Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Alternating Copolymerization of Styrene and N-(4-Bromophenyl)Maleimide

Z. Janović[a]; T. T. Matusinović[a]; F. Ranogajec[b]
[a] Faculty of Technology University of Zagreb, Zagreb, Croatia [b] Ruder Bošković Institute, Zagreb, Croatia

To cite this Article Janović, Z. , Matusinović, T. T. and Ranogajec, F.(1992) 'Alternating Copolymerization of Styrene and N-(4-Bromophenyl)Maleimide', Journal of Macromolecular Science, Part A, 29: 9, 801 — 811
To link to this Article: DOI: 10.1080/10601329208054117
URL: http://dx.doi.org/10.1080/10601329208054117

J.M.S.—PURE APPL. CHEM., A29(9), pp. 801–811 (1992)

ALTERNATING COPOLYMERIZATION OF STYRENE AND *N*-(4-BROMOPHENYL)MALEIMIDE†

Z. JANOVIĆ* and T. T. MATUSINOVIĆ

Faculty of Technology
University of Zagreb
Zagreb, Croatia

F. RANOGAJEC

Ruder Bošković Institute
Zagreb, Croatia

ABSTRACT

Free radical copolymerization of styrene (St) and *N*-(4-bromophenyl)maleimide (4BPMI) in dioxane solution gave an alternating copolymer in all proportions of feed comonomer compositions. The monomer reactivity ratios were found to be $r_1 = 0.0218 \pm 0.0064$ (St) and $r_2 = 0.0232 \pm 0.0112$ (4BPMI), and the activation energy of the copolymerization reaction for the equimolar ratios of comonomer was $E_a = 51.1$ kJ/mol. The molecular weights of the copolymers obtained are relatively high, the T_g's showed similar values (490 K), and the thermal stability is higher than that of polystyrene. The initial rate of copolymerization depends on the total concentration of the comonomers and the maximum occurred at higher 4BPMI mol fractions; however, the overall conversion is highest at equimolar comonomer composition. It has been shown that a charge-transfer complex participates in the process of copolymerization. The initial reaction rate was measured as a function of the monomer molar ratios, and the participation of the charge-

---

†Dedicated to Professor Otto Vogl in honor of his 65th birthday.

transfer complex monomer and the free monomers was quantitatively estimated.

INTRODUCTION

Free radical copolymerizations of styrene with various *N*-phenylmaleimides have been reported in many papers, and it has been shown that in all cases a nearly alternating copolymerization took place, leading to copolymers with great structural stiffness and high thermal stability [1-3]. Also, alternating copolymers, particularly those of maleic anhydride derivatives, have been used in the preparation of pure head-to-head polymers [4, 5].

Several approaches have been used in the literature to treat the kinetic data of systems with the anticipated participation of a charge-transfer complex (CTC) in the copolymerization process [6-9]. The treatment proposed by Shirota et al. [9] has the view that alternation in the resulting copolymers is brought about by stabilization of the transition state in cross reactions of the free monomers and the complex. This treatment has been adopted in the present study.

Some work dealing with *N*-(4-bromophenyl)maleimide (4BPMI) has noted that copolymers are readily formed with styrene and butadiene of alternating structure [10] and random copolymers with methyl acrylate [11]. However, no adequate attention has been paid to the kinetics of the reactions or to the properties of the copolymers obtained. In a previous paper [12] we described the copolymerization of styrene and *N*-(2,4,6-tribromophenyl)maleimide and some properties of the copolymer.

This paper details the copolymerization of 4BPMI with styrene in dioxane with 2,2′-azobis(isobutyronitrile) (AIBN) as initiator by following the course of the reactions by microcalorimetry. The participation of the CTC monomer and the free monomers in the initial rate of copolymerization was quantitatively estimated. Measurements of some characteristic properties of the copolymers were also made.

EXPERIMENTAL

Materials

Styrene and solvents were purified by distillation prior to use. *N*-(4-Bromophenyl)maleimide was prepared in 75% yield in a two-stage synthesis from maleic anhydride and 4-bromoaniline [13] and was twice recrystallized from ethanol, mp 116°C. The ^{1}H-NMR spectrum in $CDCl_3$ showed a singlet at 6.85 ppm (maleic) and a quartet at 7.20–7.65 ppm (phenyl). Azobis(isobutyronitrile) was recrystallized from methanol.

Measurements

Thermogravimetric analyses (TGA, DTG) were carried out with a Perkin-Elmer TGS-2 and DSC-7 instrument in a helium and air atmosphere and at a heating rate of 20°C/min. ^{1}H-NMR spectra were measured on a 90-MHz Varian EM-90 Spectrometer in deuterated chloroform with TMS as the internal standard. The compositions of the copolymers were established by bromine and carbon analyses. The molecular weights of the copolymers were measured by gel permeation chromatography carried out on an Aerograph 8500 Varian instrument fitted with a UV detector. Styragel columns (Waters Associates) were used at a flow rate of 1 mL/min of degassed tetrahydrofuran. Retention times were calculated on polystyrene equivalents.

Polymerization Procedures

Solution polymerizations up to low conversion in dioxane (50 mL solutions) of monomers (0.025 mol) with AIBN (0.082 g) as the initiator at 50°C were carried out under a constant stream of nitrogen in a 100-mL, double-jacketed glass reactor equipped with a magnetic stirrer. After an appropriate time interval (10–100 min), when a withdrawn sample precipitated in methanol, the entire reaction mixture was poured into methanol, and the polymer was isolated by filtration, dissolved in dioxane, reprecipitated, and dried at 60°C and 0.1 mm.

Polymerizations up to high conversion were performed in a Calvet differential microcalorimeter (Setaram, France), consisting of two cylindrical cells, 20 × 80 mm, with a maximum usable volume of 10 mL. A solution of comonomers and AIBN in dioxane (2 mL) was placed into a glass ampule, cooled in an ice bath, evacuated to high vacuum, and sealed. The ampule was heated to slightly below polymerization temperature and placed into the measuring cell of the calorimeter adjusted to polymerization temperature. The electromotive force in μV was recorded. After an appropriate time, when the electric signal had reached zero value and remained unchanged for 1 h, the reaction was completed. The copolymer solution was diluted with 4 mL dioxane and added dropwise into 50 mL methanol. The precipitate was filtered off, washed with methanol, and dried overnight in vacuum at 60°C. A white polymer powder was reprecipitated. The polymerizations were performed at different monomer-to-monomer ratios but at a constant total concentration in the feed: 0.25, 0.50, and 1.0 mol/L, respectively.

The initial reaction rates were established from when the clear electrical signal reached a maximum value in the beginning of the reaction, indicating a maximum rate in an appropriate time. It was previously shown that the microcalorimeter we used to follow the course of styrene polymerization makes stable and accurate measurements [12, 14].

RESULTS AND DISCUSSION

The free radical copolymerization of styrene (St) with *N*-(4-bromophenyl)maleimide (4BPMI) was performed in dioxane solutions by using AIBN as initiator. The influence of molar ratios of the initial monomer mixture (f) on the composition (F) and some properties of copolymers obtained at low conversions are summarized in Table 1 and the copolymerization diagram in Fig. 1. By using the Kelen-Tüdös equation, the monomer reactivity ratios and the confidence interval [15] were calculated from the results in Table 1. The values $r_1 = 0.0218 \pm 0.0064$ (M_1 = St) and $r_2 = 0.0232 \pm 0.0012$ were obtained and were related to the polarity (e) and to the resonance effect (Q) in the Alfrey–Price scheme for 4BPMI

TABLE 1. Copolymerization of Styrene (M_1) and *N*-(4-Bromophenyl)maleimide (M_2) in Dioxane at 50°C with AIBN as Initiator[a]

f_2	Conversion, %	Br, %	F_2	$\overline{M}_w \times 10^{-3}$ [b]	$\overline{M}_n \times 10^{-3}$ [b]	T_g,[c] °C
0.10	8.3	21.23	0.455			
0.20	7.2	21.78	0.475	194.3	90.6	213.0
0.30	7.8	22.14	0.488			
0.40	8.9	22.37	0.497	244.8	113.5	214.8
0.55	9.1	22.45	0.500			216.7
0.65	9.0	22.82	0.510	387.7	180.1	
0.75	8.8	23.09	0.520			
0.90	7.3	23.78	0.545	177.2	63.3	228.8
0.95	5.9	23.91	0.558			

[a] Polymerization conditions: Dioxane solutions (50 mL) of monomers (0.025 mol) and AIBN (0.082 g), 50°C.

[b] Determined by GPC.

[c] Determined by DSC.

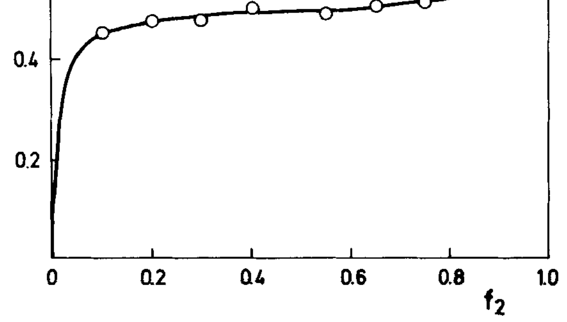

FIG. 1. Monomer–copolymer composition curve for the copolymerization of styrene (M_1) with *N*-(4-bromophenyl)maleimide (M_2) in dioxane at 50°C with AIBN as initiator. Experimental (○), calculated by r_1 and r_2 (——).

as follows: $Q = 5.05$ and $e = 1.96$. It is well documented that monomers presenting such a large e value possess electron-acceptor properties, and in combination with electron-donor monomers, of which styrene is a typical example, they readily form alternating copolymers in conventional free-radical polymerization [16]. The tendency to form an alternating St/4BPMI copolymer is evident from the copolymerization diagram in Fig. 1 and was also confirmed by the values of the glass transition temperatures (T_g) of the copolymers (Table 1). Small differences in the T_g, which is in the range of 213 to 228°C, in spite of large differences in the monomer feed composition, suggest that the copolymerization is indeed nearly alternating. The molecular weight measurements (Table 1) showed relatively high $\overline{M}_w$ and $\overline{M}_n$ of the copolymers, and also their significance increased up to about 0.7 mol fraction of 4BPMI in the monomer mixture when these values started to decrease. This behavior is in agreement with the highest initial polymerization rate at this specific monomer feed composition.

The thermal stabilities of St-4BPMI alternating copolymer were determined by TGA and DTG measurements in helium and air atmospheres (Fig. 2). They showed that the copolymer starts to decompose spontaneously in helium at 387°C and in air at 363°C, which is about 25°C above the decomposition temperature of polystyrene [17]. Some residue, 5.7% in helium and 12.0% in air, respectively, at the end of the fast decomposition indicates that depolymerization to volatile product did not go to completion, the usual characteristic of halogenated *N*-phenyl maleimide copolymers [18].

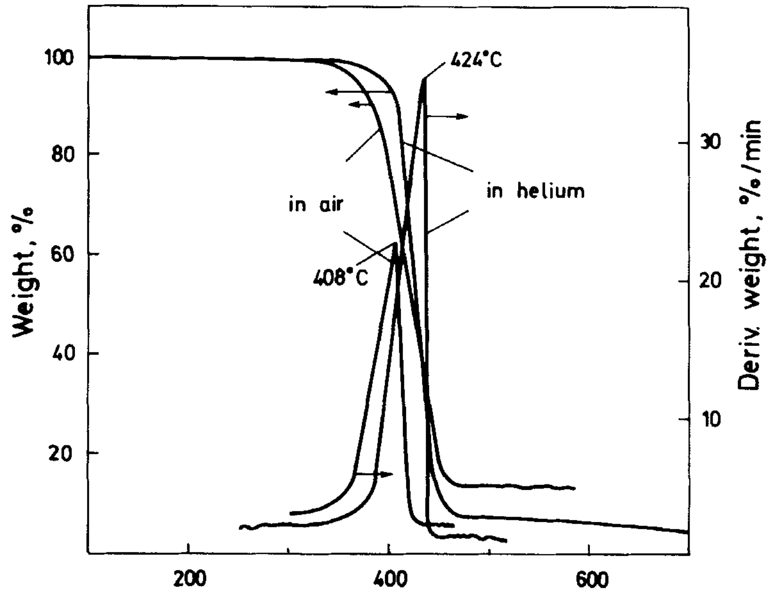

FIG. 2. Thermogravimetric analysis of alternating copolymer of styrene and *N*-(4-bromophenyl)maleimide in helium and air atmospheres.

The course of the copolymerization reactions up to high conversions in a homogeneous environment in dioxane solutions was followed by the microcalorimetric method. The integrated time-conversion curves were calculated and are presented in Fig. 3. It is clearly evident that in spite of the initial polymerization rate increasing by increasing the 4BPMI content in the monomer feed, the highest conversion was obtained at equimolar monomer amounts in the monomer mixture.

The initial rate of copolymerization R_p, determined by microcalorimetry at low conversions, was measured as a function of the initiator concentration [I] at constant total monomer concentration $[M_1] = [M_2] = 0.25$ mol/L in dioxane at 60°C. Figure 4 illustrates the dependence of R_p on $[AIBN]^{0.5}$. A straight line passing through the origin demonstrates the bimolecular termination of the copolymerization process. The temperature dependence of conversion was established in dioxane at 40, 50, and 60°C for an equimolar monomer mixture with a total concentration of 0.5 mol/L. Overall rate constants were determined as slopes of straight lines from a plot of ln $[M_0]/[M_t]$ against time, and they gave the values $k_{40} = 0.79$

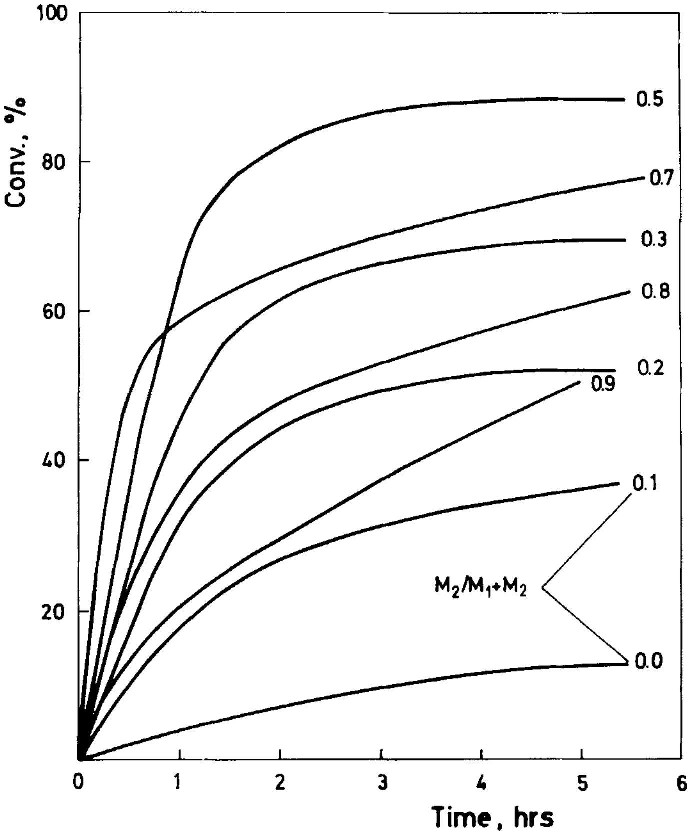

FIG. 3. Influence of the monomer mixture composition on the conversion versus reaction time in the copolymerization of styrene (M_1) and N-(4-bromophenyl)maleimide (M_2) at 60°C. [M] = 0.5 mol/L, [AIBN] = 1×10^{-2} mol/L in dioxane.

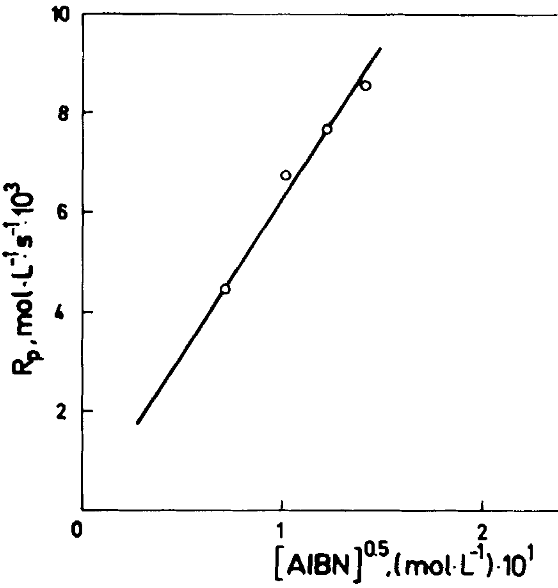

FIG. 4. Initial rate of copolymerization (R_p) of styrene (M_1) and *N*-(4-bromophenyl)maleimide (M_2) versus $[AIBN]^{0.5}$ at 60°C. $[M_1]$ = $[M_2]$ = 0.25 mol/L in dioxane.

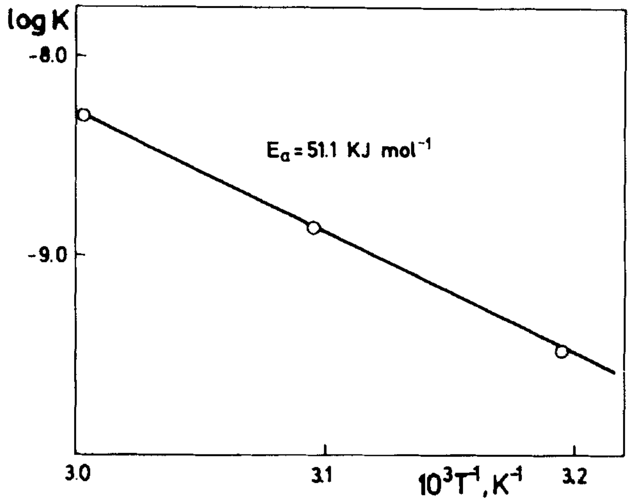

FIG. 5. Arrhenius plot of copolymerization of styrene (M_1) and *N*-(4-bromophenyl)maleimide (M_2). $[M_1]$ = $[M_2]$ = 0.5 mol/L, [AIBN] = 1 × 10^{-2} mol/L in dioxane.

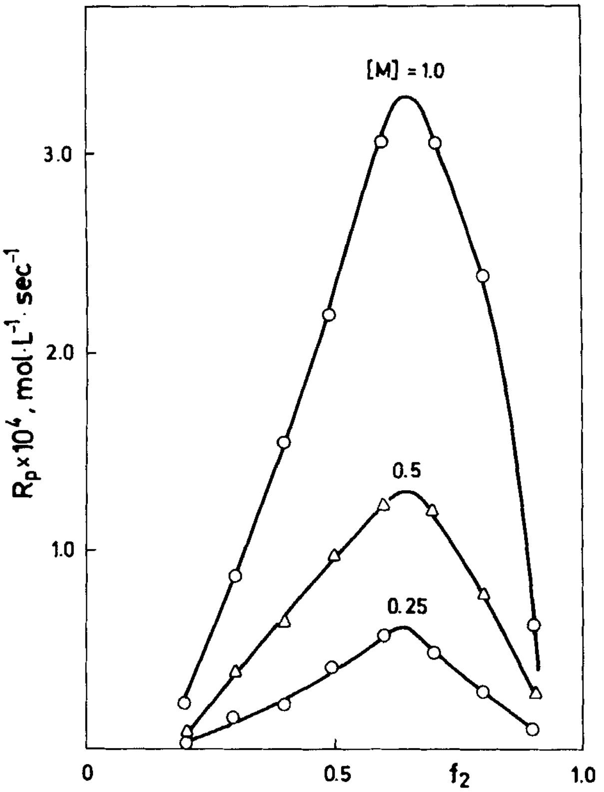

FIG. 6. Dependence of the initial reaction rate, R_p, of monomer feed composition in the copolymerization of styrene (M_1) and N-(4-bromophenyl)maleimide (M_2) at various total monomer concentrations of [M] = 0.25, 0.5, and 1.0 mol/L. [AIBN] = 1×10^{-2} mol/L at 60°C in dioxane.

$\times 10^{-4}$, $k_{50} = 1.43 \times 10^{-4}$, and $k_{60} = 2.53 \times 10^{-4}$ s^{-1}, respectively. The overall energy of activation for the given monomer feed as calculated from Fig. 5 was 51.1 kJ/mol.

To illustrate the role of the CTC monomer in the copolymerization process, the initial rates were measured for various monomer feeds but at total monomer concentrations of 0.25, 0.50, and 1.0 mol/L, respectively, as shown in Fig. 6. The reaction rate, R_p, does not maximize at the equimolar feed ratio but at approximative 0.6-0.7 mol fraction of 4BPMI. It is also somewhat dependent on the total monomer concentration. In the case of a bimolecular termination, the following equations were derived by Shirota et al. [9] to quantify the degree of participation of the free monomers and the CTC monomer in the copolymerization reaction:

$$R_p = A(X)K\{k_{1c}/k_{12} + (k_{2c}/k_{21})X\}[M_1]^2 + A(X)[M_1] \quad (1)$$

$$R_p(f) = A(X)[M_1] \quad (2)$$

$$R_p(\mathrm{CT}) = A(X)K\{k_{1c}/k_{12} + (k_{2c}/k_{21})X\}[M_1]^2 \quad (3)$$

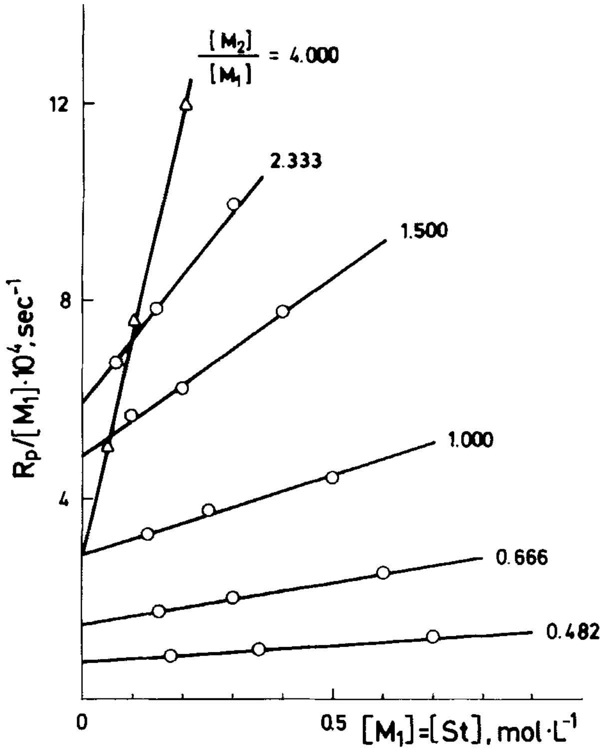

FIG. 7. Dependence of the initial reaction rate, R_p/[St], on [St] at various monomer feed ratios in the copolymerization of styrene and *N*-(4-bromophenyl)maleimide in dioxane.

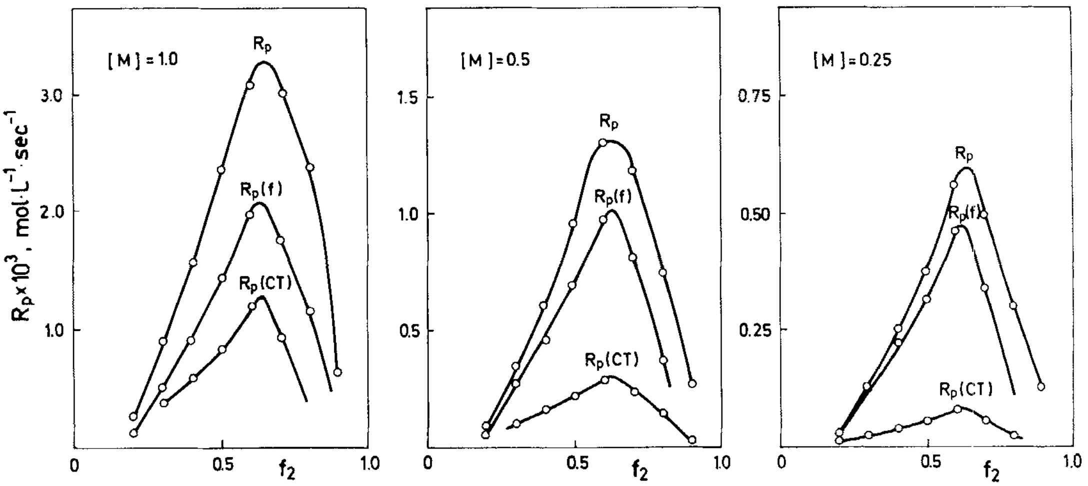

FIG. 8. Relative participation of free (*f*) and complexed (*c*) monomers in the copolymerization of styrene (M_1) and *N*-(4-bromophenyl)maleimide (M_2) at different monomer feed concentrations in dioxane at 60°C.

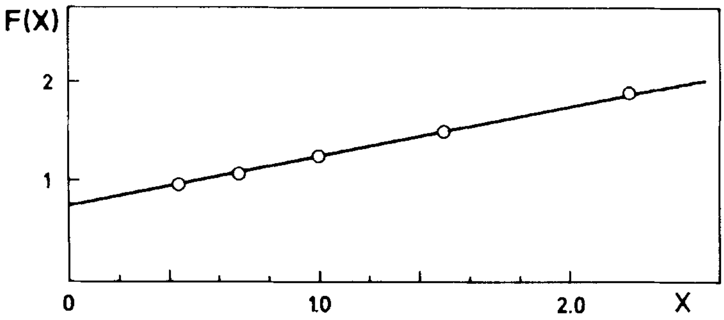

FIG. 9. Plot of $F(X) = K(k_{1c}/k_{12} + k_{2c}/k_{21}X)$ versus X in the copolymerization of styrene (M_1) and *N*-(4-bromophenyl)maleimide (M_2) in dioxane at 60°C.

$$A(X) = 2k_{21}k_{12}R_i^{1/2}X/(k_{t11}k_{21}^2 + 2k_{t12}k_{21}k_{12}X + k_{t22}k_{12}^2X^2)^{1/2} \tag{4}$$

$$R_i = 2k_d fI$$

$$[M_2] = X[M_1]$$

$$R_p/[M_1] = A(X)K\{k_{1c}/k_{12} + (k_{2c}/k_{21})X\}[M_1] + A(X) \tag{5}$$

$$F(X) = K\{k_{1c}/k_{12} + (k_{2c}/k_{21})X\} \tag{6}$$

Here X is the monomer feed molar ratio as represented above; K is the equilibrium constant for the formation of CTC monomer; R_i is the rate of initiation; k_d is the initiator decomposition rate constant; f is the initiator efficiency, k_{1c}, k_{2c}, and k_{12} are the corresponding propagation reaction rate constants; and k_{t11}, k_{t22}, and k_{t12} are the rate constants for the bimolecular, homo, and cross-termination reactions of growing polymer radicals, respectively. The overall initial rate R_p is the superposition of the reaction rates of the free monomer $R_p(f)$ and of the CTC monomer $R_p(\mathrm{CT})$. The plot of $R_p/[M_1]$ against $[M_1]$ gives straight lines for each given ratio of monomer concentration, as shown in Fig. 7, where $[M_1]$ and $[M_2]$ are molar concentrations of St and 4BPMI, respectively. The slope of the lines is $A(X)K(k_{1c}/k_{12} + k_{2c}/k_{21}X)$ and their intercept is $A(X)$. By substituting the values of the slope and the intercept in the above equations, the contributions of free and complexed monomers as a function of the various monomer feed compositions were obtained and presented in Fig. 8. These data indicate that the copolymerization of styrene and *N*-(4-bromophenyl)maleimide in dioxane at total monomer concentration of 0.25, 0.50, and 1.0 mol/L proceeds predominantly via cross propagation of free monomers but that increasing monomer concentrations promote the participation of the CTC monomer. The average contribution of R_p (CT) calculated from Fig. 8 is 20% (0.25 *M*), 25% (0.50 *M*), and 38% (1 *M*). From Eq. (6) it is possible to get a qualitative estimation of the relative reactivity between the St-4BPMI complex and the free monomers. The numerical values of the reactivity ratios determined from the intercept and slope of the straight line in Fig. 9 are $K(k_{1c}/k_{12}) = 0.75$ and $K(k_{2c}/k_{21}) = 0.50$, respectively. The ratio $(k_{1c}k_{21})/(k_{2c}k_{12}) = 1.50$ indicates a somewhat faster formation of St radicals in the propagation reactions.

CONCLUSION

The free radical copolymerization of St with 4BPMI showed a strong tendency toward alternation and follows the mechanism proposed by Shirota et al. [8, 9]. The reaction proceeds predominantly via the cross propagation of free monomers but an increase of the total monomer concentration permits participation of the CTC in the overall initial reaction rate. The average contribution of the CTC copolymerization rate in the overall copolymerization rate is 20% (0.25 *M*), 25% (0.50 *M*), and 38% (1 *M*). Kinetic analysis provides evidence that the formation rate of St free radicals is somewhat greater than the formation rate of 4BPMI radicals. However, the strong tendency toward alternating copolymerization indicates that the St free radicals are preferentially formed through complex addition whose concentration, under the experimental condition used, is presumably small.

REFERENCES

[1] A. Matsumoto, T. Kubota, and T. Otsu, *Macromolecules, 23*, 4508 (1990).

[2] A. A. Mohamed, F. H. Jebrael, and M. Z. Elsabee, *Ibid., 19*, 32 (1986).

[3] J. M. Barrales-Rienda, J. I. Gonzales De La Campa, and J. Gonzales Ramos, *J. Macromol. Sci.—Chem., A11*, 267 (1977).

[4] O. Vogl and S. Grossman, in *Encyclopedia of Polymer Science and Engineering*, Vol. 7 (H. F. Mark, N. M. Bikales, C. G. Overberger, and G. Menges, eds.), Wiley, New York, 1987, p. 626.

[5] T. Florianczyk, C. Sullivan, Z. Janović, and O. Vogl, *Polym. Bull., 5*, 521 (1981).

[6] J. A. Sliner and M. Litt., *Macromolecules, 4*, 308 (1971).

[7] R. Arnaud, C. Caze, and J. Fossey, *J. Macromol. Sci.—Chem., A14*, 1269 (1980).

[8] Y. Shirota, M. Yoshimura, A. Matsumoto, and H. Mikawa, *Macromolecules, 7*, 4 (1974).

[9] M. Yoshimura, H. Mikawa, and Y. Shirota, *Ibid., 11*, 1085 (1978).

[10] M. Bezdek and F. Hrabak, *J. Polym. Sci., Polym. Chem. Ed., 17*, 2857 (1979).

[11] J. D. Patel and M. R. Patel, *Ibid., 21*, 3027 (1983).

[12] Z. Janović, F. Ranogajec, and J. Kučišec-Dolenc, *J. Macromol. Sci.—Chem., A28*, 1025 (1991).

[13] N. E. Searle, U. S. Patent 2,444,536 (1948); *Chem. Abstr., 42*, 7340d (1948).

[14] M. Barić, F. Ranogajec, and I. Dvornik, *Croat. Chem. Acta, 52*, 61 (1979).

[15] F. Tüdös, T. Kelen, and B. Turcsanyi, *J. Polym. Sci., Polym. Chem. Ed., 19*, 1119 (1981).

[16] M. Hirooka, H. Yabuuchi, S. Kawasumi, and K. Nakaguchi, *Ibid., 11*, 1281 (1973).

[17] R. H. Hansen, in *Thermal Stability of Polymers*, Vol. 1 (R. T. Conley, ed.), Dekker, New York, 1970, p. 153.

[18] F. Hrabak, I. Masarik, K. Bouchal, and M. Slaviček, *Eur. Polym. J., 13*, 509 (1977).

Received November 20, 1991
Revision received February 25, 1992