Copolymerization of N-Arylmaleimide with Vinyl Acetate—Effect of the Total Monomer Concentration on the Reactivity Ratios of the Copolymerization

M. Z. ELSABEE, M. W. SABAA, and S. MOKHTAR

*Department of Chemistry, Faculty of Science,
University of Cairo, Giza, Egypt*

ABSTRACT: The copolymerization of N-2-chlorophenylmaleimide with vinyl acetate was investigated at different total monomer concentrations. The reactivity of the maleimide was enhanced greatly with an increase in total monomer concentration. The overall initial copolymerization rate for the above system in two different solvents was also measured as a function of total monomer concentration, which was varied between 0.5—2.0 mol l^{-1}.
    KEY WORDS   Copolymerization   /   N-2-Chlorophenylmaleimide–Vinyl
Acetate / Reactivity Ratios / Effect of Concentration /

The copolymerization of N-arylmaleimide with vinyl acetate was investigated in different solvents.[1] The solvent was found to affect the reactivity of the maleimide due to the molecular association of solvent/monomer molecules. Moreover, the overall rate of the copolymerization was found to increase as the ability of the solvent to associate with the maleimide increased. The effect of total monomer concentration on the reactivity ratios of the copolymerization is now being studied since preliminary studies show that the reactivity ratios of the copolymerization of N-arylmaleimide with vinyl acetate changes noticeably with the total concentration of the two monomers. For this, the system of N-2-chlorophenylmaleimide(2CMI)–vinyl acetate(VAC) was chosen using two different solvents. Maleimides are known to be electron acceptors[2] and vinyl acetate as an electron donor. It is very likely that these two monomers can associate to form a charge-transfer complex and are polymerized according to an alternating copolymerization scheme.[3,4] The ability of various maleimide monomers to alternate with

electron donor monomers has been reported.[5-7] Moreover, the charge-transfer complex (CTC) was found to play a role in the alternating copolymerization of N-substituted maleimides with vinyl ethers.[8] It was thus considered worthwhile to investigate the 2CMI/ VAC system from both the standpoint of the solvent–maleimide interaction and that of association of monomers at different concentrations.

EXPERIMENTAL

Materials

Synthesis of the maleimide was carried out in two stages according to the method developed by Searle.[9] The final product was dried and purified by repeated recrystallization from aqueous ethanol. The melting point and analysis agreed well with the published data. Vinyl acetate (Prolabo, France) was purified by distillation according to ordinary methods following removal of the inhibitor. Azobisisobutyronitrile (AIBN) (Fluka A.G.) was purified by recrystallization from methanol and

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then dried in the dark. Solvents of the highest grade available were purified according to standard methods. The purity was checked with refractive index measurements.

Copolymerization

Polymerization ampoules of pyrex glass were charged with the monomers, solvent and the initiator (AIBN), 0.2% by weight of the two monomers. The ampoules were then cooled and purified nitrogen gas was bubbled through the solution to eliminate dissolved oxygen. The ampoules were then sealed. Polymerization was carried out in a water bath thermostated at $70 \pm 0.1°C$. Polymerization was brought to a stop by opening the glass ampoules and immediately pouring the content into a large amount of ethanol. The precipitated materials were washed with ethanol and dried at 60°C until constant weights were attained. The polymerizations were homogeneous in all cases.

Rates of Copolymerization

Copolymerization rates were determined by calibrated dilatometers immersed in a transparent Dewar flask connected to an ultra-thermostat. The dilatometers were charged under normal atmospheric conditions and oxygen was eliminated by a usual cooling and thawing technique. The decrease in volume was followed as a function of time at a constant temperature. After a required time, the dilatometer was connected to a vacuum line and the contents was withdrawn and immediately poured into excess of ethanol to precipitate the copolymers. The copolymers were then filtered, washed, purified by reprecipitation from a dioxane solution into alcohol, and dried to constant weights. The rates were determined from the percent conversion and time of copolymerization.

Copolymer Analysis

Copolymer compositions were calculated on the basis of nitrogen content of the copolymers. Nitrogen analysis was performed at the central microanalytical unit, Cairo University.

RESULTS AND DISCUSSION

The composition of the copolymers as a function of the initial monomer mixtures, and the analysis of the copolymerization data ac-

Table I. Copolymerization data for $2CMI(M_1)$–$VAC(M_2)$ in dioxane at 70°C, $[M_1]+[M_2]=1$ mol l^{-1}

| No. | Monomer composition | | Conversion | | Copolymer composition | | | |
| | mol% | | wt% | N% | wt% | | mol% | |
	2CMI [M₁]	VAC [M₂]			2CMI [m₁]	VAC [m₂]	2CMI [m₁]	VAC [m₂]
1	5	95	4.5	3.10	50.00	50.00	29.30	70.70
2	10	90	10.60	3.8	61.29	38.71	39.62	60.38
3	20	80	8.40	4.1	66.13	33.87	44.73	55.27
4	30	70	7.60	4.2	67.74	32.26	46.53	53.47
5	40	60	20.00	4.5	72.58	27.42	52.31	47.99
6	50	50	16.00	4.65	75.00	25.00	55.50	44.50
7	60	40	23.00	4.7	75.81	24.19	56.50	43.50
8	70	30	26.00	4.1	66.13	33.87	59.73	55.27
9	80	20	21.00	5.05	81.45	18.55	64.54	35.46
10	90	10	9.00	5.1	82.74	17.74	65.78	34.42

Table II. Copolymerization data for 2CMI(M_1)–VAC(M_2) in
dioxane at 70°C, $[M_1]+[M_2]=2.5$ mol l^{-1}

No.	Monomer composition		Conversion		Copolymer composition			
	mol%		wt%	N%	wt%		mol%	
	2CMI [M_1]	VAC [M_2]			2CMI [m_1]	VAC [m_2]	2CMI [m_1]	VAC [m_2]
1	5	95	6.7	4.0	64.52	35.48	43.00	57.00
2	10	90	5.7	4.4	70.97	29.03	50.33	49.67
3	20	80	2.0	4.6	74.19	25.91	54.36	45.94
4	30	70	—	4.8	77.42	22.58	58.69	41.30
5	40	60	—	4.9	79.03	20.97	60.97	39.03
6	50	50	3.9	5.1	82.26	17.74	65.78	34.22
7	60	40	2.2	5.3	85.48	14.52	70.93	29.07
8	70	30	22.0	5.4	87.10	12.90	73.68	26.32
9	80	20	2.2	5.5	88.71	11.29	76.51	23.49
10	90	10	10.4	6.1	98.39	1.61	96.20	3.80

Table III. Analysis of Copolymerization data
for the 2CMI(M_1)–VAC(M_2) system in dioxane
at 70°C, $[M_1]+[M_2]=1$ mol l^{-1}
by the F–R and K–T methods

x	y	G	F	η	ξ
				$\alpha=0.544$	
0.052	0.414	−0.073	0.007	−0.132	0.013
0.11	0.656	−0.058	0.018	−0.103	0.032
0.25	0.809	−0.059	0.077	−0.095	0.124
0.43	0.870	−0.064	0.212	−0.085	0.280
0.67	1.090	0.055	0.412	0.058	0.431
1.00	1.247	0.198	0.802	0.147	0.596
1.50	1.299	0.345	1.732	0.152	0.761
4.00	1.820	1.802	8.791	0.193	0.942
9.00	1.911	4.290	42.386	0.100	0.987

$X=M_1/M_2$; $Y=dM_1/dM_2$; $G=X(Y-1)/Y$; $F=X^2/Y$;
$\eta=G/(\alpha+F)$; $\xi=F/(\alpha+F)$; $\alpha=$constant.

Table IV. Analysis of copolymerization data
for the 2CMI(M_1)–VAC(M_2) system in dioxane
at 70°C, $[M_1]+[M_2]=2.5$ mol l^{-1}
by the F–R and K–T methods

x	Y	G	F	η	ξ
				$\alpha=0.088$	
0.052	0.754	−0.017	0.004	−0.185	0.043
0.11	1.013	0.001	0.012	0.010	0.120
0.25	1.183	0.039	0.053	0.277	0.376
0.43	1.421	0.127	0.13	0.583	0.596
0.67	1.562	0.241	0.287	0.643	0.765
1.00	1.922	0.480	0.520	0.789	0.855
1.50	2.44	0.885	0.922	0.876	0.913
2.33	2.799	1.498	1.939	0.739	0.957
4.00	3.257	2.772	4.912	0.550	0.975
9.00	25.316	8.644	3.222	2.582	0.973

$X=M_1/M_2$; $Y=dM_1/dM_2$; $G=X(Y-1)/Y$; $F=X^2/Y$;
$\eta=G/(\alpha+F)$; $\xi=F/(\alpha+F)$; $\alpha=$constant.

cording to Fineman–Ross and Kelen–Tüdos methods for the system *N*-2-chlorophenyl-maleimide (m_1)/vinyl acetate (m_2) (2CMI/VAC) in dioxane for total monomer concentrations of 1.0 and 2.5 mol l^{-1} are summarized in Tables I—IV, respectively. The reactivity ratios r_1 and r_2 were calculated from the data in Tables III and IV and Figures 1a and 1b as 0.229, 0.025 and 0.75, 0.027 for the 1.0 and 2.5

mol l^{-1}, respectively. The theoretical curves in Figure 2 were constructed using these values of r_1 and r_2, the points being experimental data. The shape of the copolymer composition curves differed significantly between the two different concentrations, indicating the effect of dilution on the present system.

The above results, which deviate from the

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Table V. 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 VAC(M_1)–2CMI(M_2) system in dioxane at 70°C

$x =$ $[M_2]/[M_1]$	Total monomer concentration mol l^{-1}	$[M_1] =$ [VAC] mol l^{-1}	$R_p \times 10^3$ mol l^{-1}	$R_p/[M_1] \times 10^3$ min^{-1}
9.0	2.0	0.2	0.955	4.78
	1.0	0.1	0.275	2.75
	0.5	0.05	0.083	1.66
4.0	2.0	0.4	1.32	3.30
	1.0	0.2	0.38	3.90
	0.5	0.1	0.105	1.05
2.33	2.0	0.6	1.66	2.77
	1.0	0.3	0.479	1.596
	0.5	0.15	0.132	0.88
1.50	2.0	0.8	1.995	2.494
	1.0	0.4	0.631	1.578
	0.5	0.2	0.190	0.95
1.00	2.0	1.0	1.77	1.77
	1.0	0.5	0.767	1.53
	0.5	0.25	0.20	0.80
0.66	2.0	1.2	1.25	1.04
	1.0	0.6	0.714	1.19
	0.5	0.30	0.207	0.69
0.43	2.0	1.4	1.38	0.986
	1.0	0.7	0.479	0.684
	0.5	0.35	0.162	0.462
0.25	2.0	1.6	1.202	0.751
	1.0	0.8	0.363	0.454
	0.5	0.4	0.126	0.315
0.11	2.0	1.8	1.05	0.583
	1.0	0.9	0.26	0.292
	0.5	0.45	0.094	0.222

Table VI. 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 VAC(M_1)–2CMI(M_2) system in THF at 60°C

$x =$ $[M_2]/[M_1]$	Total monomer concentration mol l^{-1}	$[M_1] =$ [VAC] mol l^{-1}	$R_p \times 10^3$ mol l^{-1}	$R_p/[M_1] \times 10^3$ min^{-1}
9.0	2.0	0.2	1.148	5.74
	1.0	0.1	0.479	4.79
	0.5	0.05	0.200	4.00
4.0	2.0	0.4	1.500	3.75
	1.0	0.2	0.575	2.87
	0.5	0.1	0.250	2.50
2.33	2.0	0.6	1.739	2.89
	1.0	0.3	0.631	2.10
	0.5	0.15	0.267	1.78
1.50	2.0	0.8	2.500	3.12
	1.0	0.4	0.724	1.81
	0.5	0.2	0.300	1.50
1.00	2.0	1.0	2.307	2.30
	1.0	0.5	0.871	1.74
	0.5	0.25	0.312	1.24
0.66	2.0	1.2	2.142	1.78
	1.0	0.6	0.724	1.20
	0.5	0.3	0.344	1.14
0.43	2.0	1.4	1.905	1.36
	1.0	0.7	0.603	0.86
	0.5	0.35	0.316	0.90
0.25	2.0	1.6	1.660	1.03
	1.0	0.8	0.437	0.54
	0.5	0.4	0.267	0.66
0.11	2.0	1.8	1.111	0.61
	1.0	0.9	0.355	0.39
	0.5	0.45	0.190	0.42

simple terminal model for the copolymerization system in which the reactivity ratios should be independent of the toral monomer concentration, indicate that a kind of molecular interactions plays an important role in the present copolymerization system. The en-

hanced reactivity of 2CMI with an increase in the total monomer concentration may indicate the participation of the charge-transfer complex (CTC) in the copolymerization on increasing the concentration of the reactive species. This CTC is more reactive than either
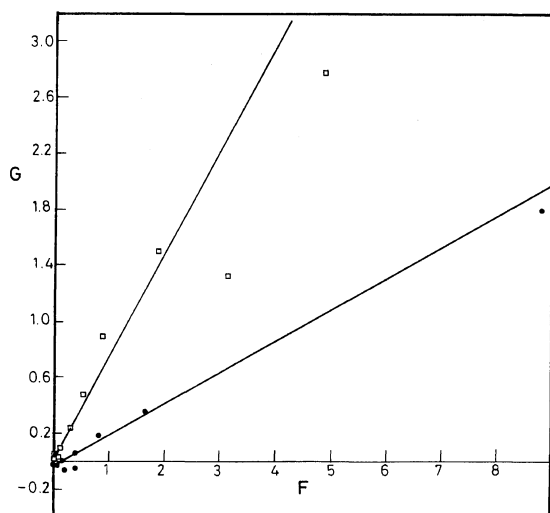
Figure 1a. Fineman and Ross plots for 2CMI(M_1)–VAC (M_2) with different total monomer concentration. ●, [M]=1 mol l^{-1}; □, [M]=2.5 mol l^{-1}.

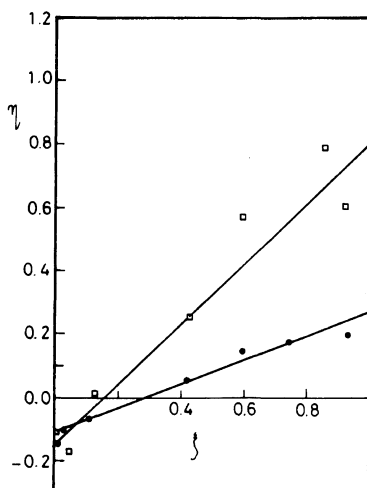**Figure 1b.** Kelen–Tüdos plots for the same systems as in Figure 1a.

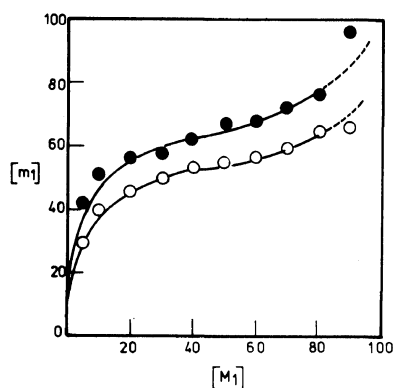**Figure 2.** Diagram for copolymerization of 2CMI with VAC in dioxane at 70°C. AIBN=1 mol%; ○, $[M_1]+[M_2]=1$ mol l^{-1}; ●, $[M_1]+[M_2]=2.5$ mol l^{-1}.

of the two monomers. However, another possibility exists from the interaction of 2CMI with the solvent itself (dioxane) to produce a weak complex[1] with relatively higher reactivity than the maleimide alone. The distinction between the two mechanisms is almost impossible since in both cases we cannot isolate any complexes. However, indirect evidence for the

participation of CTC in the copolymerization can be obtained by applying the equations proposed by Shirota et al.,[10,11] to the present system, since the reactivity ratios in all cases are <1. Moreover, the product of reactivity ratios indicates the tendency of the two monomers to alternate along the macromolecular chains, being $r_1 r_2 = 0.0057$ for the 1.0 mol l^{-1} and $r_1 r_2 = 0.0202$ for the 2.5 mol l^{-1}.

The overall initial copolymerization rate R_p for the system 2CMI/VAC in two solvents, dioxane and tetrahydrofuran (THF), 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 varied from 0.5 to 1.0 and 2.0 mol l^{-1}. M_1 stands for VAC and M_2 for 2CMI. The data obtained for this system are listed in Tables V and VI. The plot of $R_p/[M_1]$ vs. $[M_1]$ corresponding to eq 1, was found to show good linearity for each given monomer feed ratio x as shown in Figures 3 and 4.

$$R_p/[M_1] = A(x) \cdot K \left(\frac{k_{1C}}{k_{12}} + \frac{k_{2C}}{k_{21}} x \right)[M_1] + A(x)$$

(1)

Thus one can analyze quantitatively the degree of participation of the free monomer and the CTC in the copolymerization. The values of
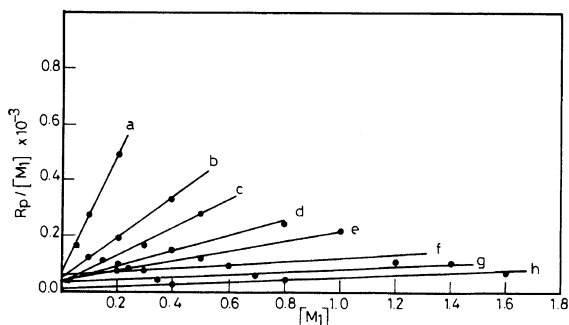
Figure 3. Plots of $R_p/[M_1]$ vs. $[M_1]$ for the system VAC–2CMI in dioxane at 70°C. The letters correspond to different values of $[M_2]/[M_1]=x$: a) -9; b) -4; c) -2.33; d) -1.5; f) -0.666; g) -0.425; h) -0.25; i) -0.111.
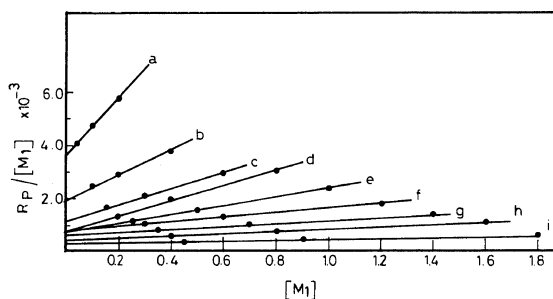

Figure 4. Plots of $R_p/[M_1]$ vs. $[M_1]$ for the VAC–2CMI system in THF at 60°C for different values of $X=[M_2]/[M_1]$.

$A(x)$ and $A(x)K(k_{1C}/k_{12}+X(k_{2C}/k_{21}))$ were obtained for each given monomer feed ratio from the intercept and slope of the linear plot. The least-squares method was used to obtain these values. The results are summarized in Tables VII and VIII, by introducing these values into eq 2 and 3, respectively.

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

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

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

Table VII. 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 VAC(M$_1$)–2CMI(M$_2$) system in dioxane at 70°C

$x=$ $[M_2]/[M_1]$	$A(x)\times$ 10^4	$A(x)K(K_{1c}/K_{12}+$ $x(K_{2c}/K_{21}))\times 10^{-3}$	$F(x)$	Confidence coefficient
9.0	6.45	20.70	32.10	
4.0	3.50	7.4	21.14	0.998
2.33	2.90	4.15	14.34	0.998
1.50	4.94	2.52	5.10	0.996
1.00	6.80	1.17	1.731	0.880
0.666	7.65	0.297	—[a]	0.50
0.428	3.11	0.489	1.573	0.995
0.250	1.66	0.364	2.195	0.999
0.111	0.765	0.0765	1.00	0.988

[a] Highly uncertain value.
Intercept of $F(x)$ vs. $x = K(K_{1c}/K_{12}) = 1.230$ ($x = 0.66$ was omitted from the least square).
Slope of $F(x)$ vs. $x = K(K_{2c}/K_{21}) = 3.72$.

Table VIII. 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 VAC(M$_1$)–2CMI(M$_2$) system in THF at 60°C

$x=$ $[M_2]/[M_1]$	$A(x)\times$ 10^3	$A(x)K(K_{1c}/K_{12}+$ $x(K_{2c}/K_{21}))\times 10^{-3}$	$F(x)$	Confidence coefficient
9.0	3.52	11.3	3.21	0.99
4.0	2.06	4.2	2.038	0.999
2.33	1.14	2.77	2.429	0.971
1.50	0.485	2.78	3.28	0.988
1.00	0.96	1.37	1.427	0.987
0.666	0.86	0.74	0.860	0.969
0.428	0.65	0.477	0.733	0.918
0.25	0.42	0.337	0.802	0.85
0.111	0.31	0.155	0.50	0.898

[a] Intercept of $F(x)$ vs. $x = 0.441 = K(K_{1c}/K_{12})$.
Slope of $F(x)$ vs. $x = 1.10 = K(K_{2c}/K_{21})$.

charge-transfer complex $R_p(CT)$ for each monomer concentration. Figures 5 and 6 show 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 of the three total mono-
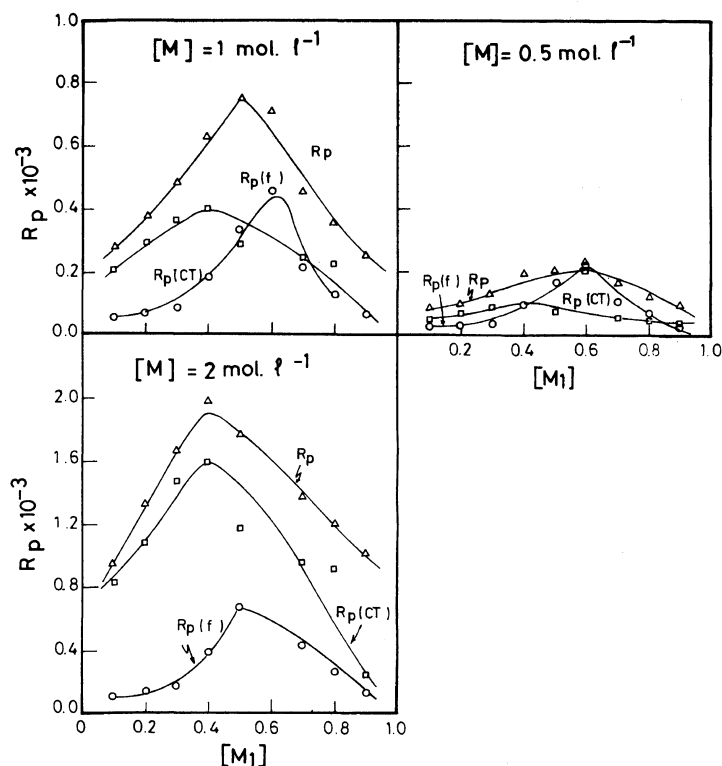
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Figure 5. Quantitative separation of the overall initial copolymerization ratè R_p into the reaction rates of the free monomer $R_p(f)$ and charge-transfer complex $R_p(CT)$ as a function of the monomer feed ratio for the VAC–2CMI system in dioxane at 70°C. Total monomer concentration varied from 0.5 to 2 mol l^{-1}.

Table IX. Quantitative separation of the overall initial copolymerization rate R_p into the reaction rates of the free monomer $R_p(f)$ and charge-transfer complex $R_p(CT)$ as a function of the monomer feed molar ratio x at the total monomer concentration of 2 for the VAC(M_1)–2CMI(M_2) system in dioxane at 70°C.

| $x =$ $[M_2]/[M_1]$	$[R_p(f)] \times 10^4$ mol l^{-1} min^{-1}	$[R_p(CT)] \times 10^4$ mol l^{-1} min^{-1}	$\dfrac{R_p(CT)}{R_p(f)}$
9	1.29	8.00	6.20
4	1.40	11.80	8.40
2.33	1.74	14.76	8.40
1.50	3.96	16.12	4.10
1.00	6.90	11.70	1.70
0.666	9.18	4.27	0.465
0.428	4.35	9.58	2.20
0.250	2.65	9.31	3.50
0.111	1.37	2.47	1.80

Table X. Quantitative separation of the overall initial copolymerization rate R_p into the reaction rates of the free monomer $R_p(f)$ and charge-transfer complex $R_p(CT)$ as a function of the monomer feed molar ratio x at the total monomer concentration of 2.0; for the VAC(M_1)–2CMI(M_2) system in THF at 60°C

$x =$ $[M_2]/[M_1]$	$R_p(f)$ $\times 10^4$	$R_p(CT)$ $\times 10^4$	$\dfrac{R_p(CT)}{R_p(f)}$
9	7.04	4.52	0.64
4	8.24	6.72	0.81
2.33	6.84	9.97	1.45
1.5	6.76	17.79	2.50
1.0	9.6	13.70	1.40
0.666	11.52	10.62	0.92
0.428	9.1	9.30	1.00
0.25	6.72	8.62	1.20
0.111	5.58	5.00	0.89
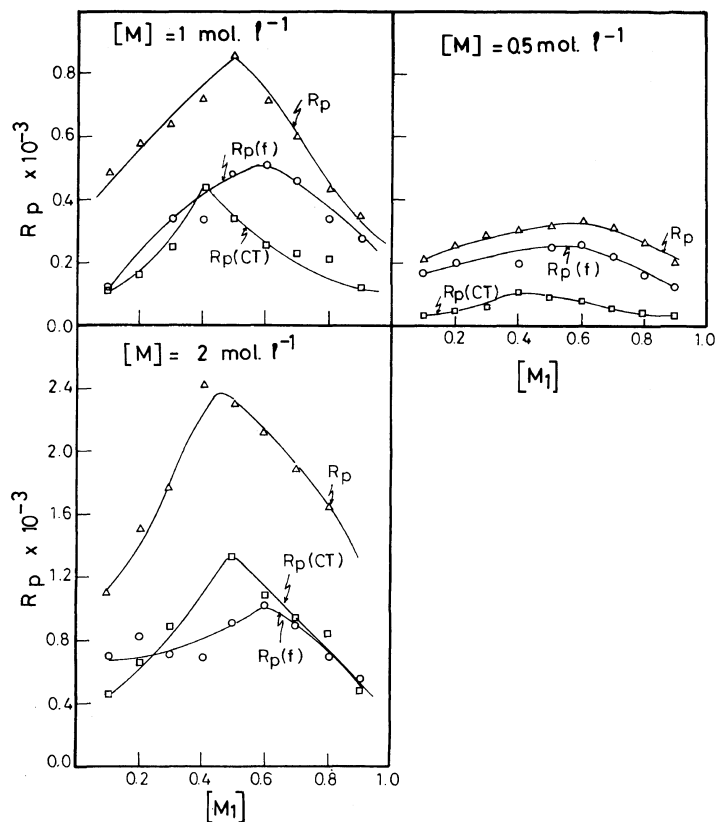
Figure 6. Quantitative separation of the overall initial copolymerization rate R_p into the reaction rates of the free monomer $R_p(f)$ and charge-transfer complex $R_p(CT)$ as a function of the monomer feed ratio for the system VAC–2CMI in THF at 60°C. Total monomer concentration varied from 0.5 to 2.0 mol l^{-1}.

mer concentrations. Tables IX and X contain some of these calculations for the total monomer concentration of 2 mol l^{-1}.

Estimation of the Relative Reactivity of the Charge-Transfer Complex to the Free Monomer

In our previous work,[12] it was found that the rate of polymerization of 2CMI changed greatly according to the type of solvent, being 1.2×10^{-4} mol l^{-1} s^{-1} and 4.63×10^{-4} mol l^{-1} s.$^{-1}$ for dioxane and THF, respectively. This was attributed to the different abilities of the solvent to associate with the monomer. The association of these solvents with the maleimide molecules occurs most probably *via* orbital overlapping with the π-cloud of the

double bond of the maleimide.[13] It is thus evident that participation of the CTC (if present) in the copolymerization is higher in dioxane than in THF, since the ability of THF to associate with the maleimide is greater than that of dioxane. (Figures 5 and 6).

Further analysis regarding the relative reactivity of the CTC to the free monomers toward growing polymer radicals was carried out with the system 2CMI/VAC in the two solvents, dioxane and THF. The value of $K(k_{1C}/k_{12} + X(k_{2C}/k_{21}))$ 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 lines in this figure are drawn by the least-squares method (one
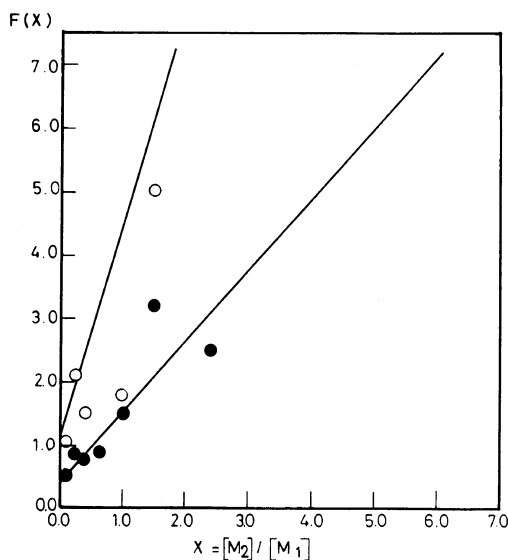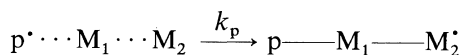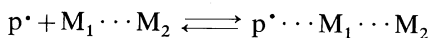
Figure 7. Plots of $F(x)$ *vs.* X for the VAC–2CMI system: ●, in THF; ○, in dioxane.

should note that the confidence of each value of $F(x)$ is not on the same level). 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 $K(k_{1C}/k_{12}) = 1.23$ and $K(k_{2C}/k_{21}) = 3.72$ for dioxane (point at $x = 0.66$ was omitted due to high uncertainty) and 0.441 and 1.10 in THF (points at $x = 0.9$ and 1.5 were omitted due to the much larger probable errors).

These values indicate that the growing maleimide radical is formed more readily than the growing VAC radical. It also indicates that the maleimide radical tends to add the complex rather than a vinyl acetate monomer. This tendency is higher in dioxane than in THF since the concentration of the complex is lower in THF than in dioxane (Figures 5 and 6). We failed to obtain any value for the equilibrium constant K for the formation of the charge-transfer complex of monomers as indicated previously. At this stage, since the overall rate of copolymerization does not follow first order kinetics with respect to the monomer concentration as shown from the application of the equation proposed by Shirota *et al.* to the present system, and since the product of the reactivity ratios of this system indicates a tendency for the alternating copolymerization together with the ability of these electron donor and electron acceptor monomers to form a CTC, one can speculate that the monomer charge-transfer complex participates in the propagation process of the polymerization. There may be the possibility that a double complex is formed between the monomer charge-transfer complex and a growing chain end. The double complex may be expressed as follows:

$$p^{\bullet} + M_1 \cdots M_2 \rightleftharpoons p^{\bullet} \cdots M_1 \cdots M_2$$

$$p^{\bullet} \cdots M_1 \cdots M_2 \xrightarrow{k_p} p \!\!-\!\!\! M_1 \!\!-\!\!\! M_2^{\bullet}$$

In any case, the data indicate that the complex (whatever its nature) has a greater reactivity relative to the free monomer towards the growing polymer radical with the 2CMI end, while toward the growing polymer radical with the VAC end, the reactivity of the complex is not enhanced very much or might be reduced with that of the free monomer.

CONCLUSIONS

1) The reactivity ratios of the 2CMI/VAC system were found to depend on the total monomer concentration.

2) The present system shows a tendency for donor-acceptor interaction between the VAC and 2CMI monomers. This is well illustrated from the deviation of the results from the simple terminal model of the copolymerization and from the fact that the system does not follow first order kinetics with respect to the monomer concentration.

3) The solvent effects the rate of polymerization and degree of complexation, since THF has a higher ability to associate with the maleimide monomer than dioxane, resulting in a decrease in the concentration of the complex in THF.

4) The nature of the monomer interaction is not very clear, since we could not isolate the

complex. It may be a very weak monomer charge-transfer, or double complex between the monomer charge-transfer complex and a growing chain end.

In general, a precise determination of the mechanism of copolymerization will require further analysis of many systems. One interesting system would be styrene–maleimide which is not capable of homopolymerization, e.g., N-4-bromophenylmaleimide or N-4-nitro-phenylmaleimide. Moreover, the value of the equilibrium constant K for the formation of the monomer charge-transfer complex should be determined spectroscopically.

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