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Ionic Copolymerizations

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ABSTRACT

It is shown that for the reported instances of "random" copolymerization in cationic systems, N values related to relative reactivity may be derived for monomers. The N values approximate reasonably well the values of the function, $\exp\{-e\} - 1.23$, where e is the polarity e of the $Q-e$ scheme for free-radical copolymerizations.

In a recent paper [1] it was shown that for the reported instances [2-4] of "random" copolymerization ($r_1 r_2 = 1$) in cationic systems, N values, related to relative reactivity, might be derived for monomers, employing styrene as a base monomer ($N = 1$). Thus

$$d[M_1]/d[M_2] = N_1[M_1]/N_2[M_2] \quad (1)$$

where $d[M_1]/d[M_2]$ is the instantaneous copolymer composition, $[M_1]/[M_2]$ is the ratio of unreacted monomers, and N_1 and N_2 are parameters related to general monomer reactivity of monomers 1 and 2, respectively, in cationic copolymerization.

It was further shown that experimentally determined N values approximated reasonably well the values of the function, $\exp \{-e\} - 1.23$, where e is the polarity e of the $Q-e$ scheme for free radical copolymerizations. The constant 1.23 arises from the adjustments of the two functions to yield a common value at $e = -0.8$ for styrene.

It is important to note that only those r_1 and r_2 values of cationic copolymerizations were utilized in which experimental conditions of catalysts, solvents, etc., resulted in random copolymerization ($r_1 r_2 = 1$). This practice was based on several factors: (1) recent recalculations of copolymerization data [2] have shown a remarkable number of instances where improved assessment of data yielded $r_1 r_2 = 1$; (2) the potentially great advantage of Eq. (1) in terms of simplicity if it could be confirmed; (3) the virtual absence of cross-over systems (azeotropes) in cationic copolymerization (which should occur if strong cross-propagation tendencies existed); (4) such systems should assure minimal contributions otherwise arising from drastic changes in dielectric constants of solvents and monomers throughout the entire compositional region.

Good correlations were obtained in "new" copolymer systems on employing N values so derived or employing e values from free-radical copolymerizations.

It is now apparent that the N values represent a measure of the relative nucleophilicity of monomers in reaction with the growing polymeric cation. Moreover, it is probable that the growing cation, under the conditions leading to random copolymerization, is substantially separated from any counterion, monomer or solvent molecule. If this circumstance were not so, it would be difficult to imagine any general scheme of reactivity so simple as that exhibited here. Closely bound counterions, monomer, or solvent molecules would drastically alter the relative reactivity of competing monomers.

Yamamoto and Higashimura [3] have presented compelling evidence of preferential attack of monomer on like polymeric cation under conditions leading to solvation by monomer (in presence of solvents of low dielectric constant) with the result of enhanced "blockiness" of copolymer ($r_1 r_2 > 1$). Thus, a comparison of reactivity ratios in the presence of solvents of low dielectric constant with those obtained under "random" conditions (generally solvents of high dielectric constant) should allow an assessment of the reactivity of monomer-solvated cations.

Thus, it may be proposed that for cationic copolymerization

$$k_{11} = \exp \{-e_1 * e_1\}$$

$$k_{12} = \exp \{-e_1 * e_2\}$$

$$r_1 = k_{11}/k_{12} = \exp \{-e_1 * (e_1 - e_2)\}$$

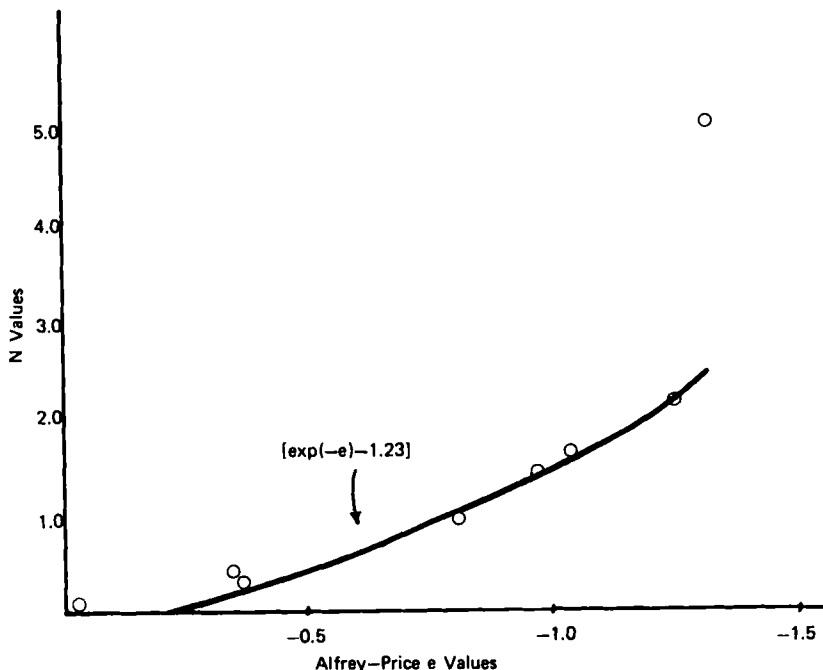


FIG. 1. Plot of N values against e values. The solid line shows the function, $\exp \{-e\} - 1.23$.

and similarly

$$r_2 = k_{22} / k_{21} = \exp \{-e_2 * (e_2 - e_1)\}$$

where reactivity of the growing cation 1 differs appreciably from the reactivity of the growing cation 2 (and from the reactivity (nucleophilicity) of monomer 1). Thus $r_1 \neq 1/r_2$.

Figure 1 shows actual N values for various monomers derived from cationic copolymerization reactivity ratios plotted against free-radical e values. The value of the function $\exp \{-e\} - 1.23$ is shown as the solid line.

The solid line may also be envisioned as a plot of the function $\exp \{-e_1 * e_2\} - 1.23$, where $e_1 * = 1$. If $e_1 *$ takes on positive values larger than unity, then the slope of the function increases sharply as e_2 becomes more negative. This result suggests the following:

(1) The e_1^* value for the nucleophilicity (reciprocal of the electrophilicity) of the growing cation 1 (styrene) is slightly larger than +1.00 [compared with an e value (e_2) for styrene monomer of -0.80]. (2) Monomer-solvation of growing cations would be especially pronounced for those derived from monomers of large negative e value. Enhanced "blockiness" ($r_1 r_2 > 1$) would result, especially in solvents of low dielectric constant. (A highly electrophilic cation derived from a highly nucleophilic monomer would tend to generate "blocky" copolymers.)

The procedure to be followed in investigating other cationic systems is clear. The principal monomer (and cation) is copolymerized with 8 to 10 comonomers (random conditions), and plots similar to Fig. 1 are made. The value of e_1^* may be determined by trial and error to give the best fit of $\exp \{-e_1^* e_2\} - 1.23$ vs. e_2 to the experimentally determined values of N . Similar assessments under "blocky" conditions (solvents of low dielectric constant) should generate information about the electrophilicity of growing cation under monomer-solvation conditions.

It is particularly illuminating that e values for propagating cations tend to be highly positive and those for the corresponding monomers, highly negative. This situation is sharply distinct from that encountered in free radical copolymerization, where e values for propagating radical and corresponding monomer are very similar. Nevertheless, the e values for monomers are evidently the same in free-radical and cationic copolymerizations, and possibly in anionic copolymerizations as well. The drastically enhanced reactivity of propagating cation with its own monomer is the net result, leading to many decades of enhanced relative reactivity in cationic systems compared with one or two in free radical systems.

REFERENCES

- [1] G. E. Ham, J. Polym. Sci. Polym. Symp. Ed., in press.
- [2] J. P. Kennedy, T. Kelen, and F. Tüdös, J. Polym. Sci. Polym. Chem. Ed., **13**, 2277 (1975).
- [3] K. Yamamoto and T. Higashimura, Polymer, **16**, 815 (1975).
- [4] T. Masuda, T. Higashimura, and S. Okamura, Polym. J., **1**, 19 (1970).

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