Using eq A11 to eliminate $P_\infty\{...-1^*-i-1^*-...\}$, $P_\infty\{...-1^*-i-2^*-...\}$, $P_\infty\{...-2^*-i-1^*-...\}$ one finally obtains, for the *total* fraction of oxidized units, the result in eq 46.

References and Notes

(1) J. J. Gonzâlez and P. C. Hemmer, *J. Polym. Sci., Polym. Lett. Ed.*, **14**, 645 (1976).
(2) J. J. Gonzâlez and P. C. Hemmer, *J. Chem. Phys.*, **67**, 2496 (1977).
(3) J. J. Gonzâlez and P. C. Hemmer, *J. Chem. Phys.*, **67**, 2509 (1977).
(4) J. J. Gonzâlez, Avhandling for den tekniske doktorgrad, Trondheim, 1977.
(5) M. F. Ishak and T. Painter, *Acta Chem. Scand.*, **27**, 1268 (1973).
(6) J. Hoffman, B. Lindberg, and T. Painter, *Acta Chem. Scand., Ser. B*, **29**, 137 (1975).
(7) J. Hoffman, B. Lindberg, and T. Painter, *Acta Chem. Scand., Ser. B*, **30**, 365 (1976).
(8) T. Painter, unpublished.
(9) I. C. M. Dea and A. Morrison, *Adv. Carbohydr. Chem.*, **31**, 241 (1975).
(10) T. Painter and B. Larsen, *Acta Chem. Scand.*, **24**, 813 (1970); **24**, 2366 (1970).
(11) T. Painter and B. Larsen, *Acta Chem. Scand.*, **24**, 2724 (1970).
(12) M. F. Ishak and T. Painter, *Acta Chem. Scand.*, **25**, 3875 (1971).
(13) The value previously reported by J. Hoffman, B. Lindberg, and T. Painter, *Acta Chem. Scand., Ser. B*, **30**, 365 (1976), was $y(\infty) = 0.80$. However, a recent experiment by T. Painter (unpublished) shows that even after 11 days the reaction has not completely stopped although it proceeds very slowly. We have performed a least-squares fit analysis on these data and by extrapolation found a suggested oxidation limit of 86%.
(14) J. J. Gonzâlez, *Biophys. Chem.*, **2**, 23 (1974).
(15) O. Smidsrød, B. Larsen, and T. Painter, *Acta Chem. Scand.*, **24**, 3201 (1970).
(16) C. B. Arends, *J. Chem. Phys.*, **39**, 1903 (1963).
(17) P. C. Hemmer, unpublished.
(18) H. Morawetz, "Macromolecules in Solution", 2nd ed, Wiley, New York, N.Y., 1975.
(19) R. J. Yu and C. T. Bishop, *Can. J. Chem.*, **45**, 2195 (1967).
(20) M. F. Ishak and T. J. Painter, *Carbohydr. Res.*, **64**, 189 (1978).
(21) A. S. Perlin, *Adv. Carbohydr. Chem.*, **14**, 20 (1959).
(22) T. Painter, unpublished.
(23) Typical computation time with a UNIVAC 1121 for 40 points of the oxidation curve for, say, guaran is 5–10 minutes if one has previously found the ideal time scale by means of eq 38. If one had to find the transformation from ideal times a posteriori, as described in p 81 ff, a computation time of two hours per oxidation curve would be unavoidable.
(24) T. Painter and B. Larsen, *Acta Chem. Scand.*, **27**, 1957 (1973).
(25) P. C. Hemmer and J. J. Gonzâlez, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 321 (1977).
(26) J. J. Gonzâlez, unpublished.
(27) J. E. Courtois and P. Le Dizet, *Bull. Soc. Chim. Biol.*, **50**, 1695 (1968); **52**, 15 (1970).
(28) T. Painter, J. J. Gonzâlez, and P. C. Hemmer, *Carbohydr. Res.*, in press.
(29) See for instance F. A. Bovey, "High Resolution NMR of Macromolecules", Academic Press, New York, N.Y., 1972.
(30) H. Grasdalen, B. Larsen, and O. Smidsrød, *Carbohydr. Res.*, **56**, C11 (1977).
(31) H. Grasdalen and T. Painter, unpublished.
(32) All results on $y_1(t)$ and $y_2(t)$ are exact by 0.2% and were obtained by numerical computation of eq 7–10. Series (10) was truncated when the required accuracy was achieved and standard numerical integration routines were applied to evaluate eq 7. For details see ref 3 and 4.

Studies on the Mechanism of Alternating Radical Copolymerization: Quantitative Separation of the Participation of the Free Monomer and the Charge-Transfer Complex Monomer in the *N*-Vinylcarbazole–Diethyl Fumarate and *N*-Vinylcarbazole–Fumaronitrile Systems

Motomu Yoshimura, Hiroshi Mikawa, and Yasuhiko Shirota*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565, Japan.

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ABSTRACT: Described is the first example of the quantitative analysis of the degree of participation of the free monomer and the charge-transfer complex monomer in the 1:1 alternating radical copolymerization which was achieved by applying the method recently developed by us to the *N*-vinylcarbazole–diethyl fumarate and *N*-vinylcarbazole–fumaronitrile systems. The results show that the reaction of the free monomer contributes to the polymerization rate to a much greater extent than that of the charge-transfer complex monomer in both systems, although the degree of participation of each of them varies significantly depending on the total monomer concentration and on the monomer feed composition. The relative reactivity of the charge-transfer complex monomer to the free monomer toward growing polymer radicals and the termination process were estimated for the *N*-vinylcarbazole–diethyl fumarate system in which the copolymerization proceeds homogeneously.

The 1:1 alternating radical copolymerization has been an area of active research in free-radical polymerizations but the mechanism has been a subject of controversy. Two different mechanisms have been proposed to explain the 1:1 alternation in the resulting copolymer. One is the cross-reaction of free monomers whose transition state is considered to be more stabilized than that of the homoreaction due to either the difference in polarity between monomer pairs or charge-transfer interactions between a growing polymer radical and a monomer.[1,2] The other is the homopolymerization of a charge-transfer complex formed between monomer pairs, i.e., a charge-transfer complex monomer which is usually detected spectrophotometrically in many 1:1 alternating radical copolymerization systems.[3] However, both mechanisms are not capable of explaining satisfactorily polymerization features such as described below.

The initial rate of the 1:1 alternating radical copolymerization does not always maximize at the monomer feed molar ratio of 1:1 under a fixed total monomer concentration as is found in, e.g., styrene–maleic anhydride,[4] *N*-vinylcarbazole (VCZ)–diethyl fumarate (DEF), or VCZ–fumaronitrile (FN) systems.[5] This is inconsistent with the mechanism of the homopolymerization of the

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charge-transfer complex monomer, since, if this mechanism operates, the copolymerization rate as a function of the monomer feed ratio under a fixed total monomer concentration should maximize at the monomer feed molar ratio of 1:1 where the charge-transfer complex formation is a maximum.[6] Furthermore, there are systems in which the copolymer composition deviates from the 1:1 alternation depending on the monomer feed composition as is found in, e.g., the VCZ–diethyl or dimethyl maleate system in which the composition of the copolymers deviates from the 1:1 alternation to the increasingly VCZ rich with the VCZ content in the monomer feed.[7] This result is strongly in favor of participation of the free monomer in the 1:1 alternating radical copolymerization. On the other hand, if only the cross-reaction of free monomers operates, the copolymerization rate should be proportional to the total monomer concentration under conditions of a fixed initiator concentration and monomer feed composition; however, this has not always been found the case, the rate usually being larger than following the first order in the monomer concentration.[8] Recently, Seiner and Litt have successfully applied their terminal-complex model to several nonalternating radical copolymerization systems in which the copolymer composition is not adequately explained in terms of the terminal model but explained in terms of the penultimate model, showing that their model which involves partial participation of the charge-transfer complex monomer gave a better fit with the experimental data than the penultimate model.[9] These experimental results have led one to propose the 1:1 alternating radical copolymerization generally involves participation of both the free monomer and the charge-transfer complex monomer.[4,5] We have proposed a new generalized model for the propagation process of the 1:1 alternating radical copolymerization which consists of the cross-reactions of both the free monomer and the charge-transfer complex monomer.[5]

It is then required to quantify how much the free monomer and the charge-transfer complex monomer contribute respectively to the polymerization in the individual 1:1 alternating radical copolymerization system; however, this has not been achieved so far. We have shown in the preceding paper a method to quantify the degree of participation of the free monomer and the charge-transfer complex monomer in the copolymerization based on our model.[10] This paper describes the results of the application of the method to the VCZ–DEF and VCZ–FN 1:1 alternating copolymerization systems which led to successful quantitative analyses of the degree of participation of the free monomer and the charge-transfer complex monomer in the copolymerization.

Experimental Section

Model for the Propagation Process and the Method for Quantitative Analyses. Although the details are described in the preceding paper,[10] a brief review at this point will serve for the present discussion. The model for the propagation process of the 1:1 alternating radical copolymerization is shown in Scheme I, where k_{12} and k_{21} and k_{1c} and k_{2c} are the rate constants for the reaction of the free monomer and of the charge-transfer complex monomer, respectively. This model is based on the view that the 1:1 alternation in the resulting copolymer is brought about by the stabilization of the transition state in the cross-reactions of both the free monomer and the charge-transfer complex monomer, and hence $m_1\cdot$ attacks the M_2 side of the complex and vice versa.

The method to quantify the model is to analyze the overall initial copolymerization rate as a function of the total monomer concentration under each fixed monomer feed composition. In the case of a bimolecular termination, the following equations (eq 1–6) are derived to quantify the degree of participation of the free monomer and the charge-transfer complex monomer in the polymerization, the reactivity ratio of the charge-transfer complex monomer to the free monomer toward a growing polymer radical, and the termination process of the polymerization.

Scheme I
Propagation Process

$$m_1\cdot + M_2 \xrightarrow{k_{12}} m_2\cdot$$

$$m_2\cdot + M_1 \xrightarrow{k_{21}} m_1\cdot$$

$$m_1\cdot + M_2M_1 \xrightarrow{k_{1c}} m_1\cdot$$

$$m_2\cdot + M_1M_2 \xrightarrow{k_{2c}} m_2\cdot$$

$$R_p = A(X)K\left(\frac{k_{1c}}{k_{12}} + \frac{k_{2c}}{k_{21}}X\right)[M_1]^2 + A(X)[M_1] \qquad (1)$$

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

$$R_p(CT) = A(X)K\left(\frac{k_{1c}}{k_{12}} + \frac{k_{2c}}{k_{21}}X\right)[M_1]^2 \qquad (3)$$

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

$$(R = 2k_d f[I])$$

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

$$R_p/[M_1] = A(X)K\left(\frac{k_{1c}}{k_{12}} + \frac{k_2c}{k_{21}}X\right)[M_1] + A(X) \qquad (4)$$

$$F(X) = K\left(\frac{k_{1c}}{k_{12}} + \frac{k_{2c}}{k_{21}}X\right) \qquad (5)$$

$$G(X) = (X/A(X))^2 = \frac{1}{4R_i}\left(\frac{k_{t22}}{k_{21}^2}X^2 + \frac{2k_{t12}}{k_{21}k_{12}}X + \frac{k_{t11}}{k_{12}^2}\right) \qquad (6)$$

Here, X is the monomer feed molar ratio as represented above, K is the equilibrium constant for the formation of the charge-transfer complex monomer, 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 copolymerization rate R_p (eq 1) is the superposition of the reaction rates of the free monomer $R_p(f)$ (eq 2) and of the charge-transfer complex monomer $R_p(CT)$ (eq 3). Equation 2 means that if the cross-reactions of only free monomers are operative, the overall initial copolymerization rate should be proportional to $[M_1]$ under the conditions of a fixed initiator concentration and monomer feed ratio. Equation 4 which is derived by dividing both sides of eq 1 by the concentration of M_1 ($[M_1]$) is the first-order function of $[M_1]$ since $A(X)$ and $A(X)K(k_{1c}/k_{12} + X(k_{2c}/k_{21}))$ are constant for a fixed X and initiator concentration. Then, the plot of $R_p/[M_1]$ vs. $[M_1]$ for each given X should be linear, and the values of $A(X)$ and $A(X)K(k_{1c}/k_{12} + X(k_{2c}/k_{21}))$ can be obtained from the intercept and slope of this linear plot, respectively. Introducing these values into eq 2 and 3, one obtains the values of $R_p(f)$ and $R_p(CT)$ for each given monomer feed ratio X under a given total monomer concentration to separate quantitatively R_p into $R_p(f)$ and $R_p(CT)$, respectively. Since the values of $A(X)$ and $A(X)K(k_{1c}/k_{12} + X(k_{2c}/k_{21}))$ are obtained for each given X as described above, the value of $K(k_{1c}/k_{12} + X(k_{2c}/k_{21}))$ which is a first-order function of X and defined here as $F(X)$ can be calculated for each given X. The plot of $F(X)$ vs. X should also give a straight line, giving the values of $K(k_{1c}/k_{12})$ and $K(k_{2c}/k_{21})$ as the intercept and slope of this linear plot, respectively (eq 5). The value K can be obtained independently by means of a spectroscopic method. Information on the termination process is given from the dependence of $A(X)$ on the monomer feed ratio X as expressed in eq 6. Thus, the plot of the function $G(X)$ which is defined as $(X/A(X))^2$ vs. X gives the relative values of k_{t22}/k_{21}^2, $k_{t12}/k_{21}k_{12}$, and k_{t12}/k_{12}^2.

Materials and Polymerization. N-Vinylcarbazole (VCZ), diethyl fumarate (DEF), fumaronitrile (FN), and 2,2′-azobis(isobutyronitrile) (AIBN) were purified as described in a

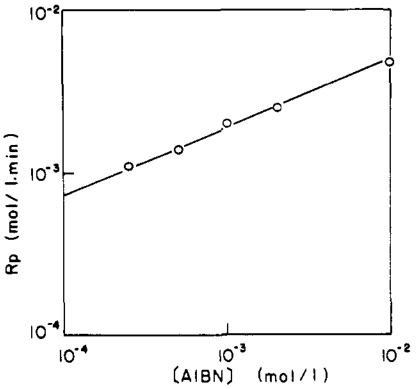

Figure 1. Dependence of the overall initial copolymerization rate on the initiator (AIBN) concentration in the VCZ–DEF system: temperature, 80 ± 0.1 °C; solvent, benzene; [VCZ] = [DEF] = 0.5 M.

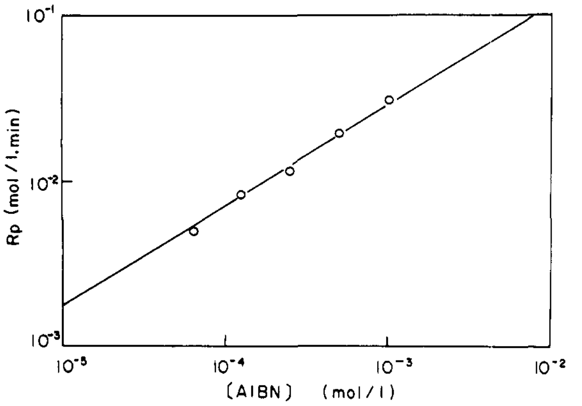

Figure 2. Dependence of the overall initiator copolymerization rate on the initiator (AIBN) concentration in the VCZ–FN system: temperature, 80 ± 0.1 °C; solvent, benzene; [VCZ] = [FN] = 0.5 M.

previous paper.[5] All copolymerizations were carried out in a benzene solution at 80 ± 0.1 °C with AIBN as an initiator. The total monomer concentration employed was 0.5, 1.0, $^5/_3$, and 2.0 M. The initiator concentration was 1.0×10^{-3} M for the VCZ–DEF system and 5.0×10^{-4} M for the VCZ–FN system. The copolymerization rate was followed gravimetrically. A polymerization solution placed in a glass tube (1.5 cm in diameter) was evacuated at 2×10^{-2} Torr by means of several freeze–pump–thaw cycles, sealed off and then allowed to stand for an appropriate time in a thermostat. The polymerization was stopped at low conversions by chilling the polymerization solution and it was poured into a large volume of methanol to precipitate the copolymer. In the VCZ–FN system the copolymer precipitated from the polymerization solution and in this case tetrahydrofuran was first added to dissolve the precipitated copolymer and then the solution was poured into a large volume of methanol to reprecipitate the copolymer. The copolymers were collected by filtration with a glass filter, washed repeatedly with methanol or benzene (in the case of the VCZ–FN copolymer), dried in vacuo, and weighed.

Results

The VCZ–DEF and VCZ–FN systems yield under a free-radical initiation 1:1 alternating copolymers regardless of the monomer feed ratio. Polymerization features and characterization of the copolymers are described in a previous paper.[5] Occurrence of the bimolecular termination in these systems was confirmed from the dependence of the initial copolymerization rate on the initiator concentration being 0.42 in the VCZ–DEF system (Figure 1) and 0.58 in the VCZ–FN system (Figure 2). The overall initial copolymerization rate R_p was measured under a constant initiator concentration at each given monomer feed ratio X ($X = [M_2]/[M_1]$) as a function of the total monomer concentration which was varied from 0.5 to 1.0, $^5/_3$, and 2.0 M. In this paper M_1 stands for the VCZ monomer and M_2 for the DEF or FN monomer.

Table I
Overall Initial Copolymerization Rate R_p and the Value of $R_p/[M_1]$ for Each Given Monomer Feed Molar Ratio at Varying Total Monomer Concentrations for the VCZ(M_1)-DEF(M_2) System[a]

$X = [M_2]/[M_1]$	total monomer concn, mol/L	$[M_1] = [VCZ]$, mol/L	$R_p \times 10^3$, mol/L min	$R_p/[M_1] \times 10^3$, min^{-1}
0.111	0.5	0.45	1.87	4.16
	1.0	0.90	3.91	4.34
	5/3	1.50	6.56	4.37
	2.0	1.80	8.06	4.48
0.250	0.5	0.40	1.60	4.00
	1.0	0.80	3.41	4.26
	5/3	1.33	5.80	4.36
	2.0	1.60	7.10	4.44
0.428	0.5	0.35	1.34	3.83
	1.0	0.70	2.83	4.04
	5/3	1.16	4.89	4.22
	2.0	1.40	6.07	4.34
0.666	0.5	0.30	1.11	3.70
	1.0	0.60	2.45	4.08
	5/3	1.00	4.35	4.35
	2.0	1.20	5.24	4.37
1.000	0.5	0.25	0.89	3.56
	1.0	0.50	2.01	4.02
	5/3	0.83	3.75	4.52
	2.0	1.00	4.60	4.60
1.500	0.5	0.20	0.64	3.20
	1.0	0.40	1.58	3.95
	5/3	0.66	2.98	4.52
2.333	0.5	0.15	0.42	2.80
	1.0	0.30	1.06	3.53
	5/3	0.50	2.06	4.12
	2.0	0.60	2.56	4.27

[a] Polymerization conditions: temperature, 80 ± 0.1 °C; solvent, benzene; $[\text{AIBN}] = 1 \times 10^{-3}$ M. R_p represents here the rate for the disappearance of the monomers which is twice the rate for the copolymer formation as is indicated from the relation, $R_p = -d([M_1] + [M_2])/dt = 2 \times d([\text{copolymer}])/dt$.

Quantitative Separation of R_p into R_p(f) and R_p(CT) in the VCZ-DEF System. The rate data obtained in this system are listed in Table I. The plot of $R_p/[M_1]$ vs. $[M_1]$ for eq 4 was found to show a good linearity for each given monomer feed ratio X as shown in Figure 3, where the plots for only three different monomer feed ratios are illustrated for the sake of simplicity. This result enabled one to analyze quantitatively the degree of participation of the free monomer and the charge-transfer complex monomer in the copolymerization. The values of $A(X)$ and $A(X)K(k_{1c}/k_{12} + X(k_{2c}/k_{21}))$ were obtained for each given monomer feed ratio X from the intercept and slope of the linear plot. The least-squares method was used in obtaining these values together with their probable errors. The results are summarized in Table II. By introducing these values into eq 2 and 3, respectively, the values of R_p(f) and R_p(CT) as a function of X were obtained for each given total monomer concentration. Thus, the overall initial copolymerization rate R_p as a function of X was quantitatively separated into the rates of the free monomer R_p(f) and of the charge-transfer complex monomer R_p(CT) for each given total monomer concentration. Figure 4 shows the result of the quantitative separation of R_p as a function of X into R_p(f) and R_p(CT) in the case

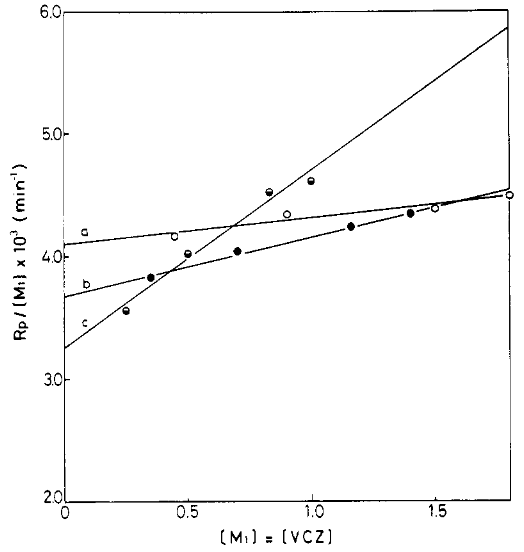

Figure 3. Plots of $R_p/[M_1]$ vs. $[M_1]$ for the VCZ–DEF system: (a) $X = 0.111$; (b) $X = 0.428$; (c) $X = 1.000$.

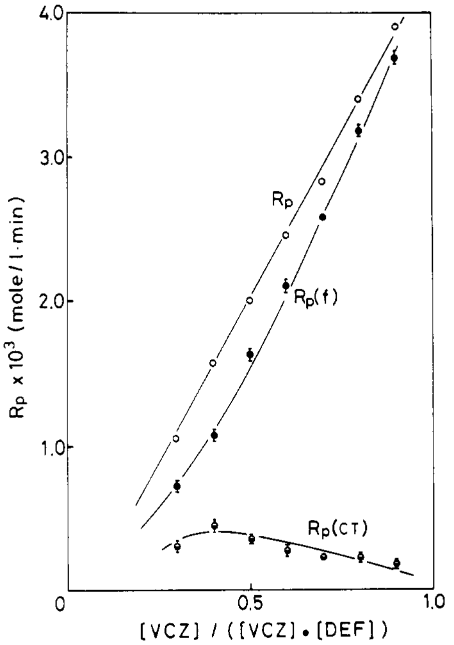

Figure 4. Quantitative separation of the overall initial copolymerization rate R_p into the reaction rates of the free monomer R_p(f) and of the charge-transfer complex monomer R_p(CT) as a function of the monomer feed molar ratio for the VCZ–DEF system. Total monomer concentration: 1.0 M.

Table II

Values of $A(X)$ and $A(X)K(k_{1c}/k_{12} + X(k_{2c}/k_{21}))$ Obtained from the Plot of $R_p/[M_1]$ vs. $[M_1]$ at Each Given Monomer Feed Molar Ratio X and the Values of $F(X)$ Calculated for the VCZ(M_1)–DEF(M_2) System

$X = [M_2]/[M_1]$	$A(X) \times 10^3 \pm \epsilon \times 10^3$ [a]	$A(X)K(k_{1c}/k_{12} + X(k_{2c}/k_{21})) \times 10^3 \pm \epsilon \times 10^3$ [a]	$F(X) \pm e$ [a]
0.111	4.10 ± 0.05	0.21 ± 0.04	0.05 ± 0.01
0.250	3.91 ± 0.05	0.34 ± 0.05	0.09 ± 0.01
0.428	3.68 ± 0.02	0.47 ± 0.02	0.13 ± 0.01
0.666	3.55 ± 0.08	0.75 ± 0.10	0.21 ± 0.03
1.000	3.26 ± 0.07	1.43 ± 0.11	0.44 ± 0.04
1.500	2.70 ± 0.11	2.82 ± 0.23	1.04 ± 0.10
2.333	2.42 ± 0.13	3.24 ± 0.31	1.34 ± 0.15

[a] ϵ is the probable error.

Table III

Quantitative Separation of the Overall Initial Copolymerization Rate R_p into the Reaction Rates of the Free Monomer R_p(f) and of the Charge-Transfer Complex Monomer R_p(CT) as a Function of the monomer Feed Molar Ratio X at the Total Monomer Concentration of 0.5 and 5/3 M for the VCZ(M_1)–DEF(M_2) System

$X = [M_2]/[M_1]$	$[R_p(f) \pm \epsilon] \times 10^3$,[a] mol/L min	$[R_p(CT) \pm \epsilon] \times 10^3$,[a] mol/L min	$R_p(CT)/R_p(f)$
(a) Total Monomer Concentration: 0.5 M			
0.111	1.85 ± 0.02	0.04 ± 0.01	0.02
0.250	1.56 ± 0.02	0.05 ± 0.01	0.03
0.428	1.29 ± 0.01	0.06 ± 0.002	0.05
0.666	1.07 ± 0.02	0.07 ± 0.01	0.07
1.000	0.82 ± 0.01	0.09 ± 0.01	0.11
1.500	0.54 ± 0.02	0.11 ± 0.01	0.20
2.333	0.36 ± 0.02	0.07 ± 0.01	0.19
(b) Total Monomer Concentration: 5/3 M			
0.111	6.15 ± 0.08	0.47 ± 0.09	0.08
0.250	5.20 ± 0.07	0.60 ± 0.09	0.12
0.428	4.27 ± 0.02	0.63 ± 0.03	0.15
0.666	3.55 ± 0.08	0.75 ± 0.10	0.21
1.000	2.71 ± 0.06	0.99 ± 0.08	0.37
1.500	1.78 ± 0.07	1.23 ± 0.10	0.69
2.333	1.21 ± 0.07	0.81 ± 0.08	0.67

[a] ϵ is the probable error.

Table IV

Overall Initial Copolymerization Rate R_p and the Value of $R_p/[M_1]$ for Each Given Monomer Feed Molar Ratio at Varying Total Monomer Concentrations for the VCZ(M_1)–FN(M_2) System[a]

$X = [M_2]/[M_1]$	total monomer concn, mol/L	$[M_1]$ = [VCZ], mol/L	$R_p \times 10^3$, mol/L min	$R_p/[M_1] \times 10^3$, min^{-1}
0.111	0.5	0.45	8.44	18.76
	1.0	0.90	18.05	20.06
	5/3	1.50	34.11	22.74
	2.0	1.80	43.79	24.33
0.250	0.5	0.40	11.48	28.70
	1.0	0.80	25.24	31.55
	5/3	1.33	46.41	34.89
	2.0	1.60	55.89	34.93
0.428	0.5	0.35	11.60	33.14
	1.0	0.70	24.92	35.60
	5/3	1.16	44.28	38.17
	2.0	1.40	57.07	40.76
0.666	0.5	0.30	11.12	37.07
	1.0	0.60	24.26	40.43
	5/3	1.00	42.56	42.56
1.000	0.5	0.25	10.52	42.08
	1.0	0.50	22.33	44.66
	5/3	0.83	40.70	49.04
1.500	0.5	0.20	8.82	44.10
	1.0	0.40	18.55	46.38
	5/3	0.66	33.70	51.06
	2.0	0.80	41.63	52.04
2.333	0.5	0.15	6.46	43.07
	1.0	0.30	14.17	47.23
	5/3	0.50	24.48	48.96
	2.0	0.60	30.11	50.18

[a] Polymerization conditions: temperature, 80 ± 0.1 °C; solvent, benzene; [AIBN] = 5×10^{-4} M. R_p represents here the rate for the disappearance of the monomers which is twice the rate for the copolymer formation.

of the total monomer concentration being fixed at 1.0 M. The results obtained at other total monomer concentrations are given in Table III.

Quantitative Separation of R_p into R_p(f) and R_p(CT) in the VCZ–FN System. The same treatment of the rate data as described above was followed for the VCZ–FN system. The rate data of this system are listed

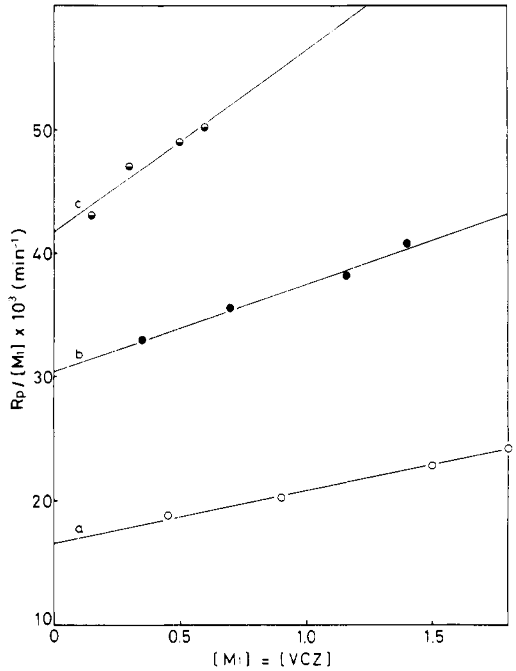

Figure 5. Plots of $R_p/[M_1]$ vs. $[M_1]$ for the VCZ–FN system: (a) $X = 0.111$; (b) $X = 0.428$; (c) $X = 2.333$.

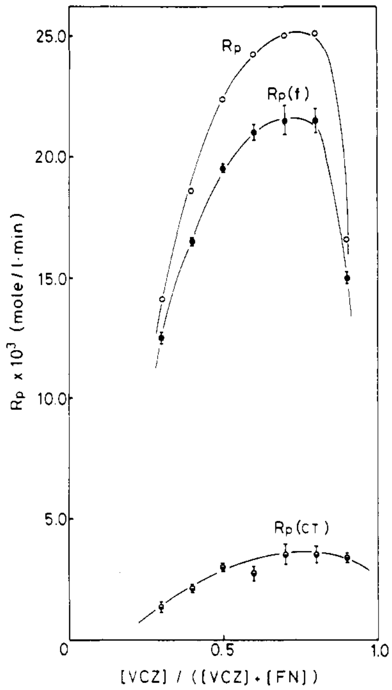

Figure 6. Quantitative separation of the overall initial copolymerization rate R_p into the reaction rates of the free monomer R_p(f) and of the charge-transfer complex monomer R_p(CT) as a function of the monomer feed molar ratio for the VCZ–FN system. Total monomer concentration: 1.0 M.

Table V
Quantitative Separation of the Overall Initial Copolymerization Rate R_p into the Reaction Rates of the Free Monomer R_p(f) and of the Charge-Transfer Complex Monomer R_p(CT) as a Function of the Monomer Feed Molar Ratio X at the Total Monomer Concentration of 0.5 and 5/3 M for the VCZ(M_1)–FN(M_2) System

$X = [M_2]/[M_1]$	$[R_p(f) \pm \epsilon] \times 10^3$,[a] mol/L min	$[R_p(CT) \pm \epsilon] \times 10^3$,[a] mol/L min	$R_p(CT)/R_p(f)$
(a) Total Monomer Concentration: 0.5 M			
0.111	7.47 ± 0.14	0.84 ± 0.05	0.11
0.250	10.76 ± 0.25	0.87 ± 0.09	0.08
0.428	10.72 ± 0.14	0.85 ± 0.05	0.08
0.666	10.54 ± 0.17	0.69 ± 0.07	0.07
1.000	9.72 ± 0.04	0.76 ± 0.02	0.08
1.500	8.25 ± 0.06	0.55 ± 0.02	0.07
2.333	6.25 ± 0.13	0.33 ± 0.05	0.05
(b) Total Monomer Concentration: 5/3 M			
0.111	24.92 ± 0.45	9.38 ± 0.52	0.38
0.250	35.78 ± 0.83	9.59 ± 0.97	0.27
0.428	35.29 ± 1.04	9.53 ± 1.08	0.27
0.666	35.14 ± 0.55	7.71 ± 0.79	0.22
1.000	32.28 ± 0.14	8.33 ± 0.20	0.26
1.500	27.22 ± 0.21	5.94 ± 0.25	0.22
2.333	20.83 ± 0.44	3.69 ± 0.52	0.18

[a] ϵ is the probable error.

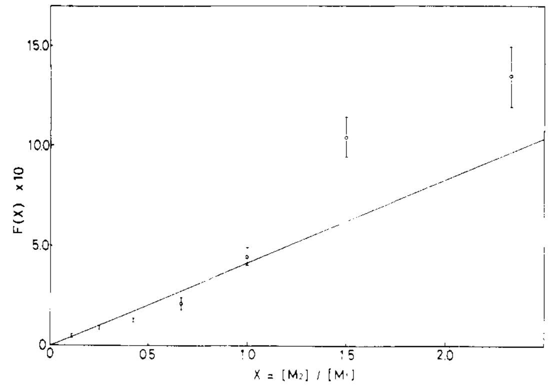

Figure 7. Plots of $F(X)$ vs. X for the VCZ–DEF system.

in Table IV. The plot of $R_p/[M_1]$ vs. $[M_1]$ for eq 4 was found to be linear for each given monomer feed ratio X as shown in Figure 5, where the plots for only three different monomer feed ratios are illustrated. As a result, the degree of participation of the free monomer and the charge-transfer complex monomer in the copolymerization was analyzed quantitatively for this system as well. The least-squares method was used in obtaining the values of the intercept and slope of the linear plot together with the values of their probable errors. Shown in Figure 6 is the result of the quantitative separation of R_p into R_p(f) and R_p(CT) in the case of the total monomer concentration being fixed at 1.0 M. The results obtained at other total monomer concentrations are summarized in Table V.

Estimation of the Relative Reactivity of the Charge-Transfer Complex Monomer to the Free Monomer and of the Termination Process for the VCZ–DEF System. Further analyses regarding the relative reactivity of the charge-transfer complex monomer to the free monomer toward growing polymer radicals and the termination process were carried out with the VCZ–DEF system in which the copolymerization proceeds homogeneously in a benzene solution. The value of $K \cdot (k_{1c}/k_{12} + X(k_{2c}/k_{21}))$ which is defined here as $F(X)$ was calculated for each given X from the values of $A(X)$ and $A(X)K(k_{1c}/k_{12} + X(k_{2c}/k_{21}))$ obtained. The plot of $F(X)$ vs. X is shown in Figure 7. The straight line in this figure is drawn by use of the least-squares method which takes into account the weight of each value since the confidence of each value of $F(X)$ is not on the same level (for example, the values at $X = 0.11$ and 0.25 are 15 times more reliable than the value at $X = 2.333$). The values of $K(k_{1c}/k_{12})$ and $K(k_{2c}/k_{21})$ obtained from the intercept and slope of the straight line are 0.004 ± 0.02 and 0.33 ± 0.05, respectively (two points at $X = 1.50$ and 2.33 which have much larger probable errors than others were omitted in obtaining these numerical values). The equilibrium constant K for the formation of the charge-transfer complex monomer was estimated spectroscopically to be in the range between ca.

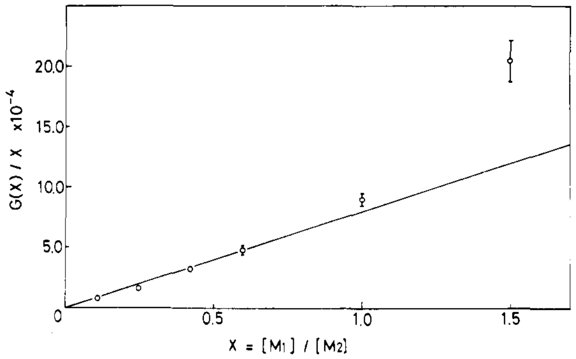

Figure 8. Plots of $G(X)/X$ vs. X for the VCZ–DEF system.

0.02 and 0.1 L/mol in a benzene solution at 35 °C for both systems but it was difficult to determine the exact value of K because of the very low value of the intercept of the Benesi–Hildebrand plot. These results show that the charge-transfer complex monomer has a greater reactivity relative to the free monomer toward the growing polymer radical with the DEF end, i.e., $\sim m_2\cdot$, but that toward the growing polymer radical with the VCZ end, i.e., $\sim m_1\cdot$, the reactivity of the charge-transfer complex monomer is not enhanced very much or might be reduced as compared with that of the free monomer.

The plot of $G(X)$ vs. X for eq 6 showed that k_{t11}/k_{12}^2 is close to zero, indicating that the bimolecular homotermination reaction between the growing polymer radical with the VCZ end is not significantly operative in the VCZ–DEF system. Then the plot of $G(X)/X$ vs. X was made which is shown in Figure 8. It is seen that the plot goes through very close to the origin although the value at $X = 1.500$ which has a much larger probable error than others deviates from the linearity. It is indicated that the termination occurs predominantly by the k_{t22} process, i.e., the bimolecular homotermination reaction between the growing polymer radical with the DEF end.

Discussion

The key observation in the present study is that the plot of $R_p/[M_1]$ vs. $[M_1]$ for eq 4 showed a good linearity for each given monomer feed molar ratio X. Linearity of the plot together with the fact that the above plot has definite values of the intercept and slope provides an indication of the validity of the proposed mechanism involving the reaction of both the free monomer and the charge-transfer complex monomer. These results enabled one to make quantitative separation of the overall initial copolymerization rate R_p into the reaction rates of the free monomer R_p(f) and of the charge-transfer complex monomer R_p(CT), respectively. It was shown that the reaction of the free monomer contributes to the polymerization rate to a much greater extent than that of the charge-transfer complex monomer in both VCZ–DEF and VCZ–FN systems, although the degree of participation of each of them varies significantly depending on the total monomer concentration and on the monomer feed ratio. It is conceivable that relative contribution of the charge-transfer complex monomer and the free monomer to the polymerization varies greatly depending on the polymerization system. It is to be noted that a larger value of K in a system than in another system does not necessarily lead to a greater contribution of the charge-transfer complex monomer to the copolymerization rate in the system with a larger value of K since the reaction rate is determined not only by the reactant concentration but also by its rate constant, i.e., reactivity. In the same polymerization system, however, the degree of participation of the charge-transfer complex monomer relative to the free monomer increases with the total monomer concentration, hence with the increase of the concentration of the charge-transfer complex monomer, as is seen from the results listed in Tables III and V.

Linearity of the plot of $F(X)$ vs. X for eq 5 which is shown in Figure 7 appears to be inferior to the plot for eq 4; however, it must be admitted that some errors are essentially involved in this plot since the values of $F(X)$ as a function of X are not the direct experimental data but the ones calculated from the intercept and slope of the linear plot of $R_p/[M_1]$ vs. $[M_1]$ for eq 4. Therefore, it must also be admitted that a small variation in the value of the slope which is inevitably accompanied by a variation in the value of the intercept in the plot of $R_p/[M_1]$ vs. $[M_1]$ yields a rather large variation in the value of $F(X)$ to be calculated. In the present study the least-squares method which takes into account the weight of each value was employed in drawing the straight line in Figure 7 since each value of $F(X)$ calculated is not on the same confidence level. The case is the same with the plot of $G(X)/X$ vs. X in Figure 8 where the k_{t11} term was shown to be almost zero. If these situations are taken into consideration, the plots shown in Figures 7 and 8 may be understood as showing a rather good linearity. In fact, the deviation from the linearity found at $X = 1.500$ and 2.333 in Figure 7 is greatly reduced if the slope of the linear plot of $R_p/[M_1]$ vs. $[M_1]$ for eq 4 in the cases of $X = 1.500$ and 2.333 is made a little bit less steep by allowing only a little bit larger error for the rate data at the total monomer concentration of 0.5 M than for others. The values of $K(k_{1c}/k_{12})$ and $K(k_{2c}/k_{21})$ obtained from the plot of $F(X)$ vs. X coupled with the value K estimated spectroscopically permit one to make an approximate evaluation of the relative reactivity of the charge-transfer complex monomer to the free monomer toward growing polymer radicals, showing that the relative reactivity of the charge-transfer complex monomer to the free monomer differs depending on the reaction pathway involved in the propagation process, i.e., between k_{1c}/k_{12} and k_{2c}/k_{21}. It was shown that in the VCZ–DEF system the charge-transfer complex monomer has a greater reactivity than the free monomer toward the growing polymer radical with the DEF end since it is certain that the equilibrium constant K for the formation of the charge-transfer complex monomer in this system is at most ca. 0.1 L/mol, but toward the growing polymer radical with the VCZ end a definite conclusion was not drawn. The detailed discussion regarding the relative reactivity must await the determination of the exact value of K.

The mechanism for the 1:1 alternating radical copolymerization has long been controversial as to whether the cross-reaction of free monomers or the homopolymerization of the charge-transfer complex monomer operates; however, recent experimental results on the polymerization features of the 1:1 alternating radical copolymerization have indicated that the mechanism involving participation of both the free monomer and the charge-transfer complex monomer is more general and probable. The present study presents the first example of quantifying the contribution of the free monomer and the charge-transfer complex monomer to the polymerization. The present quantitative treatment enables not only the separation of the overall copolymerization rate into the reaction rates of the free monomer and of the charge-transfer complex monomer, but also evaluation of the relative reactivity of the charge-transfer complex monomer to the free monomer toward growing polymer radicals and analysis of the termination process. In the present study the rate was followed gravimetrically but a more accurate method for obtaining the rate data will be desirable for precise analyses regarding the latter two subjects. The application of the present quantitative treatment to other 1:1 alternating radical copolymerization systems is now in progress to verify the generality of the proposed mechanism and to make quantitative analyses of individual systems.

References and Notes

(1) C. C. Price, *J. Polym. Sci.*, **3**, 772 (1948).
(2) C. Walling, D. Seymour, and K. B. Wolfstirn, *J. Am. Chem. Soc.*, **70**, 1544 (1948).
(3) For examples, see T. Kokubo, S. Iwatsuki, and Y. Yamashita, *Macromolecules*, **1**, 482 (1968); **3**, 518 (1970).
(4) E. Tsuchida and T. Tomono, *Makromol. Chem.*, 141, 265 (1971).
(5) Y. Shirota, M. Yoshimura, A. Matsumoto, and H. Mikawa, *Macromolecules*, **7**, 4 (1974).
(6) When the bimolecular termination of the growing polymer chain radical is assumed to occur, the polymerization rate R_p is simply expressed as $R_p = kR_i^{1/2}[\text{CT–complex}] \approx kR_i^{1/2}K[M_1][M_2]$, where k is a constant, K is the equilibrium constant for the formation of the charge-transfer complex monomer, and R_i is the rate of initiation.
(7) M. Yoshimura, H. Mikawa, and Y. Shirota, *Macromolecules*, **8**, 713 (1975).
(8) This is shown in the present paper. See also, S. Murahashi, S. Nozakura, K. Yasufuku, and K. Emura, *Kobunshi Kagaku*, **23**, 361 (1966).
(9) J. A. Seiner and M. Litt, *Macromolecules*, 4, 308 (1971); M. Litt, *ibid.*, 4, 312 (1971); M. Litt and J. A. Seiner, *ibid.*, **4**, 314, 316 (1971).
(10) M. Yoshimura, T. Nogami, M. Yokoyama, H. Mikawa, and Y. Shirota, *Macromolecules*, **9**, 211 (1976).

Importance of Mixed Dimerization in Copolymerizations Involving Lithium Salts of Living Polymers in Benzene. Comments and New Interpretation of the Work of O'Driscoll and Patsiga

A. Yamagishi and M. Szwarc*

Department of Chemistry, State University of New York, College of Environmental Science and Forestry, Syracuse, New York 13210.

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ABSTRACT: The importance of mixed dimerization of lithium salts of living polymers in benzene is shown by the results obtained for the styrene–butadiene system and for the styrene–*p*-methylstyrene system studied by O'Driscoll and Patsiga. In their work the kinetics of monomer consumption was shown to be governed by first-order law, i.e., $M_1 = M_{10}\exp(-\gamma_1 t)$ and $M_2 = M_{20}\exp(-\gamma_2 t)$, with $\gamma_1 \neq \gamma_2$. The treatment invoking mixed dimerization of living polymers predicts such relations and shows that γ_1 and γ_2 are uniquely determined by the total concentration of all living polymers and are independent of the initial composition of the feed. This conclusion is confirmed by the data reported in the literature.

As is well known, lithium salts of many living polymers exist in benzene solution in the dimeric, unreactive form. The polymerization in such systems is propagated by the minute fraction of monomeric polymers that are in equilibrium with the dimers. For example, in the polystyrene system, ${\sim}S^-$, Li^+, the rate of polymerization is given by

$$-\mathrm{d}\ln S/\mathrm{d}t = k_pK^{1/2}[{\sim}S^-,Li^+{}_{total}]^{1/2}$$

$$[{\sim}S^-,Li^+] = K^{1/2}[{\sim}S^-,Li^+{}_{total}]^{1/2}$$

The problem becomes more complex in copolymerization. In previous papers from this laboratory[1,2] the rate of cross-propagation was studied, namely,

$${\sim}S^-,Li^+ + D \rightarrow {\sim}D^-,Li^+$$

and

$${\sim}D^-,Li^+ + S \rightarrow {\sim}S,Li^+$$

where D denotes 1,1-diphenylethylene and ${\sim}D^-,Li^+$ is ${\sim}CH_2C(Ph)_2{}^-,Li^+$. It was found that the conversions of ${\sim}S^-,Li^+$ into ${\sim}D^-,Li^+$ in the first system, the reverse conversions of ${\sim}D^-,Li^+$ into ${\sim}S^-,Li^+$ in the second system, are first-order reactions, provided that the concentration of monomers is virtually constant. This condition is fulfilled if monomer concentration greatly exceeds that of living polymers. Moreover, the slopes of the first-order plots, say in the first system $\mathrm{d}\ln[{\sim}D^-,Li^+{}_{total}]/\mathrm{d}t$ or $-\mathrm{d}\ln[{\sim}S^-,Li^+{}_{total}]/\mathrm{d}t$, are given by (constant)$[D]_0/[{\sim}S^-,Li^+]_0{}^{1/2}$, where $[D]_t \approx [D]_0$ and $[{\sim}S^-,Li^+{}_{total}]_0$ = total concentration of all living polymers $[{\sim}S^-,Li^+]_t + [{\sim}D^-,Li^+]_t$.

This kinetic relation was accounted for by the following mechanism.

$$2{\sim}S^-,Li^+ \rightleftarrows ({\sim}S^-,Li^+)_2 \quad (1/2)K_1$$

$${\sim}S^-,Li^+ + {\sim}D^-,Li^+ \rightleftarrows ({\sim}S^-,Li^+,{\sim}D^-,Li^+) \qquad K_{12}$$

$$2{\sim}D^-,Li^+ \rightleftarrows ({\sim}D^-,Li^+)_2 \qquad (1/2)K_2$$

$${\sim}S^-,Li^+ + D \xrightarrow{k_p} {\sim}D^-,Li^+$$

Denoting by u and v the concentrations of the monomeric polymers, by x, y, and z the concentration of the respective dimers, by α the ratio v/u, and by f the ratio $[{\sim}S^-,Li^+{}_{total}]_t/[{\sim}S^-,L^+{}_{total}]_0$, one finds

$$-\mathrm{d}\ln f/\mathrm{d}t = \{k_p[D]_0/[{\sim}S^-,Li^+{}_{total}]_0{}^{1/2}\}\{(K_1 + 2K_{12}\alpha + K_2\alpha^2)/(K_1{}^2 + 2K_1K_{12}\alpha + K_{12}{}^2\alpha^2)\}^{1/2}$$

Only for $K_{12}{}^2 = K_1K_2$ this expression is reduced to

$$-\mathrm{d}\ln f/\mathrm{d}t = k_p[D]_0/K_1{}^{1/2}[{\sim}S^-,Li^+{}_{total}]_0{}^{1/2}$$

that agrees with experimental results.

We wish to emphasize that the first-order character of this reaction, i.e., the linear relation of $\ln[{\sim}S^-,Li^+{}_{total}]_t$ vs. time, demands the relation $K_{12}{}^2 = K_1K_2$. Indeed, we have shown in a subsequent paper[3] that the above plots

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