at fivefold dilution and constant composition at 100° are shown in Figure 5 (lower set) and indicate almost no effect.

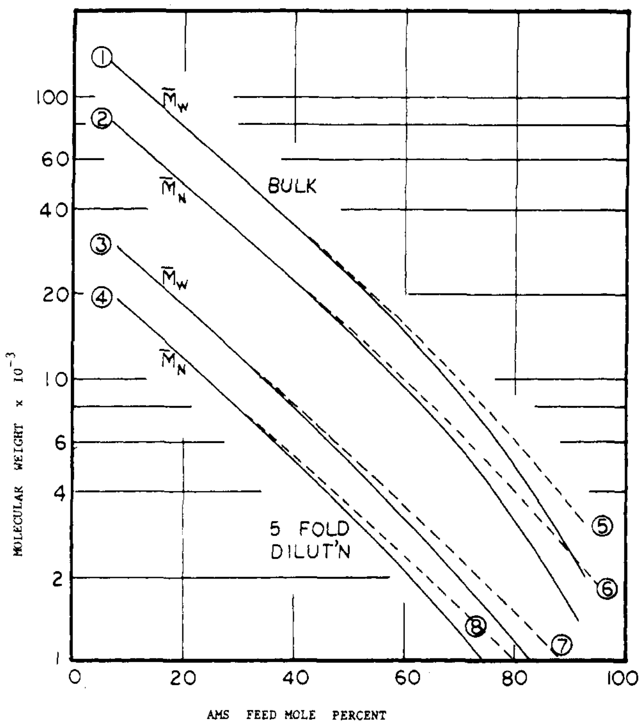

Figure 5. Results of calculation of average molecular weights as a function of AMS feed mole per cent in the bulk and solution copolymerizations of styrene with AMS at 100° using 0.04 mol/l. of *tert*-butyl perbenzoate as initiator. Solid lines are the plotted results of calculation by the reversible copolymerization model and dotted lines are those of calculation by the irreversible model. Parameters used for the calculations are given in Table III.

		Curve Numbers	
		Reversible	Irreversible
Bulk	$\bar{M}_W$	1	5
	$\bar{M}_N$	2	6
5 times Dilution	$\bar{M}_W$	3	7
	$\bar{M}_N$	4	8

The effects of increasing AMS concentration on the molecular weights will become progressively larger if the rate of chain transfer to AMS is very large. Previously, Smets and Dehaas[14] obtained the value of 0.0095 × f_{11} for the apparent rate constant for chain transfer from a polystyryl radical to AMS monomer at 74°. Later, Doak, *et al.*,[12] simplified the problem by treating AMS as solvent rather than comonomer and using the relationship $1/DP = 1/DP_0 + C_{f12}[S]/[M]$, where $C_{f12} = k_{f12}/k_{f11}$. The following values were obtained for C_{f12} from the slope of the plot of $1/DP$ *vs.* [S]/[M]: 79.5°, 4.9 × 10^{-4} and 3.2 × 10^{-4}; 99°, 8.5 × 10^{-4} and 5.6 × 10^{-4}. It was shown that AMS is approximately 5–6 times as reactive as styrene in chain transfer. They also plotted the reciprocal degree of polymerization ($1/DP$) *vs.* rate of copolymerization (R_p) based on the relationship

$$1/DP = C_f + k_t R_p / k_p{}^2 [M]^2$$

where C_f and k_p are the sum of transfer constants and propagation rate constant, respectively. By extrapolating to zero R_p, they obtained C_f as the intercept which was slightly higher than that of styrene. These results contradict the extremely high value of Smets, *et al.* Therefore, the average values of Doak, *et al.*, for C_{f12} (7.1 × 10^{-4} at 99°, 4.1 × 10^{-4} at 80°) were used for the prediction assuming that order of magnitude is correct. The value of this

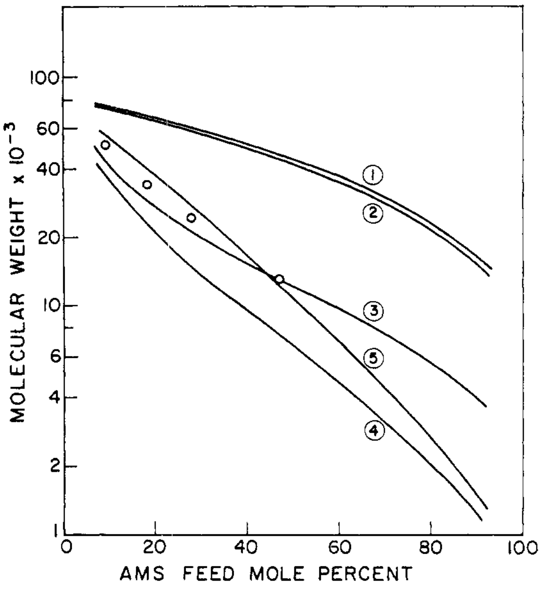

Figure 6. Results of calculations of weight average molecular weights as a function of AMS feed mole per cent at various values of combination of S and transfer constants (C_{f12}) in the bulk copolymerization of styrene with AMS at 60° using 0.05 mol/l. of AIBN as initiator. Parameters used for calculations are given in Table III. Circles are experimental results from GPC.

Curve no.	S	$C_{f12} \times 10^4$	
1	0	0	(No transfer)
2	0	2.1	(Doak's value)
3	0	95	(Smet's value)
4	2.5	95	
5	2.5	2.1	

transfer constant at 60° was estimated to be 2.1×10^{-4} by extrapolating the above values to 60°.

For calculation purposes, it was further assumed that $C_{f12} = C_{f22}$ and $C_{f11} = C_{f21}$.

To see the net transfer effect, $\bar{M}_W$ at 60° was calculated at $S = 0$ as a function of AMS feed composition. Figure 6 shows the results of calculations for three values of the transfer constants. As shown, by curve 2, the transfer effect may be considered negligible if Doak's value is of the correct order of magnitude. Predicted results using Smets' value, curve 3, show that the transfer effect would be as large as that of "indirect effect." Curve 4 is the result of calculations using Smets' values and $S = 2.5$. In this case, predicted results were very far from the experimental results.

Curve 5, repeated from Figure 4, really gives no better fit to the experimental data than does curve 3. However, the parameters used to calculate curve 5 satisfactorily explain both the rate data of Figure 3 and the molecular weight data. Curve 3, with $S = 0$, could not explain the rate data of Figure 3.

Therefore, our examination of the relative influence of S and C_{f12} on $\bar{M}_W$ suggests that the retardation effect can be quantitatively accounted for by setting $S = 2.5$ and using Doak's relatively low value of C_{f12}.

In conclusion, we may state with confidence that, within the experimental temperature range (60–100°) in the ST–AMS system, the effect of copolymerization reversibility on molecular weights mainly occurs "indirectly," *i.e.*, from an increasing apparent termination rate constant, as AMS feed concentration increases. This increase of the apparent termination rate constant may be quantitatively expressed by the parameter S, which is the slope of the plot of log (k_t/k_{t11}) *vs.* AMS feed mole fraction. To observe the "direct effect," *i.e.*, decrease of the net rate of polymerization because of depropagation, a higher temperature range may be required. This implies that reversibility need be considered only for the homopropagation reaction of AMS (reaction 7) in the temperature range 60–100°. Although reversibility is quite high for a copolymer chain with two AMS units in the terminal diad [~~(AMS)(AMS)*], this diad is infrequent, except at AMS feed concentrations appreciably greater than 0.5 mole fraction.

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