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Characterization of N-Vinyl Monomers on the Revised Q,e-Scheme

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ABSTRACT

The copolymerization behavior of N-vinyl monomers was studied on the revised Q,e-scheme in order to investigate the monomer reactivity. Using methyl methacrylate as the comonomer instead of styrene, it was shown that the N-vinyl monomers cannot be classified as typical unconjugative monomers, but are quite different from popular conjugative monomers. They could be classified as the third monomers group on the revised Q,e-map. This result is predominantly caused by the different values of e-term depending on the comonomer, which is ascribed to the different e-terms of the polymer radical and the monomer.

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The Q,e-scheme proposed by Alfrey and Price [1] is of practical use as a simple way to evaluate monomer reactivity, especially for the presumption of copolymerization [2]. Since the scheme was developed with empirical assumptions, some further revisions and/or modifications have been shown by various researchers [3-6]. One of them, the revised Q,e-values or revised Q,e-map, proposed by Kawabata et al. [7], is significant in that it enables us to distinguish the difference between the conjugative and the unconjugative monomers.

In this article we show that N-vinyl monomers can be designated as a third monomer group, being neither conjugative nor unconjugative, from elucidating the revised Q- and e-values of N-vinyl monomers.

The revised Q,e-scheme [7] has been derived from the assumption that the e-value of styrene (St) is zero in Alfrey and Price's Q,e-scheme [1] as described in the following derivation. In terms of the Alfrey-Price Q,e-scheme, the monomer reactivity ratios, r_1 and r_2, in the copolymerization of St (M_1) and comonomer (M_2) can be written [7]

$$r_1 = (Q_1/Q_2) \exp \left[-e_{R_1}[e_{M_1} - e_{M_2}]\right] \quad (1)$$

$$r_2 = (Q_2/Q_1) \exp \left[-e_{R_2}[e_{M_2} - e_{M_1}]\right] \quad (2)$$

where Q is the resonance term characteristic of the monomer, and e_R and e_M are the polarity terms characteristic of the polymer radical and monomer, respectively. When e_{R_1} and e_{M_1} are identifiable because both terms cannot be specialized in physical characteristic and they are assumed to be zero, Eq. (1) can be reduced to

$$r_1 = (Q_1/Q_2) \exp \left[-0[0 - e_{M_2}]\right] = 1/Q_2' \quad (3)$$

where Q_2' is the revised Q-value induced by altering the e-value from -0.8 to 0. The product of r_1 and r_2 is

$$r_1 r_2 = \exp [-e_{R_2} e_{M_2}] \quad (4)$$

The revised e-value, e', is defined as

$$e_2' = [e_{R_2} e_{M_2}]^{1/2} \quad (5)$$

The revised Q,e-map is given as an illustration of the e-value vs the logarithmic Q'.

In order to use the revised Q,e-scheme (Eqs. 3-5), we have the copolymerization parameters of N-vinyl monomers which have been reported by us [8] and in the literature [9]. The revised Q,e-values of

TABLE 1. Revised Q,e-Values of N-Vinyl Monomers Calculated from Copolymerization Parameters [8, 9] with Styrene (St) and Methyl Methacrylate (MMA)

		Revised Q,e			
		St		MMA	
No.	N-Vinyl monomer	e'	Q'	e'	Q'
19	N-Vinylacetanilide	0.595	0.076_9	-0.567	0.026_1
20	N-Vinyl-1-aziridinecarboxamide	0.567	0.069_0	-0.216	0.209
21	N-Vinylcarbazole	1.270	0.175	0.238	0.306
22	2-Methyl-N-vinylimidazole	0.692	0.111	-0.939	0.042_8
23	2-Phenyl-N-vinylimidazole	-	-	-0.765	0.052_9
24	N-Vinylimidazole	-	-	-0.260	0.096_9
25	N-Vinylphthalimide	0.753	0.159	-	-
26	3,5-Dimethyl-N-vinylpyrazole	0.649	0.122	-	-
27	4-(Trimethylsilyl)-N-vinylphthalimide	0.847	0.164	-	-
28	5-Methyl-N-vinyl-2-oxazolidinone	0.412	0.069_9	-	-
29	N-Vinyl-2-pyrrolidinone	0.589	0.063_7	-0.739	0.040_3
30	N-Vinyl-2-oxazolidinone	-	-	-0.113	0.066_9
31	N-Vinylsuccinimide	0.630	0.104	0.487	0.086_7

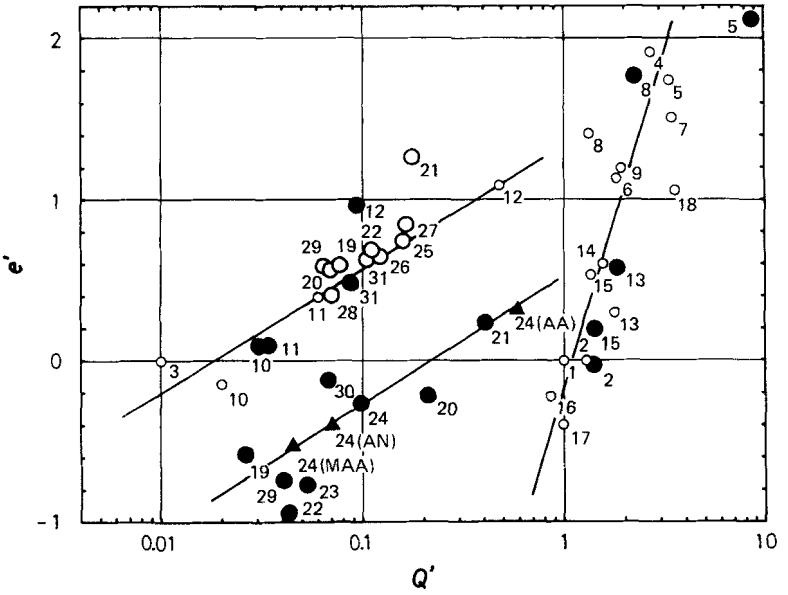

FIG. 1. Revised Q,e-map. (○) Kawabata's values [7]. (○) Revised Q,e-values of N-vinyl monomers for copolymerization with St [8, 9]. (●) Revised Q,e-values of N-vinyl monomers for copolymerization with MMA [8, 9]. (▲) Revised Q,e-values of N-vinylimidazole for copolymerization with methacrylic acid (MAA), acrylic acid (AA), and acrylonitrile (AN) [8]. Conjugative monomers [7]: (1) styrene, (2) butadiene, (4) acrylonitrile, (5) methacrylonitrile, (6) α-vinylpyridine, (7) methyl vinylketone, (8) methyl acrylate, (9) methyl methacrylate, (13) o-chlorostyrene, (14) m-chlorostyrene, (15) p-chlorostyrene, (16) p-methoxystyrene, (17) p-dimethylaminostyrene, (18) p-cyanostyrene. Unconjugative monomers [7]: (3) ethylene, (10) vinyl acetate, (11) vinyl chloride, (12) vinylidene chloride. N-Vinyl monomers: (19) N-vinylacetanilide, (20) N-vinyl-1-aziridinecarboxamide, (21) N-vinylcarbazole, (22) 2-methyl-N-vinylimidazole, (23) 2-phenyl-N-vinylimidazole, (24) N-vinylimidazole, (25) N-vinylphthalimide, (26) 3,5-dimethyl-N-vinylpyrazole, (27) 4-(trimethylsilyl)-N-vinylphthalimide, (28) 5-methyl-N-vinyl-2-oxazolidinone, (29) N-vinyl-2-pyrrolidinone, (30) N-vinyl-2-oxazolidinone, (31) N-vinylsuccinimide.

N-vinyl monomers are given in Table 1 and in the revised Q,e-map (Fig. 1), along with other reported values [7].

In Fig. 1 the revised Q,e-values of N-vinyl monomers for copolymerization with St fit well with the line of the unconjugative vinyl monomers group. The revised Q,e-values for copolymerization with methyl methacrylate (MMA) are on another line that obviously denotes a new group of unconjugative vinyl monomers. Although the new line is located between the lines for conjugative and unconjugative vinyl monomer groups, the line is parallel to the normal unconjugative line.

On the other hand, the revised Q,e-values of popular vinyl monomers copolymerized with MMA can be plotted on the ordinal conjugative and unconjugative lines in the revised Q,e-map, as shown in Fig. 1, although their plots shift somewhat from the plots for copolymerization with St. Consequently, N-vinyl monomers are a specific type of monomer that change the copolymerization behavior of the comonomer. N-vinyl monomers have at least two copolymerization modes (or selectivities) depending on the comonomer used, i.e., St and MMA.

From Fig. 1 it can be seen that the new line of N-vinyl monomers against MMA has moved from the normal conjugative line because of a change in the e-term. Similarly, movement of the revised Q,e-plots of popular vinyl monomers in regard to the comonomer St or MMA seems to be affected predominantly by the e-term, not by the Q-term. The influence of the e-term on copolymerization behavior is illustrated in Fig. 2, the difference ($\Delta e'$) between e'_{St} and e'_{MMA} vs the Alfrey-Price e-value, where those values are the same as in Table 1 and Fig. 1.

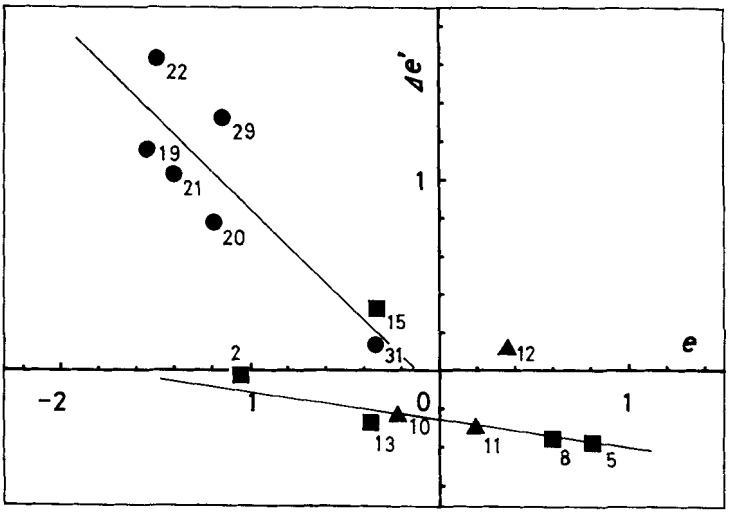

FIG. 2. Plot of $\Delta e' = e'_{St} - e'_{MMA}$ (e': revised e-value) vs Alfrey-Price's e-value. (●) N-Vinyl monomers. (■) Conjugative monomers. (▲) Unconjugative monomers.

Figure 2 clearly discloses the different character of popular conjugative monomers and N-vinyl monomers. The difference $\Delta e'$ in conjugative monomers diminishes at their lower e-values while ($\Delta e'$) in N-vinyl monomers diminishes steeply at their higher e-values.

Figure 1 shows that the characteristics of N-vinyl monomers cannot be classified as for typical unconjugative monomers, such as vinyl chloride and vinyl acetate, and are also quite different from those of popular conjugative monomers. The π-conjugative character of N-vinyl monomer between the N-atom and the vinyl group is very small, based on the electron density calculations [10]. The authors tried to find some interaction between N-vinylimidazole and St and/or MMA by applying high resolution NMR and IR spectroscopy. No spectra indicated interaction between those monomers.

N-Vinyl monomers behave as unconjugative monomers in copolymerization with St, and as another type of unconjugative monomers in copolymerization with MMA. The revised Q,e-values of N-vinyl monomers for copolymerization with acrylonitrile, methacrylic acid, and acrylic acid instead of MMA are similar to MMA (Fig. 1).

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