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Relationship between Reactivity Ratios and Configuration for Donor—Acceptor Type Copolymers

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ABSTRACT

For binary copolymers from an acrylic monomer (acceptor type, M_1) and an aromatic-substituted monomer (donor type, M_2) a linear relation between log (r_2/r_1) and the probability of "coisotactic" alternating addition is observed. This can be a proof for the influence of monomer polarity on the copolymer configuration.

In the NMR spectra of binary copolymers from an acrylic monomer and an aromatic-substituted monomer, it is possible to determine the configurational parameter σ, the probability of "coisotactic" alternating addition. In 1965, Harwood and Ritchey [1] and Ito and Yamashita [2, 3] obtained for the first time the values $\sigma = 0.48$ for methyl methacrylate (MMA)-styrene (S) copolymer and $\sigma = 0.80$ for methyl acrylate (MA)-S copolymer. There have been many studies in this field, using partially deuterated monomers and ^{13}C-NMR for spectral simplification. By analyzing Ito's table [4] together with other σ values given in the literature, we observed the simple relationship shown in Fig. 1.

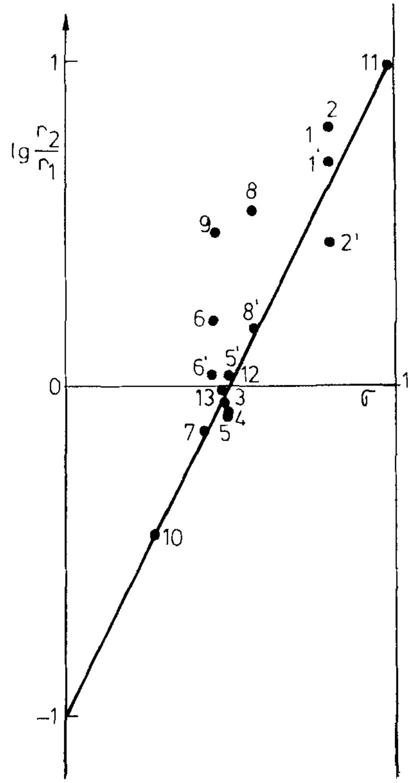

FIG. 1. Dependence of log (r_2/r_1) on σ for various copolymer systems: (1) methyl acrylate-styrene; (2) benzyl acrylate-styrene; (3) methyl methacrylate-styrene; (4) methyl methacrylate-p-methoxystyrene; (5) methyl methacrylate-p-methylstyrene; (6) methyl methacrylate-p-chlorostyrene; (7) benzyl methacrylate-styrene; (8) n-propyl methacrylate-styrene; (9) methyl acrylate-α-methylstyrene; (10) methyl methacrylate-α-methylstyrene; (1'-8') corresponding values from literature reactivity ratios [5]; (11) methyl acrylate-4-vinyl pyridine; (12) methyl methacrylate-4-vinyl pyridine; (13) methacrylic acid-styrene.

This relationship can be written:

$$\log (r_2/r_1) = 2\sigma - 1 \qquad (1)$$

where subscripts 1 and 2 refer to the acceptor monomer and the donor monomer, respectively, and σ is the probability of "coisotactic" addition between the aromatic group and the OCH_3 (or OCH_2R) group.

In Fig. 1 there are data from Ito [4] for ten systems: MA-S; benzyl acrylate-S; MMA-S; MMA-p-methoxystyrene; MMA-p-methylstyrene; MMA-p-chlorostyrene; benzyl methacrylate-S; n-propyl methacrylate-S; MA-α-methylstyrene (αMS); MMA-αMS.

The agreement with the straight line was not good for some of the copolymers. We tried to verify the values by using the reactivity ratios values given in the Polymer Handbook [5] for the copolymerization conditions given in Ito [4]. Thus, we obtained the points 1', 2', 5', 6', and 8', which better fit the straight line. Because the reactivity ratios values are generally rather spread out, it is difficult to find the real ones. For the MA-αMS copolymer there are no reactivity ratio values in Polymer Handbook, so the point 9 is the farthest from the straight line.

For the σ in the MMA-S copolymer similar values have been reported: $\sigma = 0.48$ [6]; $\sigma = 0.5$ [7].

Figure 1 shows also values for two copolymers containing 4-vinylpyridine (4VPy): MA - 4VPy ($r_1 = 0.18$; $r_2 = 1.77$; $\sigma = 0.98$) [8] and MMA - 4VPy ($r_1 = 0.23$; $r_2 = 0.24$; $\sigma = 0.5$) [9], together with the methacrylic acid-S copolymer ($\sigma = 0.47$) studied by Bockrath and Harwood [10].

The most recent studies in this field use the radical alternating copolymerization and measure σ directly: the MMA-S, MMA-αMS, MA-S, and MA-αMS copolymers [11], the methyl α-chloroacrylate-S copolymer [12], and the MMA-S, MA-S, methacrylonitrile-S, methacrylamide-S, MMA-αMS, and MA-αMS copolymers [13]. The σ values for the statistic and alternating copolymer differ sometimes. This is due to the different addition mechanism. Ikegami and Hirai [14, 15] demonstrated that the alternating copolymer configuration depends on the nature and proportion of the complexing Lewis acid. For this reason we did not include in Fig. 1 the σ values for the alternating copolymers.

An attempt to correlate the obtained equation with the Q-e scheme fails because of the well-known inapplicability of the Q-e scheme to 1,1-disubstituted ethylenes [16].

Without disagreement with the sterical determination of the alternating addition [4, 13] the relationship proposed here seems to suggest also the importance of the polar factor, both giving the reactivity ratio values.

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