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REACTIVITIES OF MONOMERS TOWARDS REFERENCE RADICALS

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Abstract—Tracer techniques have been used to compare the reactivities of monomers towards reference radicals at 60°. The monomers examined were methyl methacrylate, methyl acrylate, methyl α-chloracrylate and methyl α-bromacrylate; the reference radicals were the polymethyl methacrylate and the benzoyloxy radicals. Attempts to apply the Q and e scheme to the results were not wholly successful. It is apparent, however, that polar factors are of great importance in reactions involving the benzoyloxy radical, and that it is possible to estimate the relative reactivity of a monomer towards this radical from data obtained from study of the copolymerization of the monomer with methyl methacrylate.

This paper is concerned with comparisons of the reactivities of methyl acrylate, methyl methacrylate, methyl α-chloracrylate and methyl-α-bromacrylate towards the polymethyl methacrylate and benzoyloxy radicals. Earlier papers[1-4] have contained accounts of studies involving other series of monomers and these reference radicals. The reactivities of the monomers towards the polymer radical have been compared by examination of data concerning copolymerizations. Determinations of the relative numbers of benzoyloxy and phenyl end-groups in polymers prepared using benzoyl peroxide have provided information concerning the reactivities of the monomers towards the benzoyloxy radical.

The studies concerning the benzoyloxy radical have involved the use of two types of ^{14}C-benzoyl peroxide; R-peroxide is labelled in the benzene rings and C-peroxide at the carboxyl carbon atoms. The experimental results lead to values of the ratio of the velocity constants for the competing reactions.

$$C_6H_5.CO.O. \longrightarrow C_6H_5. + CO_2 \qquad (1)$$

$$C_6H_5.CO.O. + CH_2{:}CHX \longrightarrow C_6H_5.CO.O.CH_2.CHX. \qquad (2)$$

Copolymers have been analysed by tracer methods and monomer reactivity ratios have been calculated; the ratio r_1 is equal to k_3/k_4.

$$\left(\begin{array}{l}\text{polymethyl methacrylate}\\ \text{radical}\end{array}\right)+\left(\begin{array}{l}\text{methyl}\\ \text{methacrylate}\end{array}\right)\longrightarrow\left(\begin{array}{l}\text{polymethyl methacrylate}\\ \text{radical}\end{array}\right) \qquad (3)$$

$$\left(\begin{array}{l}\text{polymethyl methacrylate}\\ \text{radical}\end{array}\right)+\left(\begin{array}{l}\text{second}\\ \text{monomer}\end{array}\right)\longrightarrow\left(\begin{array}{l}\text{second polymer}\\ \text{radical}\end{array}\right) \qquad (4)$$

EXPERIMENTAL

Materials

The preparations and purifications of the labelled and unlabelled samples of methyl methacrylate (MMA) and methyl α-chloracrylate (MCA) have been described.(5) Inhibitor was removed from commercial methyl acrylate (MA) which was then washed with water, dried with Na_2SO_4 and fractionated in N_2. Methyl α-bromacrylate (MBA) was prepared by dehydrobromination of methyl α,β-dibromopropionate made by addition of Br_2 to MA. It was distilled on the vacuum line and stored frozen in liquid N_2 because of a tendency to polymerize in the liquid state even at −25°.

The preparation of the R- and C-labelled samples of benzoyl peroxide (BP), the purification of these and the unlabelled material have been described.(6) Azoisobutyronitrile (AZBN) was purified by recrystallization from diethyl ether. Solvents and precipitants were of AR grade.

Polymerizations were performed in sealed dilatometers in the complete absence of air and allowed to proceed to about 5 per cent conversion. Copolymers and homopolymers of MCA and MBA were purified by precipitation in hexane from solutions in dioxane; other polymers were purified by precipitation in methanol from solutions in benzene. Tests showed that two precipitations were sufficient to remove uncombined labelled monomers or initiators from polymers.

Materials containing ^{14}C were assayed by gas counting. A counting rate of 9000 counts/min is equivalent to a specific activity of about 1 $\mu c/g$ of carbon. The assay of ^{36}Cl has been described.(5)

RESULTS

Methyl acrylate

^{14}C-MMA was copolymerized with MA at 60°, using benzene solutions (containing 60% by volume of the diluent) and B.P. (at 1 g/l.) as initiator. Results are shown in Table 1. The Fineman–Ross(7) plot (Fig. 1) leads to

TABLE 1. COPOLYMERIZATION OF ^{14}C-MMA WITH MA

Mole fraction MMA in feed	Count/min for polymer	Mole fraction MMA in product
1·00	5156	1·00
0·86	4770	0·91
0·80	4666	0·88
0·70	4364	0·82
0·60	4074	0·75
0·50	3655	0·66
0·35	2915	0·51
0·20	2175	0·37
0·05	736	0·12

$$r_1 = 1{\cdot}69 \text{ and } r_2 = 0{\cdot}34$$

For this and other copolymerizations, MMA is regarded as monomer$_1$.

MA was polymerized at 60° in benzene solutions, using monomer concentrations up to 2·87 mole/l. In certain experiments, R-BP was used at 1 g/l.; in parallel experiments, C-BP was used. Even for dilute solutions of monomer, there was autoacceleration (see Fig. 2) leading to difficulties in connection with calculations of rates of initiation, but the corresponding polymerizations with the two types of labelled BP gave very similar conversion/time plots and were allowed to proceed to the same total conversion. An experiment with R-BP leads to a value for the ratio

$$\frac{\text{no. of monomer units}}{\begin{pmatrix}\text{no. of benzoyloxy}\\ \text{end-groups}\end{pmatrix}+\begin{pmatrix}\text{no. of phenyl}\\ \text{end-groups}\end{pmatrix}} = p$$

The corresponding experiment with C—BP leads to a value for

$$\frac{\text{no. of monomer units}}{\text{no. of benzoyloxy end-groups}} = q$$

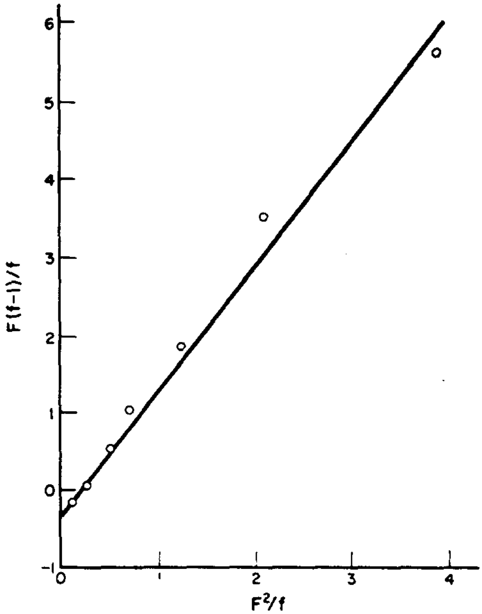

FIG. 1. Fineman-Ross plot for copolymerization of MMA with MA. F = [MMA]/[MA] in feed; f = [MMA]/[MA] in copolymer. Equation used in form: $F(f-1)/f = r_1F^2/f - r_2$

Results are summarized in Table 2. The fraction (x) is equal to

$$\frac{p}{q} = \frac{\text{no. of benzoyloxy end-groups}}{\begin{pmatrix}\text{no. of benzoyloxy}\\ \text{end-groups}\end{pmatrix} + \begin{pmatrix}\text{no. of phenyl}\\ \text{end-groups}\end{pmatrix}}$$

and varies with the concentration of monomer in the reaction mixture (see Fig. 3). The reciprocal of the slope of the line, equal to k_2/k_1, is 0·12 mole^{-1} litre^{+1}.

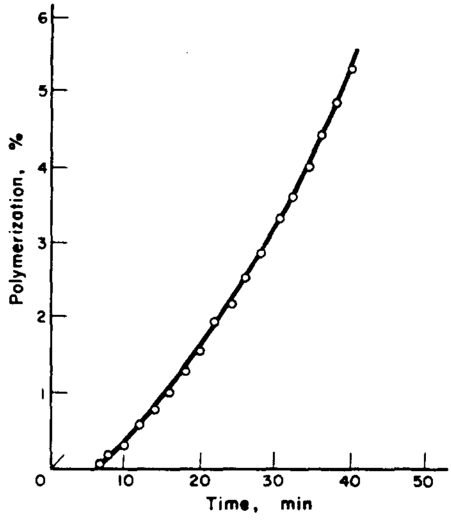

FIG. 2. Conversion vs. time plot for polymerization at 60° of MA at a concentration of 2·87 mole/l. in benzene.

TABLE 2. EXPERIMENT WITH ^{14}C-BP AND MA

[Monomer] in mole/l.	Type of ^{14}C-BP	Count/min for polymer	p	q	x
0·71	R	463	795	—	0·08
0·71	C	32	—	10200	
0·85	R	349	1060	—	0·10
0·85	C	31	—	10600	
1·02	R	349	1060	—	0·11
1·02	C	33	—	9920	
1·21	R	302	1220	—	0·12
1·21	C	33	—	9920	
1·58	R	221	1670	—	0·16
1·58	C	31	—	10600	
2·87	R	80	4600	—	0·20
2·87	C	14	—	23400	

Count/min for R-peroxide = 210,500; count min for C-peroxide = 187,100; p, q, and x are defined in the text.

Methyl α-chloracrylate

A tracer study of the copolymerization of MMA and MCA has been described already.(5) One set of experiments involved the use of ^{14}C-MMA and another the use of ^{36}Cl-MCA. Results are shown in Table 3 and the Fineman–Ross plot (See Figure 4) leads to

$$r_1 = 0{\cdot}15 \text{ and } r_2 = 2{\cdot}00$$

The reactivity of MCA towards the benzoyloxy radical was assessed by a procedure similar to that used in the case of MA. Parallel experiments involved R-BP and C-BP

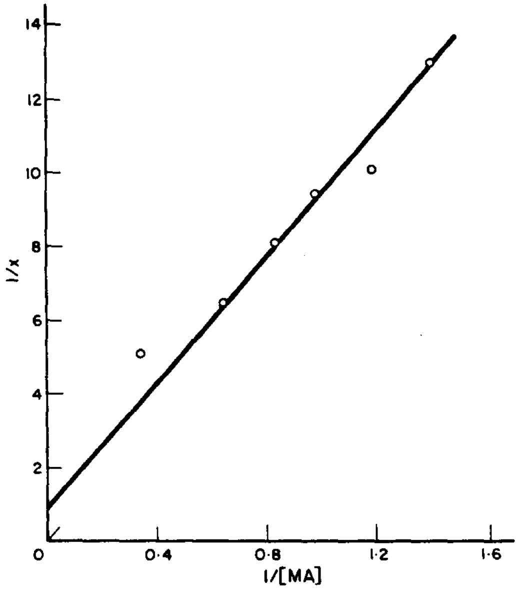

FIG. 3. Relationship between x and [MA] for polymerization at 60°. x = (no. of benzoyloxy end-groups)/(total no. of benzoyloxy and phenyl end-groups).

TABLE 3. COPOLYMERIZATIONS OF MMA WITH MCA

Mole fraction of MMA in feed	Count/min for polymer (^{14}C)	Count/min for polymer (^{36}Cl)	Mole fraction of MMA in product
1·00	3526	—	1·00
0·86	2129	—	0·55
0·86	—	43*, 44	0·64*, 0·64
0·80	1966	—	0·50
0·70	1827	—	0·46
0·70	—	63*, 65	0·45*, 0·44
0·60	1202	—	0·29
0·60	—	71*, 76	0·37*, 0·35
0·50	1070	—	0·26
0·50	—	81*, 81	0·27*, 0·29
0·35	740	—	0·18
0·35	—	87*, 90	0·21*, 0·20
0·20	416	—	0·10
0·20	—	96*, 97	0·11*, 0·11
0·06	135	—	0·03
0	—	106*, 105	0*, 0

* Assay for ^{36}Cl by scintillation counting.
Other assays for ^{36}Cl by sleeve counter.

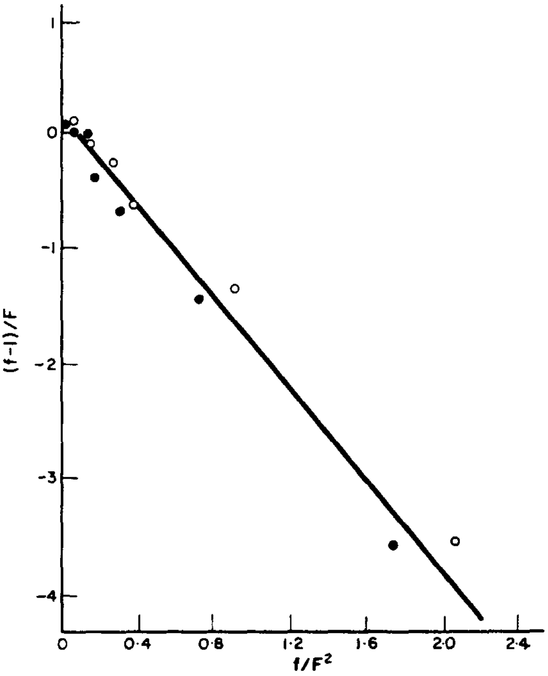

FIG. 4. Fineman–Ross plot for copolymerization of MMA with MCA. F = [MMA]/[MCA] in feed; f = [MMA]/[MCA] in copolymer. Equation used in form: $(f-1)/F = r_1 - r_2 f/F^2$; ○, ^{36}Cl by scintillation counting; ●, ^{14}C by gas counting.

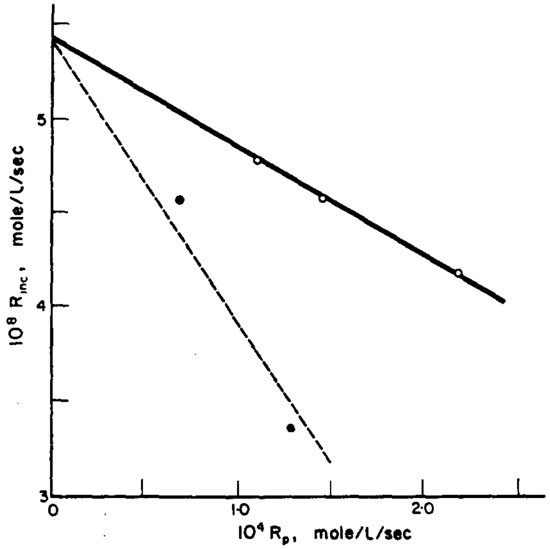

FIG. 5. Relationship between rate of polymerization of MCA and rate at which fragments derived from BP are incorporated in polymer; AZBN used in second initiator; [R–BP] = 2g/l.; ○, MCA = 2·87 mole/l. in benzene; ●, MCA = 1·57 mole/l. in benzene.

at 2 g/l.; the concentration of monomer ranged between 9·54 m/l. (bulk) and 1·57 m/l. (in benzene). There was good agreement between the rates of contraction observed in experiments differing only in the position of the labelling atoms in the initiator. At the lower concentrations of monomer, polymer was precipitated during the reaction. Rates of polymerization were calculated on the assumption that 26 per cent contraction corresponded to 100 per cent polymerization; this factor was based upon a measurement of the density of the polymer in solution in DMF. The quoted rates of polymerization must be regarded as only approximate.

TABLE 4. EXPERIMENTS WITH ^{14}C-BP AND MCA

[Monomer] in mole/l.	Type of ^{14}C-BP	Count/min for polymer	P	q	x
1·57	R	497	741	—	0·16
1·57	C	71	—	4610	
2·01	R	392	940	—	0·17
2·01	C	59	—	5550	
2·87	R	276	1330	—	0·22
2·87	C	53	—	6180	
4·01	R	153	2410	—	0·36
4·01	C	49	—	6680	
6·48	R	75	4910	—	0·51
6·48	C	34	—	9630	
9·54	R	46	8010	—	0·44
9·54	C	18	—	18200	

Count/min for R-peroxide = 210,500; count/min for C-peroxide = 187,100; p, q and x are defined in the text.

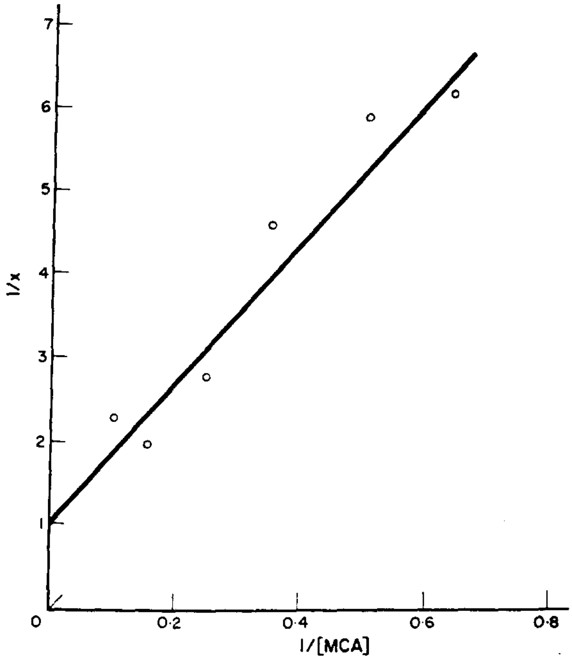

FIG. 6. Relationship between x and MCA for polymerization at 60° (see legend to Fig. 3).

The significance of transfer to initiator during the polymerization of MCA was assessed from mixed initiator experiments.(8) Results are displayed in Fig. 5; it is concluded that, for this monomer at 60°, transfer to BP is unimportant.

The results from experiments involving the two types of labelled peroxide are shown in Table 4 and Fig. 6; k_2/k_1 is equal to 0·11 mole^{-1} litre^{+1} at 60°.

Methyl α-bromacrylate

Copolymerizations of ^{14}C-MMA and MBA at 60° involved solutions of the monomers in benzene (60% by volume) and AZBN (at 0·3 g/l.) as initiator. Results shown in Table 5 and Fig. 7 lead to

$$r_1 = 0{\cdot}23 \text{ and } r_2 = 2{\cdot}08$$

TABLE 5. COPOLYMERIZATIONS OF ^{14}C-MMA WITH MBA

Mole fraction of MMA in feed	Count/min for polymer	Mole fraction of MMA in product
1·00	1167	1·00
0·83	773	0·61
0·80	744	0·58
0·76	679	0·53
0·72	587	0·45
0·64	520	0·39
0·51	389	0·29
0·36	263	0·19
0·25	183	0·13

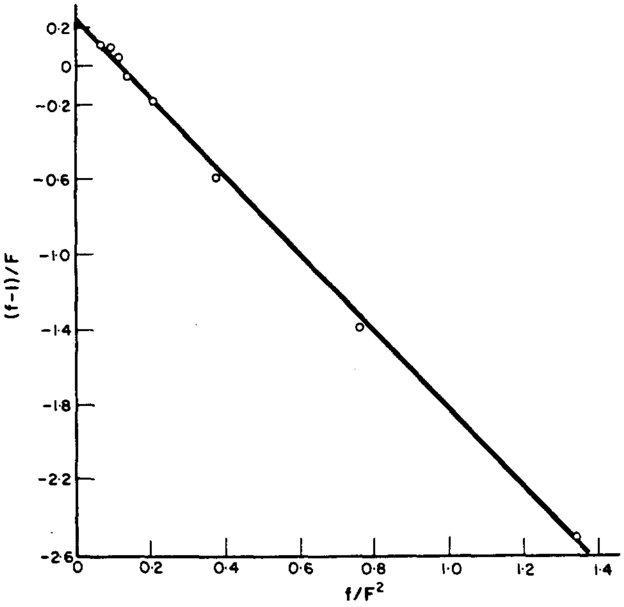

FIG. 7. Fineman–Ross plot for copolymerization of MMA with MBA. F = [MMA]/[MBA] in feed; f = [MMA]/[MBA] in copolymer. Equation used in form: $(f-1)/F = r_1 - r_2 f/F^2$.

The reactivity of MBA towards the benzoyloxy radical was found by the procedure used for MA and MCA. Polymerizations were performed at 60° with various concentrations of monomer in benzene and either R-BP or C-BP at 2 g/l. Polymers were not precipitated during the reactions and conversion time plots were linear. The rates of reaction were not always reproducible and there were occasionally differences of as much as 10 per cent between the rates observed in parallel experiments. These differences are attributed to varying contributions from alternative methods of initiation. Results are given in Table 6; from Fig. 8, k_2/k_1 is 0·23 mole^{-1} litre^{+1} at 60°.

TABLE 6. EXPERIMENTS WITH ^{14}C-BP AND MBA

[Monomer] in mole/l.	Type of ^{14}C-BP	Count/min for polymer	p	q	x
0·70	R	673	533	—	0·10
0·70	C	64	—	5110	
0·85	R	468	767	—	0·16
0·85	C	66	—	4960	
1·00	R	476	754	—	0·23
1·00	C	99	—	3310	
1·25	R	435	825	—	0·26
1·25	C	104	—	3150	
1·60	R	457	785	—	0·22
1·60	C	91	—	3600	
2·80	R	213	1680	—	0·60
2·80	C	116	—	2820	

Count/min for R-peroxide = 205,000; count/min for C-peroxide = 187,100; p, q and x are defined in the text.

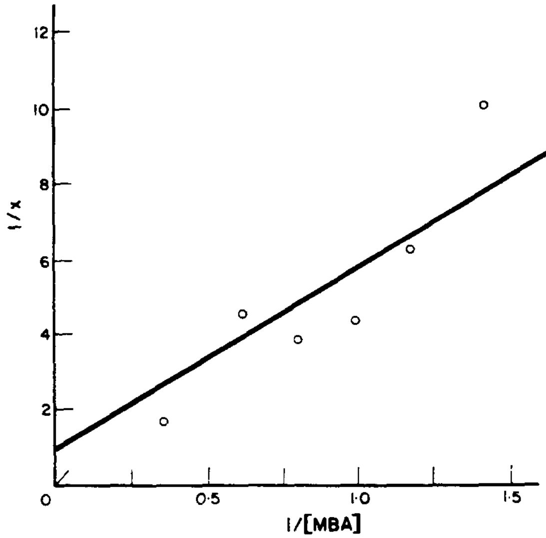

FIG. 8. Relationship between x and [MBA] for polymerizations at 60° (see legend to Fig. 3).

DISCUSSION

The results of the experiments involving labelled BP must be considered in some detail. The auto-acceleration observed during the homo-polymerizations of MA does not affect the validity of the results concerning the benzoyloxy radical. The acceleration is connected with the termination step in the polymerization and not with the initiation processes. The close agreement between the conversion/time plots for parallel experiments with R- and C-BP and the fact that parallel polymerizations were run to the same conversion and for the same time ensure the validity of the comparisons between the numbers of benzoyloxy and phenyl end-groups.

There were only minor differences between the rates of parallel polymerizations involving MCA even in those cases where polymer was precipitated. The differences between the rates in some of the pairs of experiments involving MBA were not very large.

The mixed initiator experiments for MCA provide no indication that transfer to BP is important. If transfer to initiator had been significant, the lines in Fig. 5 would have had positive slopes. The negative slopes are attributed to errors in the calculations of rates of polymerization. It is believed that the conversion factor varied with the solvent power of the reaction medium and the average molecular weight of the polymer.

From the values of r_1 (i.e. k_3/k_4) for the various copolymerizations, the relative reactivities towards the polymethyl methacrylate radical of MMA, MA, MCA, and MBA are 1·00 (standard), 0·59, 6·67, and 4·35 respectively. On this scale, the relative reactivities towards the same reference radical of styrene, vinyl acetate and acrylonitrile are 2·2, 0·05 and 0·74 respectively. The relative reactivities of MMA,(1) MA, MCA and MBA towards the benzoyloxy radical are derived from the values of k_2/k_1; they are 1·00, 0·40, 0·37 and 0·77 respectively. On this scale, the corresponding relative reactivities of styrene, vinyl acetate and acrylonitrile(2) are 8·33, 3·00 and $\leqslant 0{\cdot}42$ respectively and those of the ethyl, phenyl, benzyl and cyclohexyl esters of methacrylic acids(3) are, respectively 1·14, 1·94, 1·22 and 1·74.

These comparisons of the reactivities of monomers towards reference radical show that although MCA and MBA are comparatively reactive towards the polymethyl methacrylate radical, they are comparatively unreactive towards the benzoyloxy radical. On the other hand, vinyl acetate is rather unreactive towards the reference polymer radical but is quite reactive towards the benzoyloxy radical. These apparent anomalies can be accounted for when it is recognized that the rates of reactions between radicals and monomers are controlled in part by the intrinsic reactivities of the reactants and in part by polar factors.

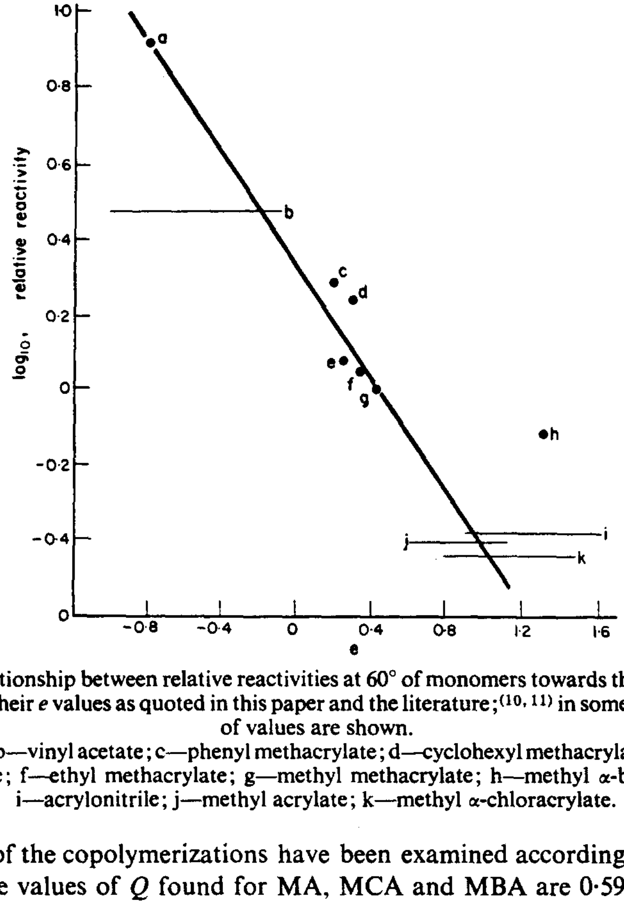

FIG. 9. Relationship between relative reactivities at 60° of monomers towards the benzoyloxy radical and their e values as quoted in this paper and the literature;(10, 11) in some cases, ranges of values are shown.

a—styrene; b—vinyl acetate; c—phenyl methacrylate; d—cyclohexyl methacrylate; e—benzyl methacrylate; f—ethyl methacrylate; g—methyl methacrylate; h—methyl α-bromacrylate; i—acrylonitrile; j—methyl acrylate; k—methyl α-chloracrylate.

The results of the copolymerizations have been examined according to the Q and e scheme.(9) The values of Q found for MA, MCA and MBA are 0·59, 8·20 and 4·54 respectively; the corresponding values of e are 1·1, 1·5 and 1·3. The present values of Q and e for MA and MCA are not in close agreement with those reported previously,(10) but the comparatively large positive values of e for MCA and MBA are expected because of the electron accepting properties of Cl and Br.

If the Q and e scheme were applied to the reactions of the benzoyloxy radical with monomers, the velocity constant for such a reaction would be expressed thus:

$$\ln k_2 = \ln P_b + \ln Q_m - e_b e_m$$

where P_b and e_b refer to the benzoyloxy radical and Q_m and e_m to the monomer. Relative values of k_2 have been determined for monomers for which the values of Q_m

and e_m have been found from copolymerizations. It is not possible to assign a value to e_b consistent with all the experimental results so that the Q and e treatment cannot properly be applied to the reaction under consideration.

Figure 9 shows, however, that k_2 generally decreases as e_m for the monomer is made more positive. The diagram contains data referring to ethyl, phenyl, benzyl and cyclohexyl methacrylates; the values of e for these monomers have been found to be 0·32, 0·18, 0·24 and 0·28 respectively based on e for MMA being 0·4. Without attaching any theoretical significance to the relationship between $\log k_2$ and e_m, it is clear that the benzoyloxy radical might be assigned a comparatively large and positive value for e_b, and that polar factors are of prime importance in its reactions. It seems that the relative reactivity of a monomer towards the benzoyloxy radical could be estimated from the value of e_m for the monomer; this value is derived from data on copolymerizations and so it is possible to correlate reactivities of monomers towards polymer radicals with those towards the benzoyloxy radical.

An attempt has been made to apply to the reactions of monomers with the benzoyloxy radical a more recent treatment(12) which allows for the influence of the polarities of reactants upon the rates of radical reactions. It has been shown already(13) that on this scheme the benzoyloxy radical must be assigned a comparatively large value for the parameter σ, in keeping with the view that polar factors are very significant in connection with reactions involving this radical. It is possible for data derived from copolymerizations to be used to predict very approximately the relative reactivities of monomers towards the benzoyloxy radical, but the correlation between observed and calculated reactivities is rather poor.

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Résumé—On a utilisé la technique des traceurs pour comparer la réactivité des différents monomères avec les radicaux considérés (à 60°). On a examiné comme monomères le méthyl méthyacrylate, le méthyl acrylate, le méthyl α-chloracrylate et le méthyl α-bromacrylate, et comme radicaux le polyméthyl méthacrylate et le benzoyloxy. On n'arrive pas à avoir une concordance satisfaisante entre les résultats obtenus et ceux donnés par les schémas Q et e. Toutefois, il apparait que les facteurs de polarité sont très importants pour les réactions avec le radical benzoyloxy et qu'à partir des résultats obtenus d'après l'étude de la copolymérisation du monomère avec le méthyl métacrylate, il est possible d'évaluer la réactivité relative d'un monomère envers ce radical.

Sommario—Si sono adottate le techniche dei traccianti per confrontare le reattività dei monomeri rispetto alle radicali di riferimento a 60°. I monomeri esaminati furono il metacrilato metilico, l'acrilato metilico, l'α-cloracrilato metilico e l'α-bromacrilato metilico; le radicali di riferimento furono il metacrilato polimetilico e le radicali benzoilossiche. I tentativi di applicare lo schema *Q* ed *e* ai risultati ebbero solo esito parziale. E' chiaro però che i fattori polari sono di grande importanza nelle reazioni interessanti la radicale benzoilossica e che è possibile stimare la reattività relativa di un monomero rispetto a questa radicale in base ai dati ottenuti in seguito allo studio della copolimerizzazione del monomero con il metacrilato metilico.

Zusammenfassung—Tracer-Technik wurde angewendet, um die Reaktionsfähigkeit von Monomeren gegenüber Bezugsradikalen bei 60° zu vergleichen. Die untersuchten Monomere waren Methylmethacrylat, Methylacrylat, Methyl-α-chloracrylat und Methyl-α-bromacrylat; die Bezugsradikale Polymethylmethacrylat und die Benzoyloxyradikale. Versuche, das *Q*-*e*-Schema auf die Ergebnisse anzuwenden, waren nicht völlig erfolgreich. Es scheint jedoch, daß polare Faktoren von großer Bedeutung für Reaktionen mit dem Benzoylradikal sind und daß es möglich ist, die relative Reaktionsfähigkeit eines Monomers gegenüber diesem Radikal nach Daten, die sich aus der Untersuchung der Copolymerisation des Monomers mit Methylmethacrylat ergeben, annähernd zu bestimmen.