RADICAL POLYMERIZATIONS INVOLVING ESTERS OF VINYL ALCOHOL—II.

COPOLYMERIZATIONS

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Abstract—[14]C-vinyl acetate has been used in studies at 60° of radical copolymerizations with methyl methacrylate and with vinyl formate, propionate, butyrate, phenylacetate and benzoate. ^{14}C-methyl methacrylate has been used similarly with the series of vinyl esters. Monomer reactivity ratios have been calculated. Comparisons have been made of the reactivities of the various monomers towards the polyvinyl acetate, polymethyl methacrylate and benzoyloxy radicals.

[14]C-VINYL acetate has been used in studies of radical copolymerizations with methyl methacrylate, vinyl formate, vinyl propionate, vinyl butyrate, vinyl phenylacetate and vinyl benzoate; ^{14}C-methyl methacrylate has been similarly used with vinyl acetate and these other esters of vinyl alcohol. Tracer techniques are particularly useful for the analysis of copolymers derived from systems such as these. Other methods of analysis are unreliable either because the comonomers have very similar compositions and structures, or because only small quantities of one of the monomers enter the copolymers.

The work described here forms part of a study of the reactivities, towards reference radicals, of monomers having closely related structures. It has been shown already[1] that the esters of vinyl alcohol differ significantly in their reactivities towards the benzoyloxy radical.

EXPERIMENTAL

The labelled samples of methyl methacrylate and vinyl acetate were prepared by exchange processes involving the unlabelled monomer with ^{14}C-methanol and ^{14}C-acetic acid respectively. The procedure for ^{14}C-methyl methacrylate has been described.[2] A mixture of vinyl acetate (300 g), acetic acid (53 g), ^{14}C-sodium acetate (2 mg, 0·2 mc), cupric acetate (0·1 g), mercuric acetate (3·5 g) and conc. H_2SO_4 (0·5 g) was stirred at 75° for 15 min and then at 30° for 60 hr. The labelled monomer was recovered and purified by fractional distillation in nitrogen, followed by pre-polymerization; it was distilled on the vacuum line immediately before use. Unlabelled monomers were purified similarly. The specific activities of labelled samples of the monomers lay between 0·1 and 0·2 $\mu c/g$.

Copolymerizations were performed at 60° in dilatometers in the complete absence of air; 70 per cent solutions of monomers in benzene were used with benzoyl peroxide at 1 g/l. as initiator. Reactions were stopped at about 5 per cent conversion (based on total monomer); copolymers were recovered by precipitation in n-hexane and purified by reprecipitation from benzene solutions. Gas counting was used for the assay of ^{14}C; a corrected counting rate of 9000 counts/min is equivalent to a specific activity of about 1 $\mu c/g$ of carbon.

Calculation of the composition of a copolymer from the counting rates for the copolymer and the homopolymer derived from the labelled monomer is illustrated by considering the case of vinyl formate with ^{14}C-vinyl acetate. Let the copolymer be represented by the empirical formula

$(C_3H_4O_2)_{1-x}(C_4H_6O_2)_x$; for assay by gas counting, it is necessary to consider only the carbon contents of the labelled and unlabelled units so that

$$\frac{\text{counting rate for copolymer}}{\text{counting rate for polyvinyl acetate}} = r = \frac{4x}{4x + 3(1-x)}$$

so that

mole fraction of vinyl acetate in copolymer $= x = 3r/(4-r)$.

The procedure of Fineman and Ross[3] was used for determination of monomer reactivity ratios. The slopes and intercepts for the lines were calculated by the method of least squares.

RESULTS

Table 1 refers to the system of ^{14}C-vinyl acetate with vinyl formate. Eight copolymerizations were similarly performed for each of the other vinyl esters with ^{14}C-vinyl acetate. The Fineman–Ross plots are shown in Figs. 1–5 and the derived monomer

TABLE 1. COPOLYMERIZATIONS OF ^{14}C-VINYL ACETATE AND VINYL FORMATE

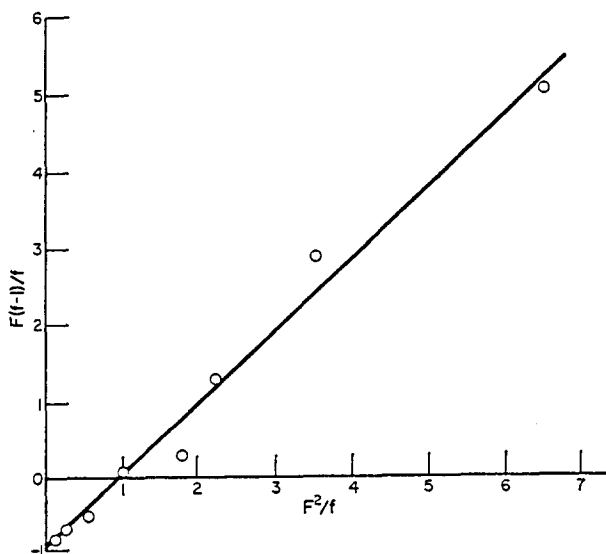| Mole fraction of vinyl acetate in feed	Counts/min for copolymer	Calculated mole fraction of vinyl acetate in copolymer
1·00	2052	1·00
0·86	1814	0·85
0·79	1732	0·80
0·69	1551	0·70
0·60	1280	0·55
0·51	1192	0·51
0·35	832	0·34
0·20	537	0·21
0·10	274	0·10

FIG. 1. Fineman–Ross plot for radical polymerization at 60° of vinyl acetate (monomer—1) and vinyl formate (monomer—2). $F = (M_1)/(M_2)$ in feed
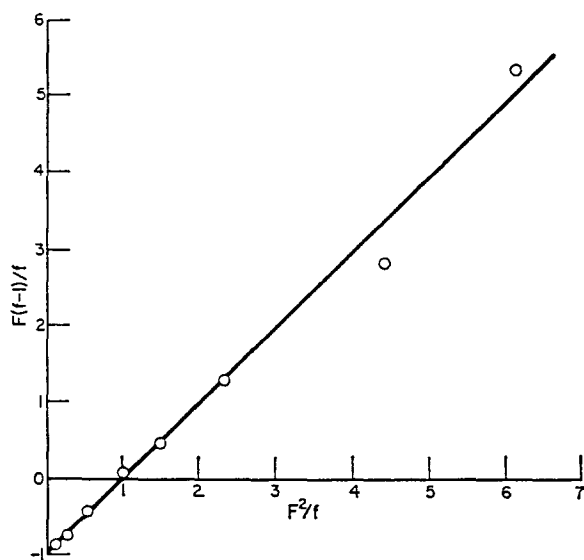$f = (M_1)/(M_2)$ in copolymer.

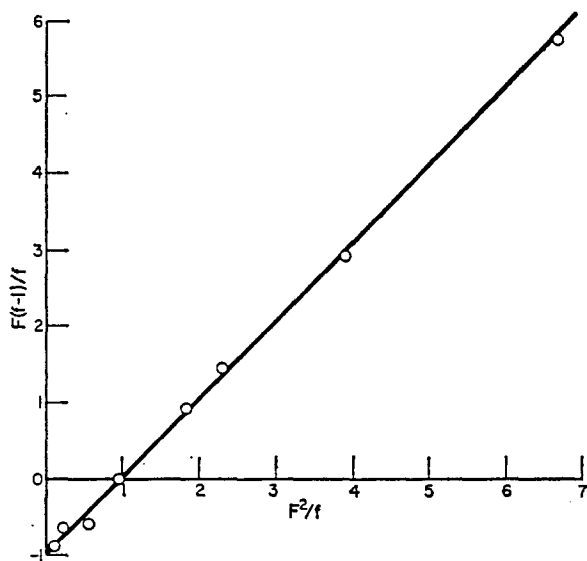FIG. 2. See Fig. 1, monomer—1 = vinyl acetate
monomer—2 = vinyl propionate.

FIG. 3. See Fig. 1, monomer—1 = vinyl acetate
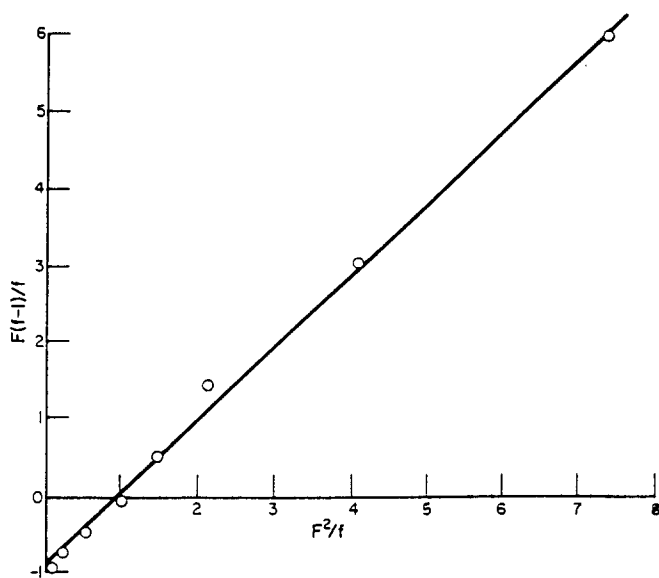monomer—2 = vinyl butyrate.

FIG. 4. See Fig. 1, monomer—1 = vinyl acetate
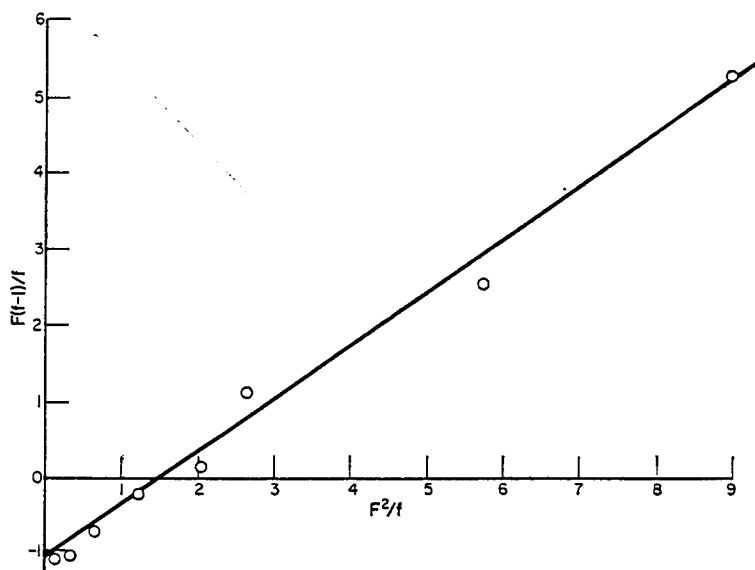monomer—2 = vinyl phenylacetate.

FIG. 5. See Fig. 1, monomer—1 = vinyl acetate
monomer—2 = vinyl benzoate.

reactivity ratios are given in Table 2. The probable error in each of the monomer reactivity ratios is estimated to be less than 0.07.

TABLE 2. MONOMER REACTIVITY RATIOS FOR COPOLY-
MERIZATIONS WITH VINYL ACETATE (MONOMER—1)

Monomer—2	Reactivity ratios	
	r_1	r_2
vinyl formate	0·94	0·95
vinyl propionate	0·98	0·98
vinyl butyrate	1·00	0·97
vinyl phenylacetate	0·96	0·92
vinyl benzoate	0·70	1·13

The copolymerization of methyl methacrylate with vinyl acetate was examined by performing one set of experiments with ^{14}C-methyl methacrylate and another with ^{14}C-vinyl acetate; Fig. 6 shows that there was satisfactory agreement. Other vinyl
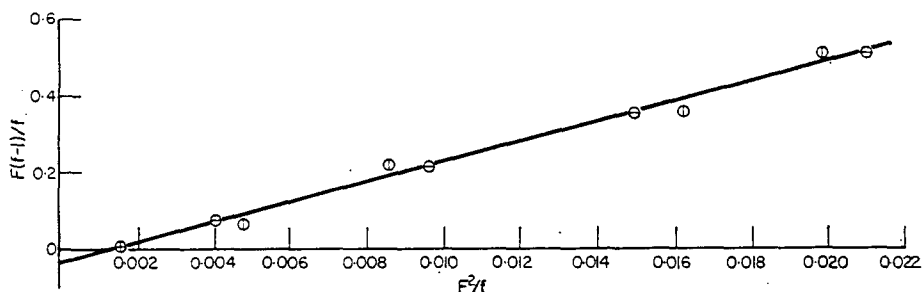
FIG. 6. See Fig. 1, monomer—1 = methyl methacrylate
monomer—2 = vinyl acetate
⊖—labelled vinyl acetate
⊕—labelled methyl methacrylate.

esters were studied using ^{14}C-methyl methacrylate (see Table 3); for each system, five copolymerizations were performed. It is estimated that the probable errors in r_1 and r_2 are 2.5 and 0.01 respectively.

TABLE 3. MONOMER REACTIVITY RATIOS FOR
COPOLYMERIZATIONS WITH METHYL METHACRYLATE
(MONOMER—1)

Monomer—2	Reactivity ratios	
	r_1	r_2
vinyl formate	28·6	0·05
vinyl acetate	26·0	0·03
vinyl propionate	24·0	0·03
vinyl butyrate	25·0	0·03
vinyl phenylacetate	26·4	0·03
vinyl benzoate	20·3	0·07

DISCUSSION

The monomer reactivity ratios in Table 2 are regarded as quite reliable although those referring to vinyl acetate with vinyl benzoate disagree with values previously reported[4] ($r_1 = 0.35 \pm 0.09$, $r_2 = 0.99 \pm 0.13$). The copolymerizations involving methyl methacrylate are associated with fairly large errors arising from the use of labelled methyl methacrylate. That monomer enters the copolymers preferentially and, in many cases, the analysis of a copolymer depends upon comparison of the rather similar counting rates for copolymer and labelled homopolymer.

From the sets of values of r_1 in Tables 2 and 3, the velocity constants for the additions at $60°$ of the vinyl esters to polyvinyl acetate and polymethyl methacrylate radicals can be compared (see Table 4 which also refers to the reactivities of the monomers towards the benzoyloxy radical[11]). The monomers, except for vinyl benzoate, are very similar in their reactivities towards the polymer radicals but there are significant differences between their reactivities towards the benzoyloxy radical.

TABLE 4. RELATIVE VALUES OF VELOCITY CONSTANTS AT $60°$ FOR ADDITION OF MONOMERS TO REFERENCE RADICALS

Monomer	Relative velocity constant for addition to		
	polyvinyl acetate radical	polymethyl methacrylate radical	benzoyloxy radical
vinyl formate	1·06	0·89	0·83
vinyl acetate (standard)	1·00	1·00	1·00
vinyl propionate	1·02	1·08	1·11
vinyl butyrate	1·00	1·03	2·42
vinyl phenylacetate	1·04	0·97	1·81
vinyl benzoate	1·43	1·26	0·94

Attention has already been drawn[5] to the similarity between the reactivities of the vinyl esters in copolymerizations. This situation is expected and has been confirmed for other series of monomers thus many esters of methacrylic acid have similar reactivities towards polymer radicals although there are distinct differences for the phenyl ester;[6] for these monomers also, there are larger differences between their reactivities towards the more polar benzoyloxy radical.[7]

The rather high values for r_1 and low values for r_2 in Table 3 confirm that the vinyl esters are considerably less reactive than methyl methacrylate towards the polymethyl methacrylate radical and also towards their conjugate polymer radicals.

Monomer reactivity ratios are commonly used to derive values for the monomers of the parameters Q and e[8] or α and β.[9] These parameters are frequently very useful for correlation of the reactivities of monomers.

The vinyl esters considered here are found to have values of Q close to 0.03 and values of β of about 3; these values reflect the low general reactivity of the monomers. The values of e and α are scattered and inconsistent; they do not agree with published values[10,11] some of which were deduced from monomer reactivity ratios which may not have been reliable.[10] It must be concluded that the treatments of Alfrey and

Price[8] and Bamford, Jenkins and Johnston[9] cannot properly be applied to discriminate between the small differences between members of sets of closely related monomers.

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Résumé—De l'acétate de vinyle marqué au ^{14}C a été utilisé dans des études de copolymerisations radicalaires à 60° avec le méthacrylate de méthyle et les formiate, propionate, butyrate, phénylacétate et benzoate de vinyle. Du méthacrylate de méthyle marqué au ^{14}C a été aussi utilisé dans une étude similaire avec les esters vinyliques. On a calculé les rapports de réactivité des monomères et on a comparé les réactivités des différents monomères vis-à-vis des radicaux poly(acétate de vinyle), poly-(méthacrylate de méthyle) et benzoyloxy.

Sommario—L'acetato di vinile ^{14}C è stato usato in studi a 60° di copolimerizzazioni radicaliche con metacrilato di metile e formiato, propionato, butirrato, fenilacetato e benzoato di vinile. Il metacrilato di metile ^{14}C è stato usato allo stesso modo con le serie di esteri di vinile. Sono stati calcolati i rapporti della reattività del monomero. Sono state paragonate le reattività dei vari monomeri verso l'acetato di polivinile, il polimetil metacrilato e i radicali benzoilossilici.

Zusammenfassung—^{14}C-Vinylacetat wurde verwendet bei Untersuchungen der Radikal-Copolymerisationen mit Methylmethacrylat und mit Vinylformiat, -propionat, -butyrat, -phenylacetat und—benzoat bei 60°. ^{14}C-Methylmethacrylat wurde in entsprechender Weise mit dieser Serie von Vinylestern verwendet. Die Reaktivitätsverhältnisse der Monomeren wurden berechnet. Die Reaktivitäten der verschiedenen Monomeren gegenüber Polyvinylacetat, Polymethylmethacrylat und Benzoylradikalen wurden verglichen.