

REACTIVITIES OF ACRYLATES AND METHACRYLATES

The monomer reactivity ratios for copolymerizations have been used by several authors for comparison of the reactivities of monomers towards reference radicals (1,2); one such study involved various esters of methacrylic acid with the poly(methyl methacrylate) radical (3). The procedure essentially involves determination of the products arising from competing reactions and very great sensitivity can be achieved; thus a reactivity ratio of 1.10 indicates that the velocity constants for the competing growth reactions differ by 10% which, for reactions at 60°C., could be accounted for by a difference of only about 60 cal./mole between the activation energies.

Composition of copolymers can be determined accurately by a tracer method involving isotopically labelled monomers (4). The method is reliable so that confidence can be placed in results which indicate only small differences between the reactivities of monomers towards a particular polymer radical. It is particularly useful in cases where the monomers have very similar compositions and structures.

Table I reports new results for radical polymerizations at 60°C. involving methyl methacrylate with other methacrylates and with acrylates. Table II shows the relative reactivities, given by $1/r_A$, for various monomers towards the poly(methyl methacrylate) radical. A later paper will contain full discussion of these results and those for other series of related monomers with other reference radicals, but attention must now be drawn to the significant differences between the reactivities of various alkyl methacrylates and the much smaller differences found for the corresponding acrylates. This feature is illustrated in Figures 1 and 2 which show that the results for n-butyl and isobutyl acrylates are almost identical, whereas those for the methacrylates are clearly separated. The difference between the reactivities of the methacrylates would be more pronounced if, for the system involving the isobutyl ester, no attention were paid to the point corresponding to the highest value of F^2/f . It is considered that the smaller monomer reactivity ratios in Table II are probably accurate to 4%; the probable error in the larger ratios is about 2½%.

Notes on Experimental Procedures

In all cases, ^{14}C -methyl methacrylate was used as the labelled monomer. It was prepared by exchange between the unlabelled monomer and ^{14}C -methanol; the specific activities of the various samples were in the region of 0.08 $\mu\text{curies/g.}$ Certain unlabelled monomers, e.g., furfuryl

TABLE I

Monomer Reactivity Ratios for Radical Copolymerizations at 60°C.

Monomer A	Monomer B	r_A	r_B
Methyl methacrylate	Furfuryl methacrylate	0.75	1.19
"	n-Butyl methacrylate	0.79	1.27
"	Isobutyl methacrylate	0.91	1.09
"	Ethyl acrylate	1.83	0.47
"	n-Butyl acrylate	1.74	0.20
"	Isobutyl acrylate	1.71	0.20

TABLE II

Relative Reactivities of Monomers Towards the Poly(methyl Methacrylate) Radical at 60°C.

Ester	Reactivity of	
	Acrylate	Methacrylate
Methyl	0.50 ^a	1.00 (reference)
Ethyl	0.55 ^b	1.09 ^c
n-Butyl	0.57 ^b	1.26 ^b
Isobutyl	0.58 ^b	1.10 ^b

^a Reference 6.^b Present work.^c Reference 3.

methacrylate, were also prepared by ester exchange. Polymerizations were performed in the complete absence of air in dilatometers; azoisobutyronitrile at 0.3 g./l. was used as initiator and polymerizations were allowed to proceed to 5% conversion. Normal kinetic behavior was found. Polymers were recovered by precipitation in methanol, purified by reprecipitation from benzene solution, and dried in vacuum. Labelled materials were assayed by gas counting. Monomer reactivity ratios were deduced from the analytical data by the method due to Finemann and Ross (5). There were no differences between the results of experiments in bulk and those in which benzene was present as diluent.

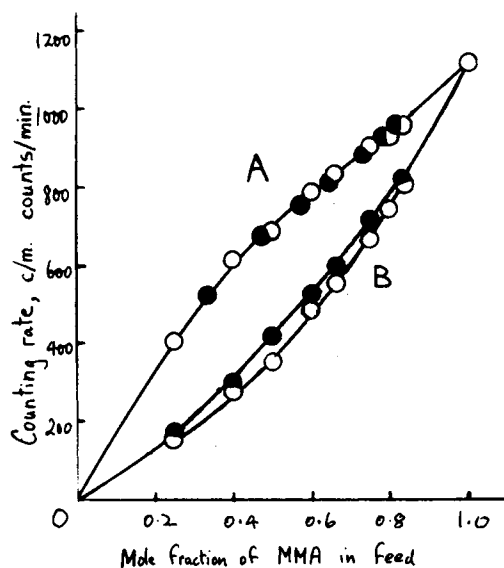


Fig. 1. Plots of specific activity of copolymer against composition of feed for copolymerizations of ^{14}C -methyl methacrylate ($0.074 \mu\text{-curies/g.}$) with methacrylates and acrylates. A: (○) n-butyl acrylate; (●) isobutyl acrylate. B: (○) n-butyl methacrylate; (●) isobutyl methacrylate.

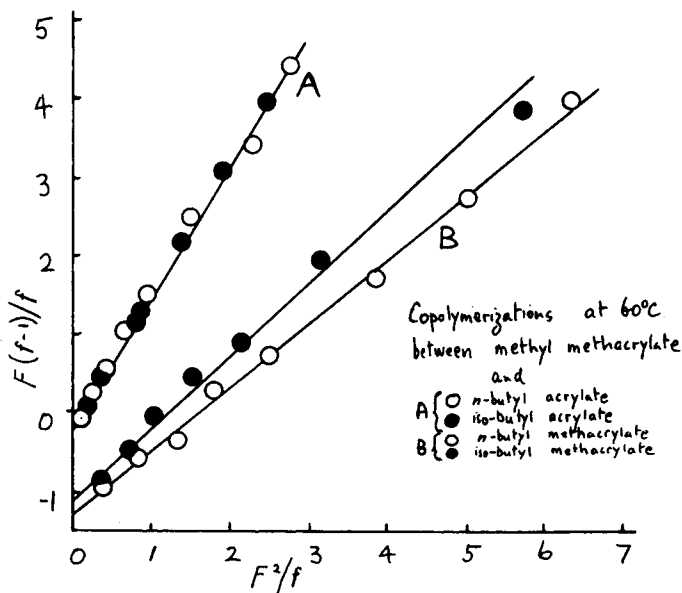


Fig. 2. Finemann-Ross plots derived from data shown in Fig. 1. Points distinguished as in Fig. 1.

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References

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