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

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To cite this Article Tanaka, Jiro and Yamada, Akira(1983) 'Copolymerization Reactivity and Behavior of N-Vinylimidazole with α,β-Disubstituted Monomers', Journal of Macromolecular Science, Part A, 19: 3, 453 — 471

To link to this Article: DOI: 10.1080/10601328308056527

URL: http://dx.doi.org/10.1080/10601328308056527

J. MACROMOL. SCI.–CHEM., A19(3), pp. 453-471 (1983)

Copolymerization Reactivity and Behavior of N-Vinylimidazole with α,β-Disubstituted Monomers

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ABSTRACT

The copolymerization of N-vinylimidazole (NVIm) with 11 different comonomers was investigated. The monomer reactivity ratios of each copolymerization system were determined by the Kelen-Tüdös method illustrated in the copolymerization diagrams. Those values were more reliable than those determined by the Fineman-Ross method. Alfrey-Price's Q and e values for NVIm were given as 0.128 ± 0.003 and -0.879 ± 0.038, respectively, from NVIm-styrene and NVIm-methyl methacrylate systems. Those copolymerization parameters suggest that the reactivity of NVIm for the growing radical of the comonomer was proportional to the Hammett's para-substituent constant for substituent of the comonomer and that alkyl fumarates were more reactive than alkyl maleates in copolymerization with NVIm. Although the charge transfer (CT) interaction between NVIm and comonomers with e values greater than 1.8 was observed by the spectroscopic "continuous variation method," the CT alternating

0022-233X/83/1903-0453$3.50/0

copolymerization mechanism cannot be utilized in this study, as explained in the discussion of the run number, as an index of the alternating tendency, the copolymer composition, and the rate of copolymerization.

INTRODUCTION

Studies on synthetic polymers which show enzyme-like catalytic activity are getting much attention in the life science field [1]. With this in view, the imidazole-containing compounds, which are key chemical species [2] in all living creatures, are worthy of notice in the polymeric catalyst design field. N-Vinylimidazole (NVIm) was selected for the above reasons.

In this study the copolymerization reactivity of NVIm was investigated in order to synthesize alternating and random copolymer catalysts containing NVIm. Although there are studies [3-7] on the copolymerization of substituted NVIm with some comonomers, the copolymerization reactivity of NVIm has not been investigated systematically heretofore and there are no reports [8] vis-a-vis its copolymerization parameters. Therefore, the copolymerization of NVIm with styrene (St) and methyl methacrylate (MMA) was carried out in order to determine the copolymerization parameters of NVIm. The copolymerization of NVIm with α,β-disubstituted monomers was examined in order to increase the functionality of the copolymer catalyst from the viewpoint of its polymer design. By evaluating the results of the sequence control in the copolymerization of NVIm with α,β-disubstituted monomers, the copolymerization conditions for the alternating copolymer are made clear.

EXPERIMENTAL

Chemicals

NVIm from BASF was purified by distillation (bp 48.0°C/3 mmHg, purity above 99.5%). The other monomers were purified according to normal procedure before use. Those purities were more than 99.5% confirmed by gas chromatography or spectroscopy. All solvents were purified by distillation. α,α'-Azobisisobutyronitrile used as an initiator was recrystallized from methyl alcohol.

Copolymerization

Known amounts of freshly purified monomers, initiator, and solvent were placed in a Pyrex ampule. After complete evacuation by a freeze-thaw technique, the ampule was sealed under reduced pressure.

Copolymerization was then carried out at 60 ± 0.02°C until conversion reached 5%. The copolymers of NVIm were precipitated in a suitable nonsolvent, and the copolymers having carboxyl groups were purified three times in a solution of distilled water poured into acetone. The copolymers of NVIm with α,β-disubstituted comonomers were purified similarly from a corresponding alcohol solution of the alkyl group of comonomers into diethyl ether. The copolymer containing St was precipitated in a mixed solvent of n-hexane/diethyl ether and purified three times by precipitation from a toluene/methyl alcohol solution poured into the n-hexane/diethyl ether solvent. Since there is no solvent for dissolving the copolymers of NVIm with acrylonitrile (AN) and maleic acid (MA), the former was purified by washing in acetone repeatedly and the latter was dissolved in 3% aqueous NH_4OH and then dialyzed using Seamless Cellulose Tubing (pore size: 24 Å, Union Carbide Co.) in running distilled water for 1 week and then the copolymer solution was freezedried. The copolymer composition (molar fraction of monomeric unit) was determined by N analysis. The copolymer composition of NVIm with AN was determined by the intensity of IR absorption due to the nitrile groups in AN units.

Measurements

In order to study and determine the composition of charge-transfer (CT) complexes between NVIm and acceptors (M_2), ultraviolet and visible spectra were measured with a Varian Cary-14 spectrophotometer using a continuous variation method [9] utilizing a 1-cm quartz cell with $[NVIm] + [M_2] = 0.1$ mol/L at room temperature.

The number-average molecular weight ($\overline{M}_n$) of the copolymers was determined by the VPO method.

RESULTS AND DISCUSSION

Copolymerization Results

In order to study the reactivity and behavior of NVIm, the copolymerization of NVIm with 11 different comonomers with a wide e-value range was investigated. Copolymerization was stopped at low conversion (less than 5%), i.e., at the initial stage of copolymerization. The apparent rate constant of copolymerization (R_p*) is calculated on the basis of the concentration of monomer feed, conversion, and copolymerization time. All the copolymerization results including the copolymer composition (molar fraction of M_2 in the copolymer: $[M_2]_p$), are summarized in Table 1.

R_p* was low compared to the apparent rate constant of homopolymerization of NVIm ($R_p^* = 2.0 \times 10^{-5}$ mol/L/s). The average

TABLE 1. Copolymerization of NVIm (M_1) with Comonomer (M_2)

	Comonomer			Copolymerization		Copolymer		
No.	M_2	e_2[a]	$[M_2]_f$	Conversion (wt/wt%)	R_p* (mol/L/s)[b]	N (%)	$[M_2]_p$	$\overline{M}_n$
1	Styrene	-0.80	0.100_3	2.8	2.3×10^{-5}	16.07	0.402_4	8360
			0.200_5	2.7	2.4×10^{-5}	8.99	0.657_0	
			0.300_4	2.2	2.2×10^{-5}	5.78	0.776_8	
			0.399_5	1.2	2.3×10^{-5}	3.74	0.854_5	
			0.499_9	3.2	3.5×10^{-5}	2.79	0.888_0	
			0.599_7	2.2	4.0×10^{-5}	1.96	0.923_2	
			0.700_1	1.6	2.9×10^{-5}	1.32	0.948_2	
			0.799_8	1.5	3.6×10^{-5}	0.98	0.961_5	
			0.899_6	1.9	5.7×10^{-5}	0.55	0.978_3	
2	Methyl methacrylate	0.40	0.072_1	1.0	0.8×10^{-5}	13.35	0.508_5	-
			0.247_8	0.7	0.7×10^{-5}	9.81	0.636_0	
			0.356_6	0.5	0.6×10^{-5}	7.53	0.719_2	
			0.497_2	0.5	0.5×10^{-5}	4.72	0.822_9	
			0.640_2	1.2	1.3×10^{-5}	3.28	0.876_5	
			0.748_6	1.6	1.6×10^{-5}	2.14	0.919_2	

			0.847_6	3.4	3.6×10^{-5}	1.26	0.952_3	
			0.925_8	2.4	2.5×10^{-5}	0.43	0.983_7	
3	Methacrylic acid	0.65	0.075_2	0.9	0.8×10^{-5}	17.17	0.409_1	
			0.147_6	1.6	1.7×10^{-5}	14.99	0.487_7	5520
			0.244_7	3.3	2.5×10^{-5}	12.99	0.569_1	
			0.503_9	2.3	1.4×10^{-5}	7.29	0.723_5	
			0.751_4	4.9	3.7×10^{-5}	4.93	0.836_7	
			0.846_1	1.4	1.2×10^{-5}	3.21	0.894_3	
			0.928_7	1.8	2.3×10^{-5}	1.63	0.946_6	
4	Acrylic acid	0.77	0.125_4	3.1	4.3×10^{-5}	17.37	0.445_3	4340
			0.249_4	4.2	6.3×10^{-5}	14.36	0.554_5	
			0.375_3	2.4	7.3×10^{-5}	11.85	0.640_9	
			0.499_0	2.5	5.2×10^{-5}	8.52	0.749_6	
			0.625_6	8.4	25.3×10^{-5}	6.74	0.804_9	
			0.749_8	5.3	19.7×10^{-5}	4.64	0.868_2	
			0.873_5	3.8	14.1×10^{-5}	2.52	0.929_6	
5	Acrylonitrile	1.20	0.068_8	3.4	0.2×10^{-5}	(27.64)	0.438	-
			0.150_4	3.9	0.2×10^{-5}	(27.41)	0.638	
			0.247_7	4.2	4.0×10^{-5}	(27.03)	0.673	

(continued)

TABLE 1 (continued)

	Comonomer			Copolymerization		Copolymer		
No.	M_2	e_2 [a]	$[M_2]_f$	Conversion (wt/wt%)	R_p* (mol/L/s)[b]	N (%)	$[M_2]_p$	$\overline{M}_n$
			0.748_4	6.3	5.5×10^{-5}	(26.61)	0.917	
			0.851_4	1.4	1.0×10^{-5}	(26.49)	0.964	
			0.926_8	4.2	5.0×10^{-5}	(26.38)	0.977	
6	Diethyl fumarate	1.25	0.070_6	3.4	9.9×10^{-6}	12.70	0.397_7	
			0.151_2	4.5	7.3×10^{-6}	10.63	0.472_4	
			0.251_0	5.8	7.5×10^{-6}	9.40	0.520_2	8390
			0.501_3	23.0	-	8.11	0.573_3	
			0.747_0	26.5	7.7×10^{-6}	6.93	0.624_8	
			0.841_4	2.5	0.1×10^{-6}	6.29	0.654_0	
7	Dimethyl maleate	1.27	0.070_0	1.0	2.0×10^{-6}	21.97	0.152_9	
			0.151_6	1.6	3.2×10^{-6}	19.68	0.217_3	
			0.247_6	1.1	3.2×10^{-6}	17.21	0.291_3	
			0.500_5	7.1	2.6×10^{-6}	13.79	0.403_0	
			0.747_8	0.8	0.3×10^{-6}	10.51	0.521_4	7440
			0.849_9	5.3	0.4×10^{-6}	9.73	0.551_4	
			0.932_5	3.9	0.2×10^{-6}	8.71	0.591_8	

8	Dimethyl fumarate	1.49	0.067_9	5.4	1.2×10^{-7}	13.84	0.401_3	
			0.151_8	4.0	0.3×10^{-7}	11.14	0.497_7	2090
			0.251_4	5.3	5.8×10^{-7}	10.80	0.510_4	
			0.498_7	4.4	5.3×10^{-7}	8.98	0.580_9	
			0.741_8	1.7	1.6×10^{-7}	7.69	0.633_5	
			0.850_7	1.8	0.2×10^{-7}	6.99	0.663_0	
			0.929_5	Trace	-	-	-	
9	Diethyl maleate	1.49	0.072_0	0.9	14.7×10^{-6}	17.50	0.247_8	
			0.150_0	3.1	1.0×10^{-6}	14.54	0.336_7	
			0.263_5	12.1	3.9×10^{-6}	12.00	0.422_2	
			0.496_0	13.3	0.2×10^{-6}	9.65	0.510_3	5730
			0.754_1	0.8	0.1×10^{-7}	8.32	0.568_2	
			0.929_4	1.3	0.1×10^{-6}	6.01	0.667_1	
10	Fumaric acid	1.87	0.070_5	1.8	2.0×10^{-7}	14.03	0.446_8	
			0.149_4	1.2	1.4×10^{-7}	12.61	0.496_7	1770
			0.249_2	2.0	0.7×10^{-7}	11.78	0.528_2	
			0.500_2	2.1	1.0×10^{-7}	10.59	0.570_5	
			0.752_7	1.6	0.7×10^{-7}	8.61	0.646_7	
11	Maleic acid	2.60	0.072_4	1.8	7.6×10^{-7}	15.06	0.411_4	

(continued)

TABLE 1 (continued)

	Comonomer			Copolymerization		Copolymer		
No.	M_2	e_2[a]	$[M_2]_f$	Conversion (wt/wt%)	R_p^* (mol/L/s)[b]	N (%)	$[M_2]_p$	$\overline{M}_n$
			0.130_2	3.8	17.4×10^{-7}	13.36	0.470_1	
			0.251_4	1.2	18.7×10^{-7}	12.91	0.487_3	
			0.402_7	1.0	6.5×10^{-7}	12.93	0.486_6	
			0.541_8	3.6	20.7×10^{-7}	12.30	0.509_3	1860
			0.749_2	1.1	4.0×10^{-7}	10.79	0.564_6	
			0.856_2	0.9	2.2×10^{-7}	9.97	0.595_1	
			0.921_5	1.2	3.3×10^{-7}	7.56	0.687_2	

[a] Polymer Handbook [8].

[b] The apparent rate of copolymerization.

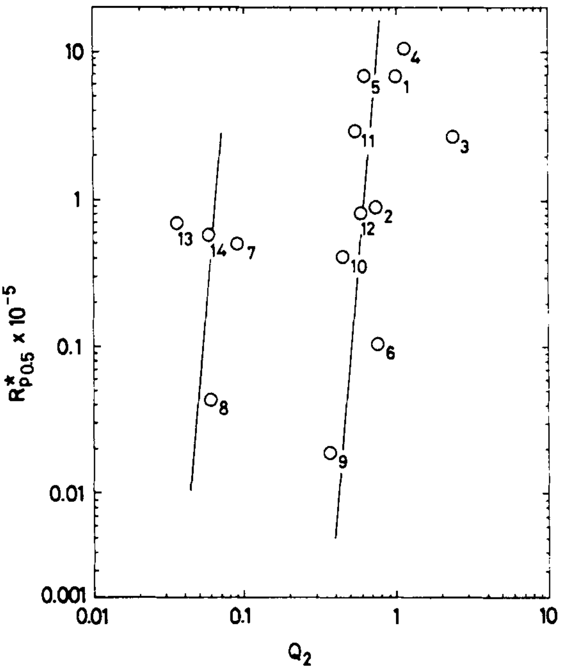

FIG. 1. Logarithmic relationship between R_p* at $[M_2]_p$ = 0.5($R^*_{p0.5}$) and Q value of comonomers (Q_2). (1) Styrene, (2) methyl methacrylate, (3) methacrylic acid, (4) acrylic acid, (5) diethyl fumarate, (6) dimethyl fumarate, (7) dimethyl maleate, (8) diethyl maleate, (9) fumaric acid, (10) maleic acid, (11) dipropyl fumarate, (12) dibutyl fumarate, (13) dipropyl maleate, (14) dibutyl maleate.

molecular weight of the copolymers of NVIm was also low. Those results seem to be induced by the chain transfer reaction in a propagation step.

R_p* at $[M_2]_p$ = 0.5, denoted by $R^*_{p0.5}$, in each copolymerization system is related to the Q_2 value of comonomer (M_2) on a full logarithmic scale as shown in Fig. 1.

The Q value can be viewed as a term of monomer reactivity in Alfrey-Price's Q-e scheme [10, 11]. The rate constant (k_{12}) for the reaction of growing NVIm radical ($\sim\dot{M}_1$*) with comonomer (M_2) is given by

$$\ln k_{12} = \ln P_1 + \ln Q_2 - e_1 e_2 \quad (1)$$

Thus there is some meaning in the proportional expression between ln $R^*_{p0.5}$ and ln Q, as shown in Fig. 1, although $R_p{}^*$ contains other rate terms such as k_{11}, k_{12}, and k_{22}. As shown in Fig. 1, only a series of copolymerization systems of NVIm with dialkyl maleates shows specific copolymerization behavior. If the Q_2 values reported for dialkyl maleates [8] are correct, the respective $R^*_{p0.5}$ values would be extremely small. However, $R^*_{p0.5}$ for dialkyl maleates are 10^{-6}-10^{-7} times greater than might be expected. The above results indicate that some interaction forces between NVIm and dialkyl maleates should accelerate the copolymerization reaction. Unfortunately, such interactions could not be found in the measurement by the spectroscopic "continuous variation method" as described below.

Monomer Reactivity Ratios of NVIm

The monomer reactivity ratios (r_1 and r_2) of each copolymerization system were determined from the copolymerization results ($[M_2]_f$, which is the molar fraction of M_2 in feed, and $[M_2]_p$) as shown in Table 1, using the linear graphic method (KT method, Eq. 2) proposed by Kelen and Tüdös [12], as follows:

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \tag{2}$$

where

$$\eta = G/(\alpha + H), \qquad \xi = H/(\alpha + H)$$

$$G = F(f - 1)/f, \qquad H = F^2/f, \qquad \alpha = \sqrt{H_{max}H_{min}}$$

$$F = [M_1]_f/[M_2]_f, \qquad f = [M_1]_p/[M_2]_p$$

To determine the r_1 and r_2 values, the Fineman-Ross method (FR method, Eq. 3) [13] was used:

$$G = Hr_1 - r_2 \tag{3}$$

The copolymerization results by the KT and FR methods are shown in Fig. 2 for the following typical copolymerization systems: (1) NVIm-St as the standard monomer in the Q-e scheme, (2) NVIm-MMA as the monomer that can be copolymerized with some N-vinyl

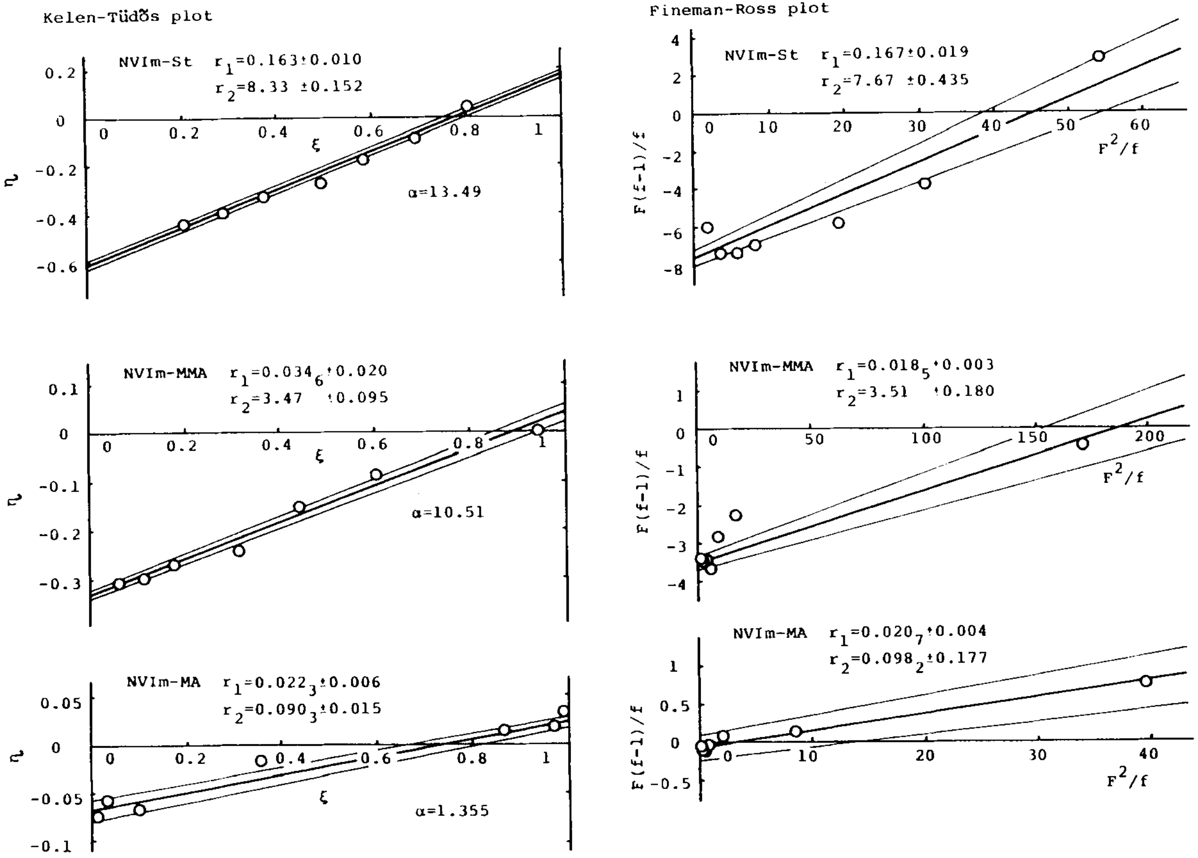

FIG. 2. Kelen-Tüdős plot and Fineman-Ross plot for the copolymerization of NVIm with comonomers.

monomers, and (3) NVIm-MA as the system that can give the most highly alternating copolymer.

In Fig. 2 the solid lines, which gave the most probable r_1 and r_2, were obtained by the least mean square method. The two fine lines on either side of the solid were obtained similarly and the width of the two fine lines denotes the range of the probable errors. The KT equation (Eq. 2) can be derived from the FR equation (Eq. 3) in order to represent graphically the homogeneous distribution of the experimental points in the region of ξ = 0-1, utilizing an appropriate α value. Therefore, the two fine lines in Fig. 2 which are calculated by the least mean square method agree well with the lines which would be drawn by eye estimation. The monomer reactivity ratios calculated by the two methods are shown in Table 2.

The r_1 and r_2 values derived by two methods based on the experimental results should agree with each other within normal errors. However, with copolymerization systems where $r_1 \gg r_2$ (or $r_1 \ll r_2$), the KT method presents more probable r_1 and r_2 than does the FR method.

Q and e Values of NVIm

The Q and e values of NVIm can be calculated from the monomer reactivity ratios in the copolymerization with St which in the standard monomer in the Q-e scheme. Unfortunately, the Q and e values of NVIm could not be derived from the monomer reactivity ratios in the copolymerization with St because the product of r_1 and r_2 was greater than 1 as shown in Table 2. This being the case, the copolymerization of NVIm was carried out with MMA which can be copolymerized with a number of N-vinyl monomer [8] and which has reliable Q and e values. The Q and e values of NVIm were obtained using Eqs. (4) and (5) based on the monomer reactivity ratios from the copolymerization of NVIm with St and MMA:

$$r_1 = Q_1/Q_2 \exp[-e_1(e_1 - e_2)] \tag{4}$$

$$r_3 = Q_3/Q_2 \exp[-e_3(e_3 - e_2)] \tag{5}$$

The subscript numbers in Eqs. (4) and (5) correspond to the following monomers: M_1, St; M_2, NVIm; and M_3, MMA. Consequently, Q and e values of NVIm were evaluated to be 0.128 ± 0.003 and -0.879 ± 0.038, respectively. These values are shown in Table 3 with those for the other N-vinyl monomers [8].

It is known that the e value of the vinyl monomer is proportional to Hammett's para-substituent constants (σ_{para}) [14]. Unfortunately,

TABLE 2. Copolymerization Parameters in Copolymerization of NVIm (M_1) with Comonomers (M_2)

Comonomer				Copolymerization reactivity ratios			
		Q and e values[a]		Kelen-Tüdös method		Fineman-Ross method	
No.	M_2	e	Q	r_1	r_2	r_1	r_2
1	Styrene	-0.80	1.00	0.163 ± 0.010	8.33 ± 0.152	0.167 ± 0.019	7.67 ± 0.435
2	Methyl methacrylate	0.40	0.74	0.034_6 ± 0.020	3.47 ± 0.095	0.185 ± 0.003	3.51 ± 0.180
3	Methacrylic acid	0.65	2.34	0.036_5 ± 0.005	1.38 ± 0.038	0.050_2 ± 0.001	1.46 ± 0.053
4	Acrylic acid	0.77	1.15	0.120 ± 0.034	2.04 ± 0.380	0.085_4 ± 0.005	1.92 ± 0.107
5	Acrylonitrile	1.20	0.60	0.012_8 ± 0.030	3.34 ± 0.039	0.018_0 ± 0.009	3.31 ± 2.05
6	Diethyl fumarate	1.25	0.61	0.022_7 ± 0.014	0.229 ± 0.042	0.028_9 ± 0.005	0.308 ± 0.244
7	Dimethyl maleate	1.27	0.090	0.442 ± 0.057	0.117 ± 0.021	0.475 ± 0.090	0.093_3 ± 0.116
8	Dimethyl fumarate	1.49	0.76	0.016_7 ± 0.008	0.252 ± 0.069	0.010_9 ± 0.009	0.277 ± 0.449
9	Diethyl maleate	1.49	0.059	0.145 ± 0.015	0.068_6 ± 0.021	0.161 ± 0.002	0.097_7 ± 0.051
10	Fumaric acid	1.87	0.36	0.012_0 ± 0.006	0.315 ± 0.031	0.020_9 ± 0.003	0.273 ± 0.007
11	Maleic acid	2.60	0.45	0.022_3 ± 0.006	0.090_3 ± 0.015	0.020_7 ± 0.004	0.098_2 ± 0.177

[a] Polymer Handbook [8].

TABLE 3. Q and e Values [8] of N-Vinyl Monomers

Monomer	e	Q
N-Vinylsuccinimide	-0.340	0.130
3-Vinyl-2-oxazolidinone	-0.800	0.057
N-Vinylimidazole[a]	-0.879	0.128
N-Vinyl-2-pyrrolidone	-1.14	0.140
2-Methyl-N-vinylimidazole	-1.30	0.150
N-Vinylcarbazole	-1.40	0.410
2-Phenyl-N-vinylimidazole	-1.50	0.100

[a] This work.

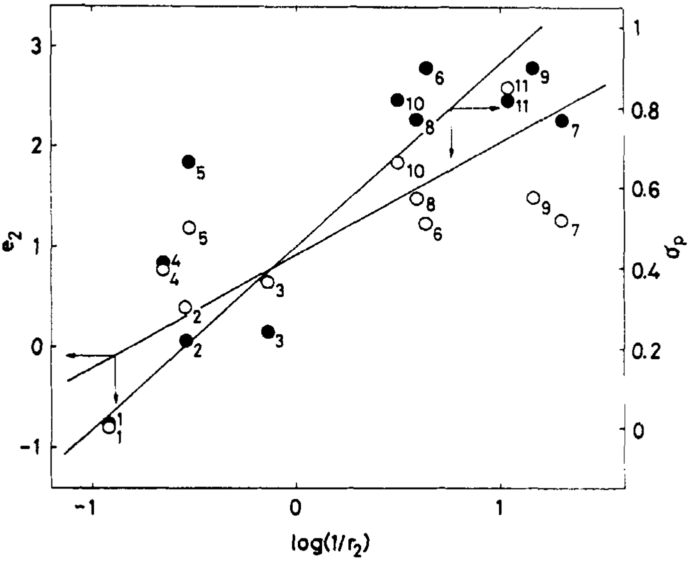

FIG. 3. The relative copolymerization reactivity (log $1/r_2$) of growing terminal radical ($\sim M_2^*$) to NVIm vs e value of comonomers (e_2) and Hammett's para-substituent constants of comonomers (σ_{para}). (1) Styrene, (2) methyl methacrylate, (3) methacrylic acid, (4) acrylic acid, (5) acrylonitrile, (6) diethyl fumarate, (7) dimethyl maleate, (8) dimethyl fumarate, (9) diethyl maleate, (10) fumaric acid, (11) maleic acid.

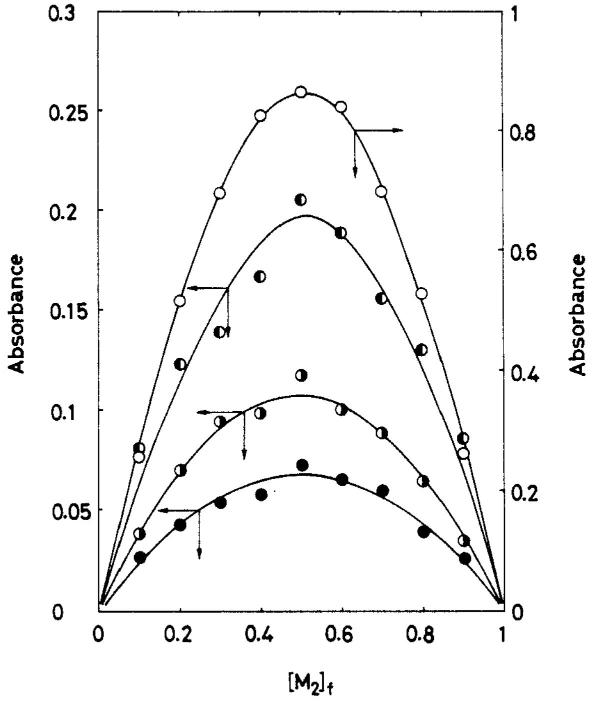

FIG. 4. Continuous variation on the absorption spectra of the charge transfer complexes of NVIm (M_1)-comonomer (M_2): [NVIm + comonomer] = 0.1 mol/L at 23°C. (○) NVIm-MA in THF at 305 nm, (◐) NVIm-Manh in methyl alcohol at 290 nm, (◑) NVIm-FN in benzene at 305 nm, (●) NVIm-FA in THF at 315 nm.

this relationship cannot provide the e value in Table 3 because the respective σ_{para} values are unknown. Only for the N-vinylimidazoles do we find that the e value of NVIm with no substituent (σ_{para} of H = O) is greater than that of 2-methyl-N-vinylimidazole with a methyl substituent (σ_{para} of methyl = -0.17) and 2-phenyl-N-vinylimidazole with a phenyl substituent (σ_{para} of phenyl = -0.01). The result shows that the e value of NVIm is suitable for a series of substituted N-vinylimidazoles.

Copolymerization of NVIm

The copolymerization reactivity of NVIm will be discussed on the basis of the copolymerization parameters in Table 2.

Log $1/r_2$, which can denote the relative copolymerization reactivity of a growing terminal radical of the comonomer ($\sim M_2^*$) to NVIm (M_1), was plotted against the e value of each comonomer as shown in Fig. 3. Simultaneously, log $1/r_2$ in each system was plotted against σ_{para} which corresponds to the substituents of M_2 in Fig. 3.

The relative copolymerization reactivity (log $1/r_2$) is approximately proportional to the values of e_2 and σ_{para}. These values are the indices concerning the electron density at C=C of the comonomer and their large magnitude means a smaller electron density. Thus the results as shown in Fig. 3 denote that the growing chain end ($\sim M_2^*$), having a smaller electron density, reacts strongly to the NVIm (M_1) with the high electron density (as express as $e_1 = -0.879$).

On the other hand, it is known that the reactivity of a trans-monomer is higher than that of a cis-monomer [15]. Table 2 shows that the ratio of r_1 values for MA/FA was 1.8, the dimethyl MA/FA was 26, and the diethyl MA/FA was 6.4. Log $1/r_1$ is representative of the relative copolymerization reactivity of M_2 toward the growing NVIm radical ($\sim$NVIm*), so the smaller r_1 indicates a greater relative copolymerization reactivity of M_2 toward $\sim$NVIm*. Therefore, the relative copolymerization reactivity of fumarates is higher than that of maleates.

Alternating Copolymerization

The CT interaction between two comonomers in the alternating copolymerization system have been observed spectroscopically [16, 17]. Here the CT interaction between NVIm (M_1) and M_2 were demonstrated by the spectroscopic "continuous variation method." The optical density observed at the wavelength assignable to the CT interaction was plotted against the molar fraction of M_2 in the feed (M_1 and M_2) composition as shown in Fig. 4.

The CT interaction with a 1:1 composition between NVIm (M_1) and M_2 [FA, fumaronitrile (FN), maleic anhydride (Manh) and MA] having large e values was observed. The relationship between the maximum optical density for the CT interaction and e_2 of M_2 is illustrated in Fig. 5.

CT absorbance appeared for comonomers with e values greater than 1.8, and the CT absorbance increased steeply with increasing e_2 values. In normal copolymerization a highly alternating sequence

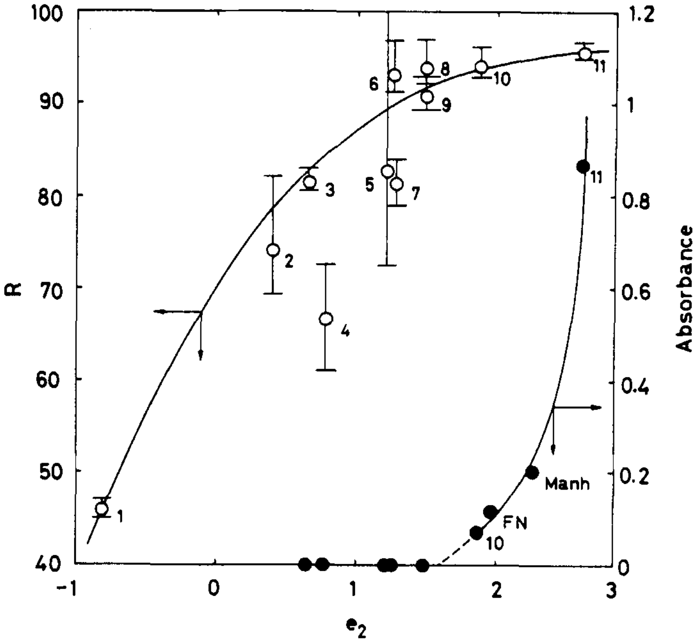

FIG. 5. e Value of comonomers (e_2) vs run number (R: ○) with experimental error and absorbance (●). (1) Styrene, (2) methyl methacrylate, (3) methacrylic acid, (4) acrylic acid, (5) acrylonitrile, (6) diethyl fumarate, (7) dimethyl maleate, (8) dimethyl fumarate, (9) diethyl maleate, (10) fumaric acid, (11) maleic acid.

of copolymers is shown by comonomer combinations having great differences between e values [10, 11], i.e., $e_1 \gg e_2$. Furthermore, when the CT alternating copolymerization mechanism occurs in the copolymerization reaction, a highly alternating sequence in such copolymers results [18]. Generally, the alternating sequence trend in the copolymer can be represented by the run number (R) [19] which is defined from monomer reactivity ratios as

$$R = 200/[2 + r_1([M_1]_f/[M_2]_f) + r_2([M_2]_f/[M_1]_f)] \tag{6}$$

In this study, each R value calculated for each copolymerization result (Table 2) was plotted for the respective e_2 values as shown in Fig. 5. The results show that R values increased with increasing e_2 values, and it is noticeable that the curve does not show any irregular variation near $e_2 = 1.8$ which denotes the critical point of the appearance of CT interaction. R is described in terms of kinetics through monomer reactivity ratios, as in Eq. (6). Therefore, from the results in Fig. 5 it can be concluded that the spectroscopic CT interaction between NVIm and other comonomers does not affect the monomer selectivity at the growing chain end, although some papers have discussed the utilization of the alternating copolymerization mechanism [20-22]. In addition, the fact that the apparent optimum rate of copolymerization does not appear at 1:1 molar fractions of feed monomers explains why this copolymerization system conforms to the normal Bernoullian process of monomer selectivity at the growing chain end.

ACKNOWLEDGMENTS

This study had been done at the Polymer Chemistry Laboratory in the Institute of Physical and Chemical Research. The authors express their thanks to Mr T. Tanno for his helpful discussion.

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Accepted by editor May 14, 1982
Received for publication July 12, 1982