Copolymerization Behavior of N-Vinylimidazole with Various Diaikyl Maleates and Fumarates

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ABSTRACT

N-Vinylimidazole was copolymerized with dialkyl maleates and
fumarates in order to investigative quantitatively the deviation
from the Alfrey-Price Q,e scheme as a function of steric hindrance
or collision frequency. There was no particular correlation ob-
served between deviations from the Alfrey-Price Q,e-scheme of
alkyl maleates (cis isomers) and fumarates (trans isomers) and
the bulkiness of those monomers. The copolymerization reactivi-
ties of these comonomers can be understood by the so-called "col-
lision theory." Maleates were more affected than fumarates in
this regard.

INTRODUCTION

Many observations vis-á-vis the radical copolymerization reactivities of α,β-disubstituted monomers have been gathered [1], and it is well known that the copolymerization reactivities of trans-form monomers are generally higher than those of the cis-form ones [2]. However, no general method to estimate the radical copolymerization reactivities of α,β-disubstituted monomers has been developed through those observations.

The present authors have recently reported on the catalytic hydrolysis of synthetic substrates by alternating and random copolymers containing N-vinylimidazole (NVIm) [3], and there was a certain difference observed between the copolymerization reactivities of cis-form and trans-form monomers [4]. A systematic experimental law to estimate the copolymerization reactivity was not found. In addition to the copolymerization results of NVIm with dimethyl, diethyl maleates, and fumarates in our work [4], the copolymerization parameters of di-n-propyl and di-n-butyl maleates and fumarates with NVIm were also studied. The copolymerization reactivities of cis- and trans-monomers with bulky substituents were discussed, using those parameters, on the basis of Lüssi's treatment [5] which evaluated steric factors on the basis of the Q,e scheme and collision theory [6].

EXPERIMENTAL

Chemicals

NVIm (BASF) was purified by distillation (bp 48.0°C/3 mmHg). Styrene (St) and di-n-butyl maleate and fumarate of chemical grade were purified by distillation (bp 47.0°C/2.6 mmHg, bp 104-107°C/2-3 mmHg, and bp 106-109°C/2-2.5 mmHg, respectively). Di-n-propyl maleate and fumarate were prepared according to accepted methods [6]. These were purified by distillation (bp 85.5-86.5°C/2 mmHg and bp 89.0-91.0°C/2.5 mmHg, respectively). α,α'-Azo-bisisobutyronitrile (AIBN), an initiator, was recrystallized from methyl alcohol.

Copolymerization

Freshly purified monomers, initiator, and toluene were placed in a Pyrex ampule. After evacuation by freeze-drying, the ampule was sealed under reduced pressure. Copolymerization was carried out at 60 ± 0.02°C until the conversion reached 7%. Copolymers of NVIm with alkyl maleates and fumarates were precipitated in n-hexane/diethyl ether solvent and then purified by reprecipitation using

an alcohol solution which corresponded to the alkyl groups of the co-monomers. The copolymers of St were precipitated in n-hexane and then purified by reprecipitation from toluene, as a solvent, with n-hexane. All the copolymer samples were dried in vacuo at room temperature. The copolymer composition $[M_2]_p$, the molar fraction of M_2 monomeric units in the copolymer, was determined by elemental analysis of N and C. The number-average molecular weight $(\overline{M}_n)$ of the copolymers was determined by the VPO method.

RESULTS AND DISCUSSION

NVIm was copolymerized with di-n-propyl and di-n-butyl maleates and fumarates under the same conditions as reported previously [4]. The results are shown in Table 1. The copolymerization results of NVIm with α,β-disubstituted monomers, i.e., dimethyl and diethyl maleates and fumarates, are cited from previous work [4].

The monomer reactivity ratios $(r_1$ and $r_2)$ of each copolymerization were determined by using the Kelen-Tüdós method [8] utilizing copolymerization results ($[M_2]_f$ (the molar fraction of M_2 in feed) and $[M_2]_p$) shown in Table 1. These ratios are shown in Table 2.

Since the copolymerization parameters of di-n-propyl maleate and di-n-propyl and di-n-butyl fumarates are not reported, St was copolymerized with these comonomers under the same conditions in order to determine the copolymerization parameters and to ascertain the reliability of the copolymerization results of NVIm with these comonomers. These monomer reactivity ratios are also shown in Table 2.

Since the stabilities of the activated intermediates of cis-isomers are, in general, less than those trans-isomers because of steric hindrance between the two ester groups in cis-isomers, the copolymerization reactivities of cis-isomers are lower than those of trans-isomers [2]. However, the relationship between the bulkiness of the ester groups of both cis- and trans-isomers and the copolymerization reactivities of these monomers has not been investigated systematically.

The monomer reactivity ratios (r_1) obtained from the copolymerization of NVIm (M_1) with maleates (cis-isomers: M_2) and fumarates (trans-isomers: M_2) and the reported r_1 [4, 9] and their ratios $(r_{1(cis)}/r_{1(trans)})$ are arranged in order of the bulkiness of the M_2 ester groups in Table 3. In Table 3, the r_1 of cis-isomers increase with the bulkiness of the M_2 ester groups, while those of the corresponding trans-isomers are constant. It can be considered that the copolymerization reactivities of trans-isomers are spared from the

TABLE 1. Copolymerization of NVIm (M_1) with Maleates (M_2) and Fumarates (M_2)

M_1	Comonomer		Conversion (wt/wt%)	N (%)	Copolymer	
	M_2	$[M_2]_f$			$[M_2]_p$	$\overline{M}_n$
NVIm	Di-n-propyl maleate	0.0700	2.0	19.03	0.1821	1060
		0.1601	2.3	15.28	0.2820	
		0.2596	1.8	14.50	0.3051	
		0.3503	3.3	12.55	0.3672	
		0.5000	9.0	10.49	0.4403	
		0.6500	7.4	9.43	0.4813	
		0.7399	7.7	8.35	0.5258	
		0.8404	7.0	7.69	0.5544	
		0.9305	1.3	5.88	0.6392	
NVIm	Di-n-butyl maleate	0.1249	3.5	17.33	0.2031	1030
		0.2498	3.6	15.22	0.2567	
		0.3720	2.8	11.25	0.3810	
		0.5003	2.6	9.57	0.4432	
		0.6271	9.4	8.90	0.4700	
		0.7501	3.9	7.66	0.5232	
		0.8745	7.4	5.64	0.6209	

NVIm	Di-n-propyl fumarate			
0.0698	4.3	11.20	0.4143	1585
0.1602	2.3	9.52	0.4777	
0.2599	4.7	8.36	0.5252	
0.3502	10.4	8.15	0.5343	
0.4999	9.9	7.84	0.5478	
0.6499	9.3	7.47	0.5641	
0.7407	11.2	6.92	0.5893	
0.8395	4.8	6.22	0.6227	
0.9302	0.6	5.06	0.6809	

NVIm	Di-n-propyl fumarate			
0.0701	3.9	11.86	0.3602	4600
0.1602	0.8	8.74	0.4765	
0.2599	7.0	7.93	0.5113	
0.3501	5.2	7.83	0.5154	
0.5003	3.8	7.29	0.5400	
0.6403	2.8	6.78	0.5638	
0.7395	7.6	5.96	0.6046	
0.8401	Trace	5.31	0.6382	
0.9299	–	–	–	

TABLE 2. Monomer Reactivity Ratios (r_1 and r_2) in the Copolymerization of NVIm (M_1) and St (M_1) with Various Maleates (M_2) and Fumarates (M_2)

M_1	M_2	$e_2{}^a$	Q_2	$r_1{}^a$	r_2
NVIm	Maleic acid[b]	2.60	0.45	0.022 ± 0.006	0.090 ± 0.015
"	Dimethyl maleate[b]	1.27	0.090	0.442 ± 0.057	0.117 ± 0.021
"	Diethyl maleate[b]	1.49	0.059	0.145 ± 0.015	0.069 ± 0.021
"	Di-n-propyl maleate[c]	0.53[c]	0.036[c]	0.348 ± 0.017	0.061 ± 0.001
"	Di-n-butyl maleate[c]	0.62	0.058	0.573 ± 0.093	0.139 ± 0.009
"	Fumaric acid[b]	1.87	0.36	0.012 ± 0.012	0.315 ± 0.031
"	Dimethyl fumarate[b]	1.49	0.76	0.017 ± 0.008	0.252 ± 0.069
"	Diethyl fumarate[b]	1.25	0.61	0.023 ± 0.014	0.229 ± 0.042
"	Di-n-propyl fumarate[c]	1.25[c]	0.54[c]	0.016 ± 0.016	0.134 ± 0.015
"	Di-n-butyl fumarate[c]	1.26[c]	0.59[c]	0.013 ± 0.012	0.169 ± 0.006
St	Di-n-propyl maleate[c]	0.53[c]	0.036[c]	9.600 ± 0.036	0.018 ± 0.000$_3$
"	Di-n-propyl fumarate[c]	1.25[c]	0.54[c]	0.357 ± 0.014	0.042 ± 0.008
"	Di-n-butyl fumarate[c]	1.26[c]	0.59[c]	0.327 ± 0.005	0.043 ± 0.009

[a]Polymer Handbook [9].
[b]Previous work [4].
[c]This work.

TABLE 3. The Ratio of Monomer Reactivity Ratio (r_1) of NVIm (M_1) and St (M_1) in the Copolymerization with Various Maleates (cis-isomer: M_2) and Fumarates (trans-isomer: M_2)

M_1	Ester group of M_2	r_1		$r_{1(cis)}/r_{1(trans)}$
		Maleate (cis)	Fumarate (trans)	
NVIm	H[a]	0.022	0.012	1.8
"	Methyl[a]	0.442	0.017	27
"	Ethyl[a]	0.145	0.023	6.4
"	n-Propyl[b]	0.348	0.016	22
"	n-Butyl[b]	0.573	0.013	43
St	Methyl[c]	8.5	0.21	40
"	Ethyl[c]	6.52	0.301	22
"	n-Propyl[c]	9.62	0.357	27

[a]Previous work [4].
[b]This work.
[c]Polymer Handbook [9]

steric effect between their two ester groups. $1/r_1$ $(= k_{12}/k_{11})$, denoting the relative copolymerization reactivity of comonomer (M_2) to the growing terminal radical of NVIm ($\sim M_1{}^*$), is obtained using Eq. (2). The ratio $(r_{1(cis)}/r_{1(trans)})$ increases with the bulkiness of the M_2 alkyl ester groups with the exception of methyl ester. A greater ratio indicates that the relative copolymerization reactivities of cis-isomers are less than those of the corresponding trans-isomers, so the results in Table 3 mean the r_1 of cis-isomers decrease in relation to the corresponding trans-isomers with increasing bulkiness of the M_2 alkyl ester. The reliability of these copolymerization results is in doubt because the ratio $(r_{1(cis)}/r_{1(trans)})$ for methyl ester was not in accord with the other M_2 alkyl esters. For this reason, the r_1 obtained from the copolymerization of St (M_1) with di-n-propyl maleate and fumarate (M_2) and the reported r_1 values [9] were added to Table 3. Although the copolymerization results of St with maleic acid (MA) and fumaric acid (FA) are lacking in Table 3, the order of the ratio $(r_{1(cis)}/r_{1(trans)})$ in the case of St system corresponds to that of NVIm systems. Therefore r_1 in the copolymerization of NVIm (M_1) with dimethyl maleate and fumarate is consistent with r_1 in those of NVIm with diethyl, di-n-propyl, and di-n-butyl maleates.

In the Alfrey-Price Q,e scheme [10, 11] the rate constant for the addition of M_2 to the radical of M_1 can be given to a fair approximation by the expression:

$$K_{12} = P_1 Q_2 \exp(-e_1 e_2) \tag{1}$$

where P_1 is characteristic of radical 1, Q_2 is the mean reactivity of M_2, e_1 and e_2 are proportional to the "charge" on the endgroup of radical 1 and on the double bond of M_2, respectively. P is referred to as the "probability" or "steric" factor. The value of P is a measure of deviation of an actual reaction from the "ideal" behavior of simple collision theory. In the Q,e scheme, assuming that the copolymerization reactivity of $\sim M_1{}^*$ for the addition of M_1 is equal to that for the addition of M_2, i.e., $P_{11} = P_{12}$, and that of $\sim M_1{}^*$ is equal to that of M_1, the monomer reactivity ratios (r_1 and r_2) are given as follows:

$$r_1 = r_{11}/r_{12} = (Q_1/Q_2) \exp\left[-e_1(e_1 - e_2)\right] \cdot \tag{2}$$

$$r_2 = r_{22}/r_{21} = (Q_2/Q_1) \exp\left[-e_2(e_2 - e_1)\right] \tag{3}$$

In this collision theory [6] the rate constant of propagation is given by

$$k = Ze^{-E/RT} \tag{4}$$

where the collision frequency or collision number Z is given by the kinetic-theory equation:

$$Z = \alpha_{1.2}^2 \left[8\pi kT\left[\frac{m_1 + m_2}{m_1 m_2}\right] \right]^{1/2} \tag{5}$$

where $\alpha_{1.2}$ is the mean molecular diameter of 1 and 2, m_1 and m_2 are the actual masses of the respective molecules, and k is Boltzman's constant. Equation (4) is modified by the introduction of the probability factor P. Thus,

$$k = PZe^{-E/RT} \tag{6}$$

P_1 in Eq. (1) is referred to as the "probability" or "steric" factor. This indicates that the copolymerization systems of monomers with bulky substituents will be inconsistent with the Q,e scheme.

Assuming that the copolymerization reactivity of $\sim M_1{}^*$ in regard to the addition of M_1 is not equal to that of the addition of M_2 with bulky substituents ($P_{11} \neq P_{12}$), Eq. (2) is modified below:

$$1/r_1 = k_{12}/k_{11} = (P_{12}/P_{11})(Q_2/Q_1) \exp\left[e_1(e_1 - e_2)\right] \tag{7}$$

In this case of the growing terminal M_2 radical, Eq. (3) is modified in the same manner as Eq. (2):

$$1/r_2 = k_{21}/k_{22} = (P_{21}/P_{22})(Q_1/Q_2) \exp\left[e_2(e_2 - e_1)\right] \tag{8}$$

P_{12}/P_{11} and P_{21}/P_{22} in Eqs. (7) and (8) are the index of deviation from the Q,e scheme, except if P_{12}/P_{11}, $P_{21}/P_{22} = 0$. Equations (7) and (8) correspond to the Alfrey-Price Q,e scheme if $P_{12}/P_{11} = $
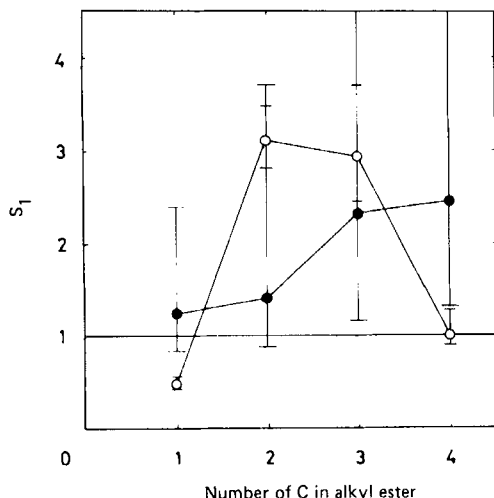
FIG. 1. Ratio $(S_1 = P_{12}/P_{11})$ of collision frequency (P_{12}) of the terminal NVIm radical $(\sim M_1{}^*)$ and M_2 and that (P_{11}) of $\sim M_1{}^*$ and M_1 in the copolymerization of NVIm (M_1) with various maleates (M_2) and fumarates (M_2) toward number of carbons (C) of alkyl ester. ⊖ : maleate, ● : fumarate.

$P_{21}/P_{22} = 1$ (see Eqs. 2 and 3). P_{12}/P_{11} and P_{21}/P_{22} are readily calculated from the copolymerization parameters (Table 2) and the Q,e values of comonomers using Eqs. (7) and (8), and those values of each copolymerization system are plotted against the chain length (number of C) of ester groups of maleates and fumarates as shown in Figs. 1 and 2.

With the assumption that P_{12}/P_{11} and P_{21}/P_{22}, S_1 and S_2, respectively, are "steric" parameters on the basis of Lüssi's idea. The S_1 values of maleates (M_2) are quite distinct from those of fumarates (M_2), even with the same substituents. The S_1 values of fumarates increase gradually with the chain length (number of C) of alkyl esters, while the S_1 values of maleates are irregular. Therefore, this behavior of fumarates and maleates cannot be explained simply by the bulkiness of alkyl esters. The negative S_1 value of dimethyl maleate might have something to do with the irregular reactivity ratios of the methyl esters shown in Table 3.
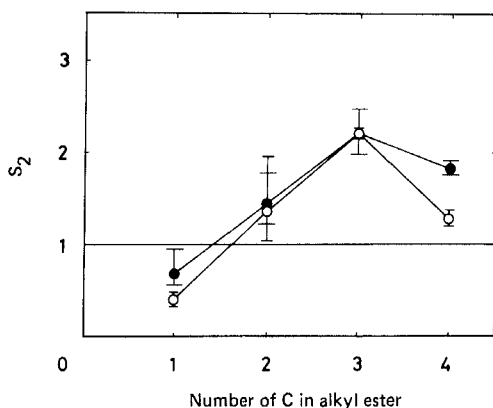
FIG. 2. Ratio $(S_2 = P_{21}/P_{22})$ of collision frequency (P_{21}) of the terminal M_2 radical $(\sim M_2^*)$ and M_1 and that (P_{22}) of $\sim M_2^*$ and M_2 in the copolymerization of NVIm (M_1) with various maleates (M_2) and fumarate (M_2) toward number of carbons (C) of alkyl ester. ⚲ : maleate, ● : fumarate.

In Fig. 2, S_2 means the ratio of each steric factor for the addition of NVIm toward the growing terminal radical of M_2. The Sp^2 orbital of the growing terminal maleate radical is clearly equal to that of fumarate, and the copolymerization behaviors of maleate and fumarate systems are almost the same within experimental error. However, it should be noted that the S_2 value of methyl ester has a different sign from that of the three other alkyl esters. S_2 values increase with the chain length of alkyl ester, although there is a sudden decrease with C_4. The influence of the steric factor on the alkyl ester was a maximum in C_3 (n-propyl).

The results of Figs. 1 and 2 showed that S_1 and S_2, considered to be "steric" factors, do not have any regular relationship to the chain length of alkyl ester, which should predominantly influence the "steric" factor. If S_1 and S_2 are "steric" factors, S_1 is expected to be less than 1 and S_2 greater than 1. However, both S_1 and S_2 are greater than 1, except for the methyl ester. In addition, the more the bulkiness of M_2, the higher the S_1 and S_2 values. The more the bulkiness of M_2, the

mor easily is NVIm copolymerized with M_2 beyond the Q,e scheme.
These results suggest that S_1 and S_2 are not related simply to the
bulkiness of the alkyl ester of M_2. Therefore, deviation from the
Q,e scheme in these copolymerization systems, i.e., S_1 and S_2, can-
not be explained by simple steric factors of alkyl ester based on
Lüssi's idea.

In the Alfrey-Price Q,e scheme, the rate constant for the addition
of M_2 to a free radical of M_1, i.e., k_{12}, can be given experientially by

$$k_{12} = A_{12} e^{-(p_1 + q_2 + e_1 e_2)} \tag{9}$$

In this expression for the propagation step, A_{12} represents a prob-
ability factor, p_1 is an activation factor related to the general reac-
tivity of the polymer endgroup, q_2 is a similar factor related to the
general monomer reactivity, and e_1 and e_2 are electrical factors.
Comparing Eq. (1) with Eq. (9), ln P_1 and ln Q_2 correspond to $-p_1$
and $-q_2$, respectively. Therefore, Eq. (1) is derived from Eq. (9)
on the assumption that A_{12} equals 1, which cannot be applied to
monomers without a vinyl group.

In the collision theory, a collision from a specific direction is re-
quired in order to induce the reaction. This is the reason why the P
factor in Eq. (6) is given a correction factor in regard to direction.
P between simple structure molecules is almost equal to 1. How-
ever, P between complicated structure molecules is considerably
less than 1, and it is therefore understood that the effective collision
frequency for the reaction decreases [6].

Since it is considered that A in Eq. (9), referred to as the "prob-
ability" factor, and P in Eq. (6), referred to as the "probability" or
"steric" factor, are looked upon as the same, S_1 and S_2 can be inter-
preted by the collision theory. Therefore, it is assumed that the cause
for the deviation from the Q,e scheme is due to the collision frequency.
The result in Fig. 1 shows that the reactivity of M_2 increases with the
bulkiness of the alkyl ester groups of M_2, contrary to expectation from
the Q,e scheme. This result suggests that the more the bulk of M_2, the
greater the collision frequency of M_2 and $\sim M_1^*$ vis-à-vis that of M_1
and $\sim M_1^*$, and this leads to interaction between $\sim M_1^*$ and M_2. By
considering the result in Fig. 2 in the same manner as Fig. 1, it is
expected that the collision frequency of M_2 toward $\sim M_2^*$ increases

with the bulkiness of the alkyl ester groups and also that P_{21}/P_{22} is less than 1. However, P_{21}/P_{22} is greater than 1, although P_{21} P_{22} increases with the bulkiness of the alkyl ester groups. This result is considered to be due to the fact that the collision frequency between the structurally complicated molecules increases with their bulkiness, while the effective collision frequency decreases with the bulkiness. From the aforementioned point of view, it should be restated that the simple collision frequency increases with the bulkiness of the alkyl ester groups of M_2 in the addition of M_2 and $\sim M_2{}^*$, while the effective collision frequency for the addition between M_2 $C{=}C$ double bonds decreases with the bulkiness of alkyl ester groups. Therefore, P_{21}/P_{22} $(\equiv A_{21}/A_{22})$ is greater than 1.

In conclusion, the deviation from the Q,e scheme is considered not to be simply due to a steric factor (steric hindrance) of alkyl ester, but is due to the assumption that A_{11} is equal to A_{12} (and A_{22} is equal to A_{21}) in the case of modification of Eq. (9). Therefore, it is thought that $A_{11} \neq A_{12}$ and $A_{22} \neq A_{21}$ in the copolymerization between monomers with bulky substituents.

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