

REACTIVITIES OF ESTERS OF METHACRYLIC ACID—III. STUDIES OF COPOLYMERIZATIONS INITIATED BY METALLIC SODIUM

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Abstract—The methyl, ethyl, cyclohexyl, benzyl and phenyl esters of methacrylic acid have been studied in copolymerizations initiated by metallic sodium. The reactions were performed at 30° with benzene as diluent. For each system, one monomer was labelled with ^{14}C ; the resulting copolymer was assayed and its composition was deduced. Monomer reactivity ratios were calculated by the procedure due to Fineman and Ross. For the copolymerization of methyl and cyclohexyl methacrylates, there are substantial differences between the monomer reactivity ratios for free radical reactions, and those initiated by the alkali metal. For the other copolymerizations examined, there were only small differences between the results obtained for the systems of the two types.

TRACER studies of radical polymerizations involving esters of methacrylic acid have been described already;^(1,2) they have been used to make comparisons of the reactivities of the various monomers towards either the benzoyloxy radical or certain polymer radicals. Metallic sodium causes the esters to polymerize by processes which in part, at least, involve anions as active centres. The monomer reactivity ratios for sodium-catalysed polymerizations of pairs of the esters have now been determined by a tracer method, and the reactivities of the monomers towards reference polymer anions have been compared for the case where the gegenion is Na^+ , the reaction mixture contains a substantial proportion of benzene, and the temperature is 30°.

The general experimental procedures have been described.^(1,2) Each reaction mixture contained benzene (60% by volume) and a piece of freshly cut sodium (about 0.1 g); the total volume was about 11 cm³. The reaction mixture was degassed thoroughly at quite low temperatures; the vessel was then sealed and transferred to a thermostat at 30° where it was shaken vigorously. A colour rapidly appeared on the metallic surface and later spread through the reaction mixture. Systems containing phenyl methacrylate developed reddish-orange colours, but others became yellowish. Rates of contraction were not measured precisely, but they depended upon the surface area of the metal and they fell with time. Reactions were allowed to proceed to about 5 per cent conversion; this required between 20 min and 8 hr, depending upon the composition of the feed. One of the monomers in each reaction mixture was labelled with ^{14}C , and the composition of the resulting copolymer was found from comparison of its specific activity with that of the monomer.

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The method of Fineman and Ross⁽³⁾ was used to derive monomer reactivity ratios from the compositions of feeds and of copolymers, assuming that changes in the compositions of the feeds during polymerization were negligible.

RESULTS AND DISCUSSION

Results of typical copolymerizations are shown in Table 1. Fineman-Ross plots for two systems are shown in Figs. 1 and 2.

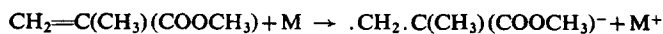
TABLE 1. RESULTS OF COPOLYMERIZATIONS

Monomer A	Monomer B	Mole fraction of A in feed	c/m for copolymer	Mole fraction of A in copolymer
¹⁴ C-MMA	EMA	1	5230	1
		0.83	4178	0.83
		0.72	3355	0.69
		0.60	2578	0.54
		0.48	2248	0.48
		0.35	1668	0.36
		0.23	1137	0.25
¹⁴ C-MMA	CMA	1	4500	1
		0.80	3586	0.89
		0.73	3308	0.85
		0.60	2644	0.74
		0.44	1915	0.60
		0.37	1780	0.57
		0.31	1440	0.48
¹⁴ C-BMA	PMA	1	3227	1
		0.82	2506	0.76
		0.76	2250	0.68
		0.68	1967	0.59
		0.38	1030	0.30
¹⁴ C-MMA	S	1	3526	1
		0.80	3560	1
		0.50	3382	0.98
		0.30	3107	0.92

MMA = methyl methacrylate;
EMA = ethyl methacrylate;
CMA = cyclohexyl methacrylate;

BMA = benzyl methacrylate;
PMA = phenyl methacrylate;
S = Styrene.

The mechanism of initiation in the polymerization of methyl methacrylate initiated by an alkali metal has been discussed already.⁽⁴⁾ The process is likely to be a one-electron transfer.



in which a radical-ion is produced. Copolymers produced in such systems might grow, in part, by anionic processes and, in part, by radical processes. Sodium promotes a rapid polymerization of styrene by itself, but attempts to copolymerize the monomer with methyl methacrylate by anionic processes lead to products containing little styrene. Results obtained in the present work (see Table 1) indicate that the experi-

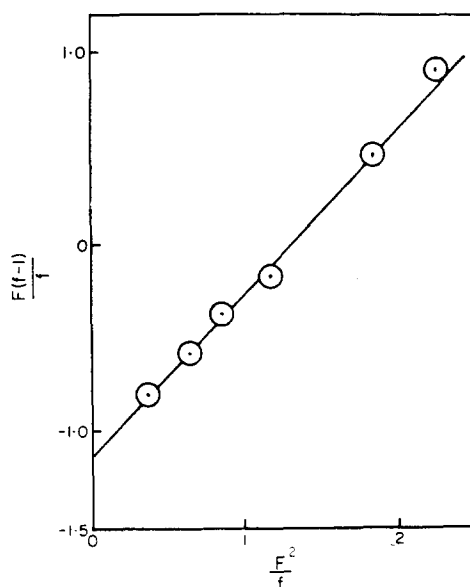


FIG. 1. Fineman-Ross plot for copolymerization of methyl and benzyl methacrylates at 30° in benzene with metallic sodium.

$$F = [\text{MMA}]/[\text{BMA}] \text{ in feed;}$$

$$f = [\text{MMA}]/[\text{BMA}] \text{ in copolymer.}$$

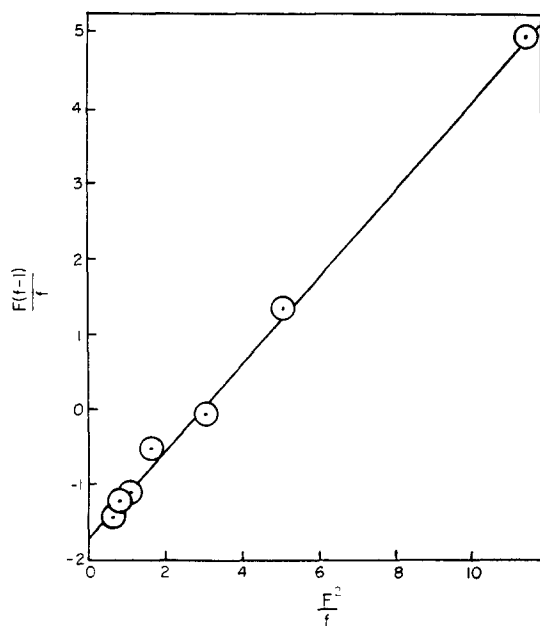


FIG. 2. Fineman-Ross plot for copolymerization of methyl and phenyl methacrylates at 30° in benzene with metallic sodium.

$$F = [\text{MMA}]/[\text{PMA}] \text{ in feed;}$$

$$f = [\text{MMA}]/[\text{PMA}] \text{ in copolymer.}$$

mental conditions were such that most of the polymer was produced by an anionic mechanism; if radical growth had been significant, substantial quantities of styrene would have been incorporated in the products.

There are close similarities between the monomer reactivity ratios for radical copolymerizations at 60° and those for copolymerizations performed at 30° with sodium in the presence of benzene, except for the case of cyclohexyl methacrylate with methyl methacrylate (see Table 2). For the radical copolymerizations of phenyl and methyl methacrylates, the values of the monomer reactivity ratios at 30° are close to those at 60°; it is very probable that the same consideration applies to the other radical copolymerizations referred to in Table 2.

TABLE 2. MONOMER REACTIVITY RATIOS

Monomer A	Monomer B	Radical		Sodium-catalysed	
		r_a	r_b	r_a	r_b
MMA	EMA	0.92	1.08 (60°)	0.98	1.09
MMA	CMA	0.86	1.15 (60°)	1.96	0.49
MMA	BMA	0.93	1.05 (60°)	0.90	1.17
MMA	PMA	0.53	1.67 (30°)	0.58	1.69
		0.56	1.72 (60°)		
BMA	PMA	0.65	1.42 (60°)	0.65	1.42

For key, see footnotes to Table 1.

As indicated already, the sodium-catalysed copolymerizations may not be purely anionic in character. Suppose that a fraction, f , of the copolymer is produced by a radical process. Let the values of a particular monomer reactivity ratio be r_1 and r_2 for radical and purely anionic reactions respectively, and let r_3 be the corresponding quantity for a system in which sodium is the catalyst; the values of r_2 and r_3 refer to systems involving the same gegenion and a reaction mixture of the same composition. It can be supposed that the relationship

$$r_3 = fr_1 + (1-f)r_2$$

would be applicable, so that

$$r_2 = (r_3 - fr_1)/(1-f) = r_3 + (r_3 - r_1)(f + f^2 + f^3 + \text{etc.})$$

When r_1 and r_3 have very similar values, as in most of the systems considered here, the monomer reactivity ratio for the purely anionic system must be close to that for the system involving metallic sodium. If r_1 and r_3 differ significantly, then r_2 must be different from r_3 by an amount depending upon the magnitude of the fraction f .

Consider the monomer reactivity ratio r_a for the copolymerization of cyclohexyl and methyl methacrylates; the values of r_1 and r_3 are 0.86 and 1.96 respectively, and so the value of r_a for a purely anionic copolymerization (i.e. r_2) must be at least 1.96. It can be argued similarly that, for the anionic copolymerization of these monomers under the conditions previously specified, r_b cannot exceed 0.49. The relationship between r_1 , r_2 , r_3 and f indicates that under certain conditions, the experimentally determined values of monomer reactivity ratios may vary with the conversion, quite apart from

any effects arising from a gradual change in the composition of the monomer mixture. Suppose that initiation involves the production of radical-ions and that the life-time of the anions is appreciably greater than that of the radicals. In the early stages of the copolymerization, f may be fairly large and r_2 and r_3 may differ significantly. At later stages, when there are more growing anions than radicals, f becomes smaller and any differences between r_2 and r_3 becomes smaller; as polymerization proceeds, therefore,⁽²⁾ the experimentally determined monomer reactivity ratios tend to values corresponding to purely anionic systems. There are clear indications that effects of this type can be detected in certain systems.⁽⁵⁾ The reactivities of the various monomers towards reference active centres can be compared (see Table 3), by considering the appropriate monomer reactivity ratios.⁽⁶⁾ In constructing Table 3, the velocity constant for the reaction of monomeric methyl methacrylate with an active centre has been taken as standard. The relative reactivities of the monomers seem to be almost independent of the nature of the reference active centre, except that monomeric cyclohexyl methacrylate is comparatively unreactive towards anions, at least in the environment considered here.

TABLE 3. RELATIVE REACTIVITIES OF MONOMERS

Reference polymer active centre	MMA (standard)	Monomer			
		EMA	CMA	BMA	PMA
MMA radical	1.00	1.09	1.16	1.08	1.78
MMA anion	1.00	1.02	≤ 0.51	1.11	1.72
EMA radical	1.00	1.08	—	—	—
EMA anion	1.00	1.09	—	—	—
CMA radical	1.00	—	1.15	1.00	—
CMA anion	1.00	—	≤ 0.49	—	—
BMA radical	1.00	—	1.14	1.05	1.62
BMA anion	1.00	—	—	1.17	1.80
PMA radical	1.00	—	—	1.21	1.72
PMA anion	1.00	—	—	1.19	1.69

For key, see footnotes to Table 1.

The rather unusual behaviour of cyclohexyl methacrylate probably results from a steric effect in anionic growth reactions, since the cyclohexyl group is unlikely to be abnormal in its electronic properties. A later paper⁽⁵⁾ will show that the monomer reactivity ratios for the sodium-catalysed copolymerization of cyclohexyl and methyl methacrylates are significantly altered if benzene is replaced by another diluent, or if sodium is replaced by another alkali metal. These observations confirm that association of the polymer anion with the gegenion and solvation of these ions can have profound effects upon the characteristics of the various growth processes in anionic polymerizations.

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REFERENCES

- (1) J. C. Bevington and B. W. Malpass, *J. Polym. Sci.* **2**, 1893 A (1964).
- (2) J. C. Bevington and B. W. Malpass, *Europ. Polym. J.* **1**, 19 (1965).
- (3) M. Fineman and S. D. Ross, *J. Polym. Sci.* **5**, 259 (1950).
- (4) K. F. O'Driscoll and A. V. Tobolsky, *J. Polym. Sci.* **37**, 373 (1959).
- (5) J. C. Bevington and F. S. Rankin, to be published.
- (6) See, for example, J. C. Bevington, *Radical Polymerization*, p. 79, Academic Press, London (1961).

Résumé—Les copolymérisations des esters de méthyl, éthyl, cyclohexyl, benzyl et phényl de l'acide méthacrylique, déclenchées par le sodium métal, ont été étudiées. Ces réactions ont lieu à 30° en milieu benzénique. Pour chaque réaction un monomère a été marqué au ^{14}C . La composition du copolymère obtenu a été vérifiée par l'analyse. Les taux de transformation ont été calculés au moyen de la relation de Fineman et Ross. Dans les cas de la copolymérisation du méthyl et de celle du cyclohexyl méthacrylate, les taux de transformation du monomère diffèrent suivant que l'on a à faire à des réactions avec radicaux libres ou à des réactions déclenchées par un métal alcalin. Dans les autres cas de copolymérisation étudiés on a seulement de légères différences suivant le type de réaction.

Sommario—Gli esteri metilici, etilici, cicloesilici, benzilici e fenilici dell'acido metacrilico sono stati studiati in copolimerizzazioni iniziate dal sodio metallico. Le reazioni avvennero a 30°, con il benzene in qualità di diluente. Per ciascun sistema, un monomero venne etichettato con ^{14}C ; il copolimero che ne risultò fu provato e se ne dedusse la composizione. Vennero calcolati i rapporti di reattività monomerica secondo Fineman e Ross. Per la copolimerizzazione dei metacrilati di metile e di cicloesile esistono notevoli differenze fra i rapporti di reattività monomerica per le reazioni radicali libere e quelle iniziate dal metallo alcalino. Per le altre copolimerizzazioni esaminate, si hanno unicamente piccole differenze fra i risultati ottenuti per i sistemi dei due tipi.

Zusammenfassung—Methyl-, Äthyl-, Cyclohexyl-, Benzyl- und Phenylester der Methacrylsäure wurden bei durch metallisches Natrium eingeleiteten Mischpolymerisationen untersucht. Die Reaktionen wurden mit Benzin als Verdünnungsmittel bei 30° durchgeführt. Für jedes System wurde ein Monomer durch ^{14}C kenntlich gemacht; das entstandene Polymer wurde geprüft und seine Zusammensetzung bestimmt. Die Reaktivitätsverhältnisse der Monomere wurden nach dem Verfahren von Fineman und Ross berechnet. Bei der Mischpolymerisation von Methyl- und Cyclohexylmethacrylaten ergeben sich beträchtliche Unterschiede zwischen den Reaktivitätsverhältnissen der Monomere für Reaktionen freier Radikale und solchen, die durch das Alkalimetall eingeleitet wurden. Bei den anderen untersuchten Mischpolymerisationen treten zwischen den für die beiden Arten von Systemen gewonnenen Ergebnisse nur geringe Unterschiede auf.