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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Kinetics of Free Radical Polymerization. XXXVIII. Solvent Effect on the Degree of Polymerization of Poly(ethyl Acrylates) and Poly(methyl Acrylates)

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To cite this Article Fehérvári, A. , Gyevi, E. Boros , Földes-Bereznich, T. and Tüdös, F.(1982) 'Kinetics of Free Radical Polymerization. XXXVIII. Solvent Effect on the Degree of Polymerization of Poly(ethyl Acrylates) and Poly(methyl Acrylates)', *Journal of Macromolecular Science, Part A*, 18: 3, 431 – 444

To link to this Article: DOI: 10.1080/00222338208056513

URL: <http://dx.doi.org/10.1080/00222338208056513>

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Kinetics of Free Radical Polymerization. XXXVIII. Solvent Effect on the Degree of Polymerization of Poly(ethyl Acrylates) and Poly(methyl Acrylates)

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A B S T R A C T

The degree of polymerization was investigated in the homopolymerization of ethyl and methyl acrylate in solution at 50°C. Molecular weights were determined by osmometry and viscometry. The mechanism of chain termination was found to be the combination of growing radicals in the polymerization of both monomers. The equation describing the degree of polymerization was derived considering the reactions of vibrationally excited radicals. Theoretical curves were found to be in good agreement with experimental data. Chain transfer constants were determined

accordingly; in the EA/AIBN/DMF/50°C system $C_M = 9.0 \times 10^{-5}$, $C_S = 1.0 \times 10^{-5}$, $C_S^* = 8.3 \times 10^{-5}$, and in the MA/AIBN/DMF/50°C system $C_M = 8.0 \times 10^{-5}$, $C_S = 3.4 \times 10^{-5}$, $C_S^* = 12.5 \times 10^{-5}$.

Solvent effect on the polymerization kinetics of ethyl and methyl acrylates in benzene and dimethylformamide was the subject of a series of our recent publications [1-4]. The investigations are now extended to the mechanism of chain termination and chain transfer in these systems.

EXPERIMENTAL

Purification of monomers, solvents, and initiator, method of polymerization, and precipitation of polymers were described earlier [1-4, 8]. Polymers were dried to constant weight in vacuum at 40°C.

The molecular weight of poly(methyl acrylate) (PMA) samples and poly(ethyl acrylate) (PEA) samples of low molecular weight (in chain termination studies) were determined by a HP 502 High Speed Membrane Osmometer at 50° in dimethylformamide (DMF) solution. The molecular weight of poly(ethyl acrylate) samples of high degree of polymerization (in chain transfer studies) were determined by viscosimetry in methyl ethyl ketone solution at 30°C. The number-average molecular weights were calculated from the Mark-Houwink equation:

$$\eta = 2.680 \times 10^{-5} \bar{M}_n^{0.808} \quad (1)$$

where the constants reported by Mangaraj and Patra [5] were accepted.

KINETIC CONSIDERATIONS

The equation for the degree of polymerization in case of chemical initiation in solution is given as

$$\bar{P}_n^{-1} = \frac{1 + \lambda}{2} \frac{(W_1 k_4)^{1/2}}{k_{2m}} + C_M + C_S \cdot s/m + C_X \cdot x/m \quad (2)$$

where C_M , C_S , and C_X are the chain transfer constants to monomer,

solvent, and initiator; m , s , and x are the concentrations of monomer, solvent, and initiator; W_1 is the initiation rate; k_2 and k_4 are the rate constants of chain propagation and chain termination; and λ is the probability of chain termination by disproportionation.

If the polymerization is initiated by azo-bis-isobutyronitrile (AIBN), chain transfer to initiator does not take place and consequently the last term in Eq. (2) is absent, e.g., Ref. 6. Equation (2) was shown to have inherent arithmetical deficiencies which can be avoided by a suitable transformation [7, 8]:

$$\chi_M \bar{P}_n^{-1} = \frac{1 + \lambda}{2} \frac{(W_1 k_4)^{1/2}}{k_2 m} \chi_M + C_M \chi_M + C_S (1 - \chi_M) \quad (3)$$

where χ_M is the molar fraction of monomer.

If the degree of polymerization is properly described by Eq. (2) in a system, the expression

$$\chi_M \left(\bar{P}_n^{-1} - \frac{1 + \lambda}{2} \frac{(W_1 k_4)^{1/2}}{k_2 m} \right) \quad (4)$$

calculated from experimental data versus the molar fraction of monomer χ_M should be linear, and from the slope and intercept the chain transfer constants can be determined. As Figs. 1 and 2 demonstrate, this relation is not linear either in EA/AIBN/DMF or in MA/AIBN/DMF system (relying on Ref. 10, λ was assumed to be zero in the calculations; this assumption was verified by results reported in this paper). This phenomenon cannot be caused by primary radical termination, because this would also result in initiator exponents smaller than the theoretical 0.5. In the homopolymerization of these monomers, however, the initiator exponent was found to be 0.5 within the limits of experimental error [1, 3]. The deviation from the straight line cannot be the result of an accidental systematic error in the method of molecular weight determination either, because the two curves were calculated on the basis of molecular weights by two different methods (PEA: viscosimetry, PMA: osmometry).

A similar effect was observed in the polymerization of styrene in solution, where the characteristic deviation could be interpreted by considering the reactions of hot radicals [8].

The homopolymerization kinetics of the acrylic ester monomers under investigation could also be evaluated on the basis of the theory of hot radicals [1, 4]. This theory assumes the participation of vibrationally excited, so-called hot radicals in chain propagation. The excess energy of these radicals arises from the heat and

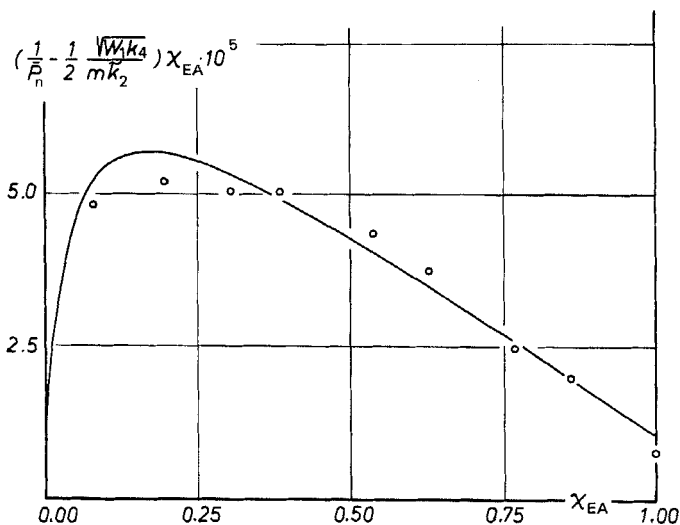


FIG. 1. Degree of polymerization in EA/AIBN/DMF/50°C system according to Eq. (2).

activation energy of propagation, and it provides the energy needed to activate the next propagation step. Since our results on the kinetics of homopolymerization indicate the effect of hot radicals on chain propagation, it is reasonable to assume that these radicals also participate in chain transfer processes.

As in the polymerization of acrylates, chain transfer to monomer also occurs, and the following elementary reactions have to be considered.

Initiation:



Reactions increasing the degree of polymerization:

Propagation:



Propagation of hot radicals:



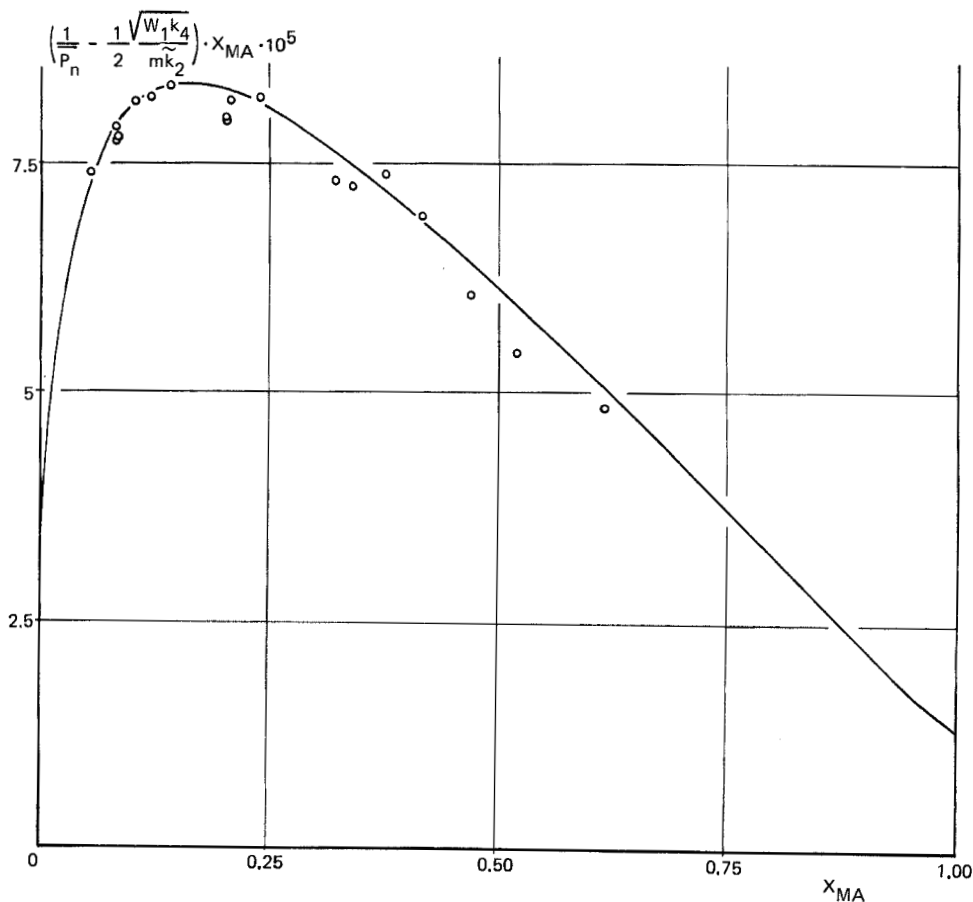


FIG. 2. Degree of polymerization in MA/AIBN/DMF/50°C system according to Eq. (2).

Reactions decreasing the degree of polymerization:

Chain transfer to monomer:



Chain transfer to solvent:



Chain transfer to monomer by hot radical:



Chain transfer to solvent by hot radical:



Chain termination:



Deactivation of hot radicals:



where \dot{R} stands for radical, \dot{R}^* for hot radical, M is monomer, S is solvent, P is polymer, and k_2 , k_3 , k_{3M} , k_{3S} , k_2^* , k_{3M}^* , k_{3S}^* , k_7 , k_7' are the rate constants of the corresponding reactions.

On the basis of the reaction scheme the differential equations describing the kinetics of these systems can be constructed:

$$-dm/dt = k_2rm + k_2^*rm + k_{3M}rm + k_{3M}^*rm \quad (15)$$

$$dr/dt = k_2rm - k_7^*rm - k_7'rs - k_{3M}^*rm - k_{3S}^*rs \quad (16)$$

$$dr/dt = 2k_1fx - k_4r^2 - k_2rm + k_7^*rm + k_7'rs + k_{3M}^*rm + k_{3S}^*rs \quad (17)$$

In the stationary state the concentrations of radicals are constant:

$$dr/dt \simeq 0 \quad \text{and} \quad dr^*/dt \simeq 0 \quad (18)$$

The sum of Eqs. (16)-(18) yields the radical concentration:

$$r = (2k_1fx/k_4)^{1/2} \quad (19)$$

The concentration of hot radicals on the basis of Eqs. (17) and (18) is given as

$$r^* = r \frac{k_2}{k_2^* \gamma + C_M^* + (\gamma' + C_S^*)s/m} \quad (20)$$

where

$$\gamma = k_7/k_2^*, \quad \gamma' = k_7'/k_2^*, \quad C_M^* = k_{3M}^*/k_2^*,$$

$$C_S^* = k_{3S}^*/k_2^*$$

The equation for the number-average degree of polymerization can be given as a ratio of the rates of reactions resulting in an increase in Eqs. (6) and (7) and a decrease in Eqs. (8)-(12) in the molecular weight:

$$\bar{P}_n = \frac{k_2rm + k_2^*rm}{\frac{1+\lambda}{2} k_4r^2 + k_{3M}rm + k_{3S}rs + k_{3M}^*rm + k_{3S}^*rs} \quad (21)$$

Equations (19) and (20) can be substituted for radical concentrations in Eq. (21), which after rearrangement become

$$\bar{P}_n^{-1} = \frac{1}{1+D} \left\{ \frac{1+\lambda}{2} \frac{(2k_1fxk_4)^{1/2}}{k_2m} + C_M + C_S^*s/m + C_M^*D + C_S^*D \cdot s/m \right\} \quad (22)$$

where the numerical value of the D deactivation function:

$$D = \frac{1}{\gamma + C_M^* + (\gamma' + C_S^*)s/m} \quad (23)$$

can be determined by the kinetic investigation of homopolymerization, see Ref. 9. It is to be noted that generally $\gamma \gg C_M^*$ and $\gamma' \gg C_S^*$ (this is also the case in the present study) and the expression for D reduces to

$$D = \frac{1}{\gamma + \gamma' s/m} \quad (24)$$

The arithmetical deficiencies of Eq. (22) can be eliminated by introducing the molar fraction of monomer as an independent variable instead of the ratio s/m , when after minor rearrangement we get

$$(1 + D) \chi_M \bar{P}_n^{-1} = \frac{1 + \lambda}{2} \frac{(2k_1 f x k_4)^{1/2}}{k_2 m} \chi_M + C_M \chi_M + C_S (1 - \chi_M) + C_M^* D \chi_M + C_S^* D (1 - \chi_M) \quad (25)$$

Our chain transfer studies were based on Eq. (25).

RESULTS AND DISCUSSION

Mechanism of Chain Termination

The degree of polymerization was studied at a constant monomer concentration as a function of the square root of initiator concentration. The numerical value of λ can be determined as the slope of the linear function described by Eq. (22) provided that the rate of initiation and the overall rate constant of polymerization are known. It is worth mentioning that identical results were obtained using Eq. (2), because the first term in Eqs. (2) and (22) are analogous wherein

$$\tilde{k}_2 = k_2(1 + D) \quad (26)$$

\tilde{k}_2 is the effective rate constant of chain propagation at the given monomer concentration, see Ref. 9.

Our experimental results according to Eq. (22) are presented in Figs. 3, 4, and 5. The values of λ calculated by linear regression from experimental data are $\lambda = -0.096$ in the system EA/AIBN/DMF, $\lambda = 0.046$ in the system MA/AIBN/DMF, and $\lambda = 0.040$ in the system of MA/AIBN/Bz. Within the limits of experimental error these

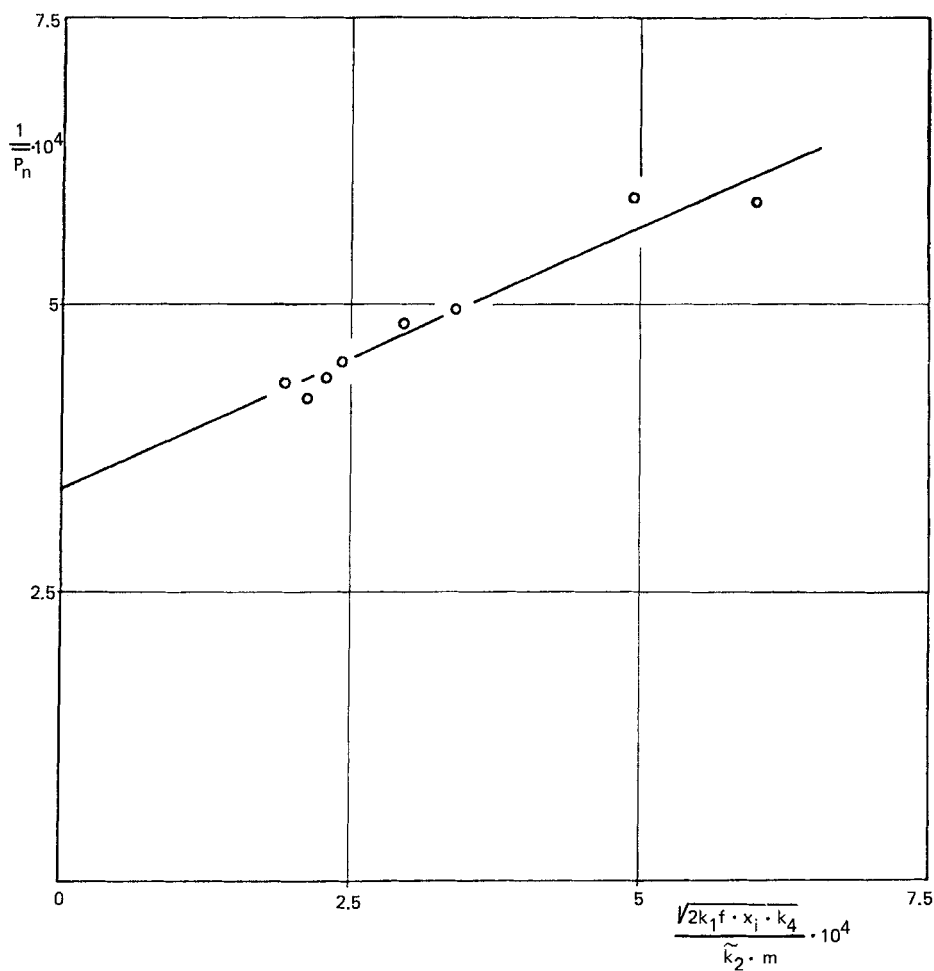


FIG. 3. Reciprocal degree of polymerization as a function of the square root of initiator concentration in EA/AIBN/DMF/50°C system at $m = 1.205 \text{ mol/dm}^3$ constant monomer concentration.

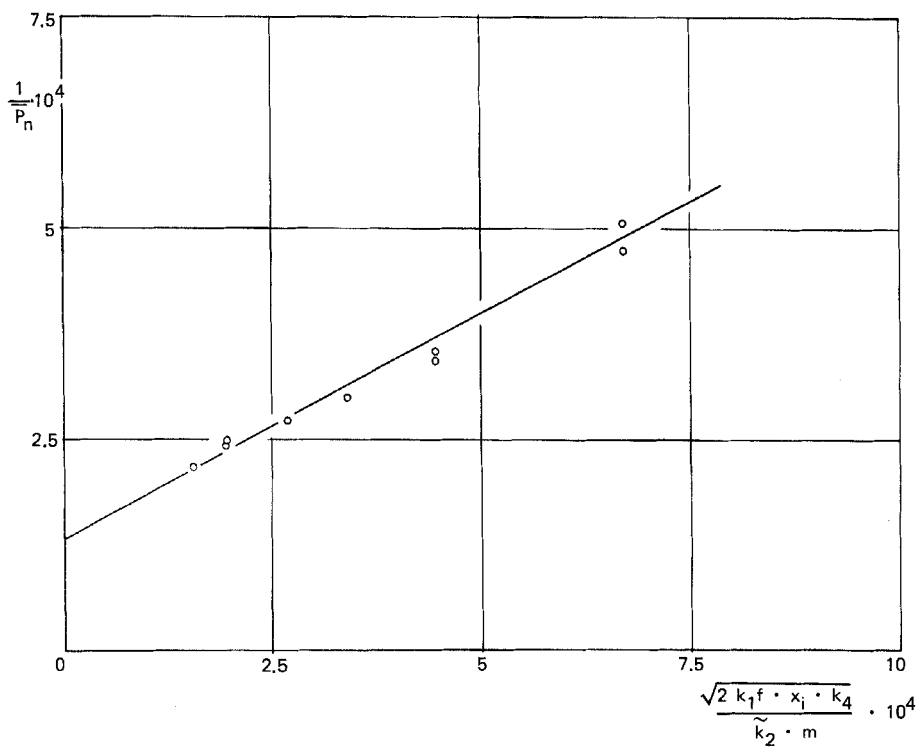


FIG. 4. Reciprocal degree of polymerization as a function of the square root of initiator concentration in MA/AIBN/Bz/50°C system at $m = 0.850 \text{ mol/dm}^3$ constant monomer concentration.

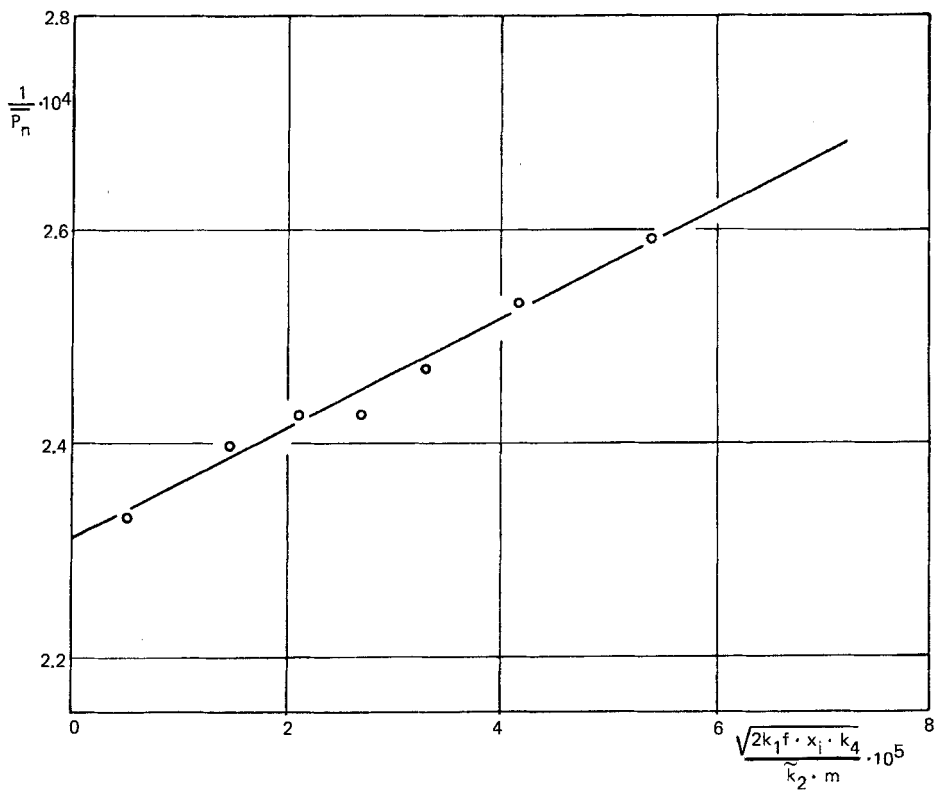


FIG. 5. Reciprocal degree of polymerization as a function of the square root of initiator concentration in MA/AIBN/DMF/50°C system at $m = 3.780 \text{ mol/dm}^3$ constant monomer concentration.

TABLE 1. Chain Transfer Studies in EA/AIBN/DMF/50°C and MA/AIBN/DMF/50°C Homopolymerizations

	$m(\text{mol}/\text{dm}^3)$	$x \times 10^4 (\text{mol}/\text{dm}^3)$	$\bar{P}_n^{-1} \times 10^5$
PEA	0.9755	69.58	80.8
	2.287	21.43	29.5
	3.398	13.70	17.8
	4.168	11.13	14.0
	5.528	6.146	8.50
	6.270	2.878	6.13
	7.309	1.511	3.34
	7.949	1.446	2.40
PMA	0.677	22.97	153.9
	1.03	1.767	96.15
	1.03	7.01	100.20
	1.03	27.33	103.4
	1.28	11.02	83.33
	1.48	12.69	72.46
	1.75	11.74	61.35
	2.47	16.90	41.49
	2.48	11.33	40.65
	2.53	11.12	40.98
	2.89	11.44	35.59
	3.82	3.54	23.31
	4.02	10.61	22.22
	4.46	47.0	21.05
	4.86	6.92	17.15
	5.39	2.67	13.19
5.99	6.10	10.79	
6.94	10.38	8.177	

TABLE 2

	EA/AIBN/ DMF/50°C	MA/AIBN/ DMF/50°C
Chain transfer: C_m	9.0×10^{-5}	8.0×10^{-5}
Constants: C_m^*	0	0
C_S	1.0×10^{-5}	3.4×10^{-5}
C_S^*	8.3×10^{-5}	12.5×10^{-5}
Constants used: $k_2/k_4^{1/2}$ in calculations: $(1/\text{mol}\cdot\text{min})^{1/2}$	1.12	1.60
γ	0.134	0.177
γ'	0.046	0.061
$2k_{1f}$ (1/min)	1.53- 1.93×10^{-4}	1.88×10^{-4}

values can be considered zero, inferring chain termination by combination of growing radicals in the polymerization of both monomers.

The same conclusion was arrived at by a different method [10], by the so-called gelation techniques in the MA/AIBN/Bz and EA/AIBN/Bz systems.

Chain Transfer Studies

Relying on our earlier data concerning the initiation and polymerization kinetics and the mechanism of chain termination, the chain transfer constants in the systems EA/AIBN/DMF and MA/AIBN/DMF were determined on the basis of Eq. (25) using the simplex method. Our experimental data and the results of computation are summarized in Tables 1 and 2. The theoretical curves calculated from Eq. (25) using these constants are presented as solid lines on Figs. 1 and 2. The deviation of experimental points from the theoretical curve remains within the limits of experimental error in molecular weight determination.

In conclusion, our results also justify the extension of the theory of hot radicals to the chain transfer processes, especially in systems where the homopolymerization kinetics of monomer indicate participation of vibrationally excited radicals in chain propagation. Remarkably, the effect of these reactions on the degree of polymerization is considerable and readily detectable even in systems where the values of chain transfer constants are relatively low (Table 2).

ACKNOWLEDGMENTS

The skillful assistance of technicians Klára Máray and Battyányi Jánosné is acknowledged.

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Accepted by editor July 28, 1981

Received for publication August 17, 1981