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Copolymerization Behavior of Some Acidic and Basic Monomers

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ABSTRACT

Copolymerization reactivity ratios of the systems 4-vinylpyridine (VP)-methacrylic acid (MA), dimethylamino methacrylate (DMAM)-MA, and VP-DMAM were obtained using the Fineman-Ross procedure. The experimental values were found to differ considerably from the values calculated from the Q-e scheme. r_1 and r_2 values calculated using seven different models for the VP-MA system have been compared with the experimental values.

The formulation of a generalized theory to predict the reactivity ratios in free radical copolymerization has attracted the attention of a large number of workers [1-9]. Although a limited amount of success has been achieved in predicting the reactivity ratios in systems containing apolar monomers, agreement with experimental values in systems involving polar monomers is an exception rather than the rule. The present study consists in the determination of reactivity ratios when the acidic monomer, methacrylic acid, was copolymerized with the basic monomers, 4-vinylpyridine and dimethylamino methacrylate. The values so obtained have been compared with values predicted from various theoretical formulations made so far.

MATERIALS AND METHODS

4-Vinylpyridine (VP), methacrylic acid (MA), and dimethylamino methacrylate (DMAM) were obtained from Rohm and Haas Co. The monomers were freshly distilled before use, under reduced pressure, to remove inhibitors. 2,2'-Azobisisobutyronitrile (AIBN) was used as initiator for the polymerization. The AIBN used was twice recrystallized from methanol.

The copolymerizations were carried out at 70°C under a nitrogen atmosphere in well-stoppered bottles. To obtain meaningful reactivity ratios, polymerizations were not allowed to proceed beyond 10%. This was achieved by controlling the initiator concentration as well as the time of reaction. At the end of the required time the bottles were withdrawn from the thermostat and the polymer precipitated in a suitable solvent. Table 1 summarizes the procedure adopted for the various systems.

TABLE 1. Conditions of Polymerization

Comonomers	Initiator (mole %)	Precipitating conditions
4VP-MA	0.8	Acetone at 0°C
MA-DMAM	0.1	Acetone at -50°C
4VP-DMAM	0.5	Water at room temperature

All the copolymers were purified by redissolving in methanol, precipitating in acetone/water twice, and were finally dissolved in water and lyophilized. The composition of the copolymer MA-DMAM was determined by the estimation of nitrogen by using the semimicro Kjeldahl method. In case of polymers containing VP, the pyridine content was estimated spectrophotometrically by measuring the absorption of the solution at 262 nm in H_2SO_4. The E_{max} at this wavelength of the VP residue, required for this calculation, was obtained by measuring the E_{max} for polyvinylpyridine in the same solvent and at the same wavelength. Poly-VP was prepared by polymerization of the monomer at 70°C with AIBN as initiator. The composition data is the average of five determinations carried out on each of the samples.

RESULTS AND DISCUSSION

As the conversions for the various combinations were kept very low (10%), the reactivity ratios of the copolymerization were evaluated using the method of Fineman and Ross [10]. According to this formulation,

$$\frac{F}{f}(f - 1) = r_1\frac{F^2}{f} - r_2$$

where f is the mole ratio of the monomers in the copolymer, F is the mole ratio of the monomers in the feed, and r_1 and r_2 are the reactivity ratios. Figures 1, 2, and 3 give the plots of the monomer feed composition vs the copolymer composition (both in mole fraction), and Figs. 4, 5, and 6 give the corresponding Fineman-Ross plots for the three systems under study: VP-MA, DMAM-MA, and VP-DMAM. It can be seen that, among the systems under investigation, only in the DMAM-MA system is an azeotropic copolymer possible. On the other hand it is interesting to note that the polymer composition and the monomer feed are almost alike in the VP-DMAM system, while in the

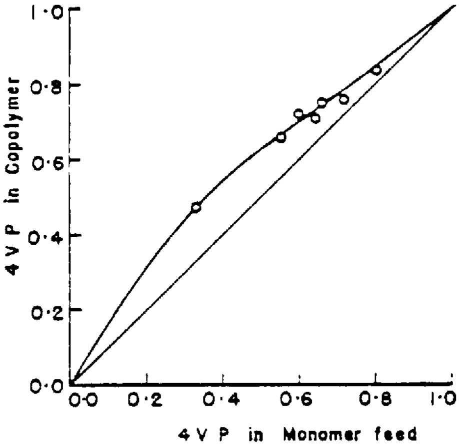

FIG. 1. Feed composition vs copolymer composition in the system VP-MA.

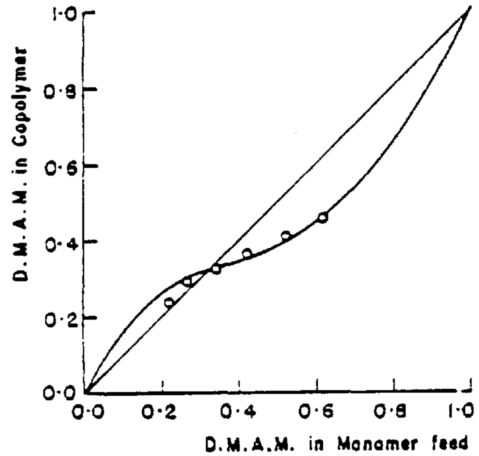

FIG. 2. Feed composition vs copolymer composition in the system DMAM-MA.

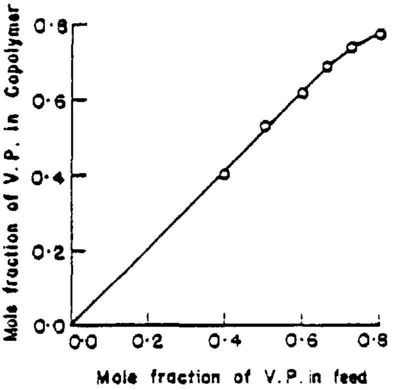

FIG. 3. Feed composition vs copolymer composition in the system VP-DMAM.

VP-MA system the polymer has the basic monomer in the higher proportion. The reactivity ratios obtained from plots are shown in Table 2. Table 2 also shows the reactivity ratios obtained using Q-e data from the compilation of Young [11].

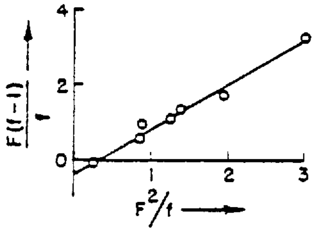

FIG. 4. Fineman-Ross plot for the system VP-MA.

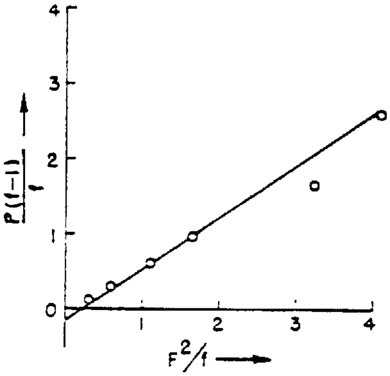

FIG. 5. Fineman-Ross plot for the system DMAM-MA.

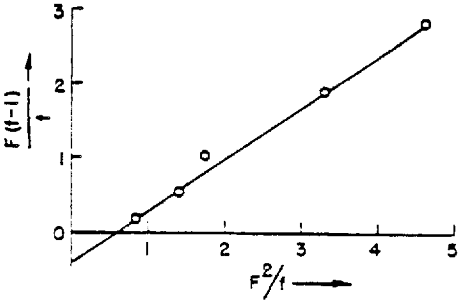

FIG. 6. Fineman-Ross plot for the system VP-DMAM.

TABLE 2. Experimental and Calculated Values of Reactivity Ratios

Monomer 1	Monomer 2	r_1(calc)	r_2(calc)	r_1(obs)	r_2(obs)
VP	MA	0.2955	1.642	1.2	0.4
VP	DMAM	1.054	0.6049	0.7	0.375
DMAM	MA	0.3162	3.043	0.2	0.7

The calculated values differ considerably from the experimental values, and in some cases even an order difference is observed. Such a large difference cannot arise only because of "inaccuracies" in the Fineman-Ross plots [12], but must involve inadequacies of the Q-e scheme proposed for the calculation of these reactivity ratios in systems involving the acidic and basic comonomers. Table 3 summarizes the results of calculations made using a variety of mathematical models proposed for the VP-MA system, the only system in the present study for which all the requisite parameters are available.

TABLE 3. r_1,r_2 Values Calculated from Various Models for the System VP-MA

Model	r_1	r_2
Q-e scheme [11]	0.2955	1.642
Ham's generalized treatment [13].	2.0	3.74
Charge transfer [7]	0.270	2.51
Electronegativity [6]	0.9955	1.005
Wall's Q-e-e* [15]	0.487	0.295
CTE model [14]	0.295	2.89
ENE model [14]	2.115	5.207
Experimental	1.2	0.4

It can be seen that not even one of the models gives a satisfactory or near satisfactory agreement between the calculated values for r_1 and r_2 and the experimental values. Perhaps this arises out of the fact that the present copolymerization scheme needs modification when applied to systems of the kind under study, where the possibility of existence of other steps, such as salt formation, may have to be considered.

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