COPOLYMERIZATION REACTIVITY RATIOS ACRYLIC AND
METHACRYLIC ACIDS WITH BUTYL ACRYLATE AND
BUTYL METHACRYLATE

The purpose of this note is to report the measurement of copolymer-
ization reactivity ratios for acrylic and methacrylic acids each with n-
butyl acrylate and n-butyl methacrylate. The recent comprehensive com-
pilation by Young (1) of r_1, r_2, and Q-e values for a multitude of mono-
mers does not include the copolymerization of either of these acids with
a corresponding ester, nor of an acrylate with the corresponding metha-
crylate. The present results show that in each case the acid monomer
lags slightly behind its ester in copolymerization. The two cases of
acrylate-methacrylate copolymerization agree very well if a small cor-
rection for the acid lag is applied.

Experimental Details

Inhibited glacial acid monomers were purified by fractional crystalli-
zation in ice; assay by base titration indicated purity of 96% for acrylic
acid and 98% for methacrylic acid. Butyl acrylate and butyl methacryl-
ate were purified by distillation under reduced pressure. Monomers were
stored at $-20°C$. until use.

Polymerizations were carried out in capped 8 oz. bottles at 50°C., us-
ing 20 g. total monomers, 40 g. ethyl alcohol as solvent, and 0.1 g. ben-
zoyl peroxide catalyst. Final conversions varied between 5 and 14%.

Polymers were purified of unreacted monomers by dialysis in Visking
cellophane tubing against about three volumes of ethyl alcohol. Titra-
tions of the extracts with base showed that residual acid monomer was
negligible after five or six extractions; presumably the extraction of
ester monomer was similarly efficient. The dialyzed polymer solution
was titrated with base to determine acid content. As soon as some of
the acid had been saponified, it was possible to add enough water, with-
out precipitating polymer, to obtain a sharp endpoint, which occurred at
pH 9 to 10. Polymer compositions were calculated from the titrations
and the total polymer content of the solutions. Reactivity ratios were
calculated by the method of Fineman and Ross using weight-fraction
compositions.

Results

The copolymer composition curves are shown in Figure 1. Table I
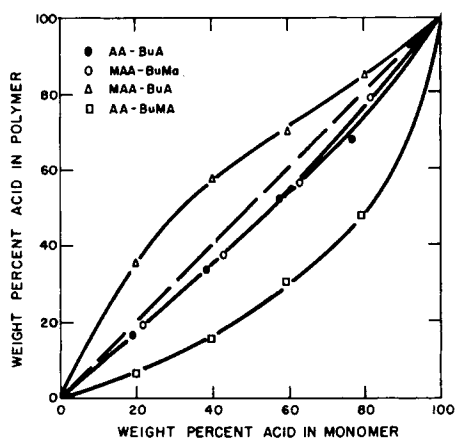lists the monomer and polymer compositions, the experimental reactivity

Fig. 1. Copolymer composition curves.

TABLE I

Monomer and Polymer Compositions and Reactivity Ratios

Per cent acid		Exptl.		Calc. (1)	
Monomer	Polymer	r_1	r_2	r_1	r_2
Acrylic acid (1)-butyl acrylate (2)					
19.3	16.5	0.58	1.07	2.73	0.35
38.6	33.9				
57.9	52.4				
77.2	67.9				
Acrylic acid (1)-butyl methacrylate (2)					
19.8	6.3	0.29	3.67	0.73	0.50
39.6	15.5				
59.4	30.5				
79.2	47.8				
Methacrylic acid (1)-butyl acrylate (2)					
20	35.3	1.31	0.35	5.82	0.15
40	57.6				
60	70.1				
80	84.6				
Methacrylic acid (1)-butyl methacrylate (2)					
22.1	18.7	0.75	1.20	1.84	0.25
43.1	37.2				
63.0	56.4				
81.9	78.9				

TABLE II

Copolymerization Parameters, Q and e, from Literature (1)

Monomer	Q	e
Acrylic acid	1.15	0.77
Butyl acrylate	0.51	1.02
Methacrylic acid	2.34	.65
Butyl methacrylate	0.72	−.23

TABLE III

Correction of Acrylate-Methacrylate Data for Acid Lag

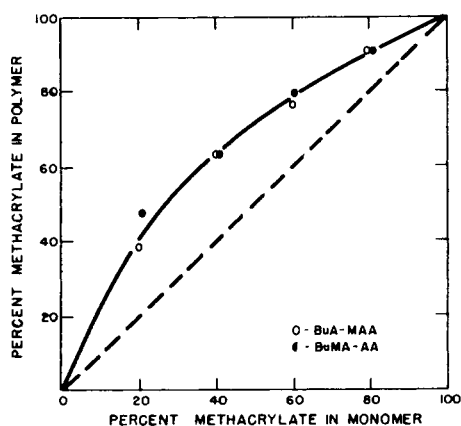| Monomer			Polymer	
% methacrylate	% acid	Δ acid	% methacrylate	Corrected % methacrylate
BuA-MAA			(BuMA-MAA)	
20	20	−3.0	35.3	38.3
40	40	−5.5	57.6	63.1
60	60	−6.0	70.1	76.1
80	80	−6.5	84.6	91.1
BuMA-AA			(BuA-AA)	
20.8	79.2	−4.5	52.2	47.7
40.6	59.4	−6.5	69.5	63.0
60.4	39.6	−5.5	84.5	79.0
80.2	19.8	−3.0	93.7	90.7

Fig. 2. Copolymerization of acrylate with methacrylate corrected for acid retardation.

ratios, r_1 and r_2, and also the reactivity ratios calculated from the Q and e values of Young (1) shown in Table II. The composition curves which may be calculated from the latter reactivity ratios are quite unlike the experimental ones, and in some cases they deviate from the ideal in the opposite direction. It is regrettable that the Q and e parameters should prove to be so unreliable.

The copolymerizations of acid monomers with the corresponding butyl esters are very nearly ideal; the entry of acid into the copolymer is slightly retarded in both cases by about the same amount. This may be due to ionic repulsion in the polar solvent ethanol, or to a lowering of the effective monomer concentration due to ionization. In any event the retardation is in qualitative agreement with the results of Alfrey, Overberger, and Pinner (2) who found that the ionized form of methacrylic acid was much less reactive than the un-ionized form.

We have polymerized an acrylic monomer with a methacrylic monomer in two cases, MAA-BuA and AA-BuMA. These are diverted from ideal behavior by two factors: the acrylate-methacrylate effect and the acid-butyl ester effect. We can correct these two composition curves for the acid effect as follows: add to the per cent methacrylate for the MAA-BuA curve the amount the MAA-BuMA curve falls below ideal, and subtract from the per cent methacrylate for the AA-BuMA curve the amount the AA-BuA curve falls below ideal. The results are shown in Figure 2 and Table III, where it is seen that the two series agree very well in describing the copolymerization of acrylate and methacrylate. Taking methacrylate as monomer 1, the reactivity ratios are $r_1 = 2.2$ and $r_2 = 0.3$.

References

(1) Young, L. J., J. Polymer Sci., 54, 411 (1961).

(2) Alfrey, T., C. G. Overberger, and S. H. Pinner, J. Am. Chem. Soc., 75, 4221 (1953).

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