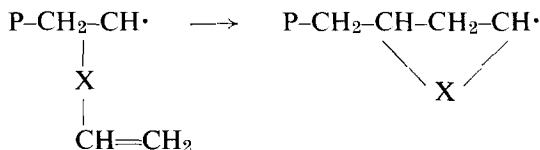


Studies of the polymerization and copolymerization of methacrylic anhydride

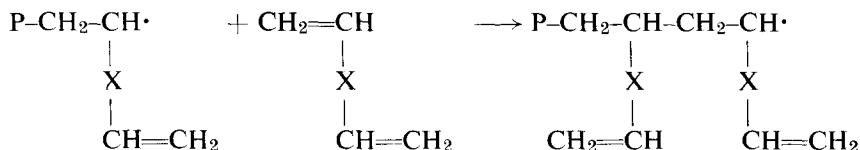
F. C. BAINES* AND J. C. BEVINGTON

Various procedures involving the use of labelled reagents have been developed for studying the behaviour of methacrylic anhydride in radical polymerizations. Studies of copolymerizations with styrene, methyl methacrylate and methyl acrylate have been correlated with studies of the initiation of homopolymerization with benzoyl peroxide; it has been shown that polar factors are prominent in the reactions of the monomeric anhydride with radicals. Tracer techniques have confirmed that there are high proportions of cyclized monomer units in homopolymers and copolymers of methacrylic anhydride.

MANY SUBSTANCES having two polymerizable groups per molecule can undergo cyclopolymerization, the intramolecular propagation



competing with the intermolecular reaction

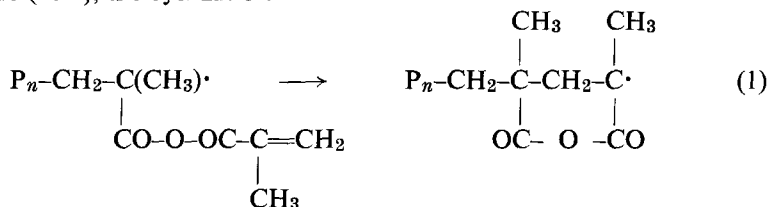


Butler and Raymond¹ performed statistical calculations, in particular for 1,6-heptadiene, showing that high degrees (>95%) of cyclization would be expected only when the monomer concentration is below about 0.10 mol/l.

For those symmetrical divinyl monomers where the nature of the group X leads to a ring of about six atoms, it is likely that the intrinsic reactivity of the pendant double bond is similar to that of a double bond in the monomer. On the other hand, the nature of X must determine whether the growing centre can acquire a configuration to permit the intramolecular propagation².

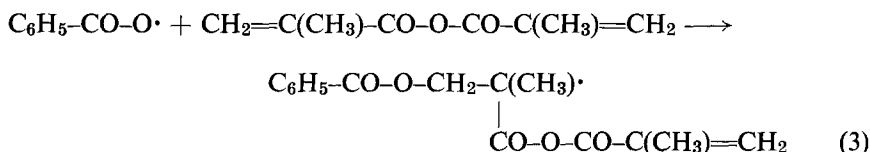
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It is known³⁻⁵ that, in radical polymerizations involving methacrylic anhydride (MAA), the cyclization



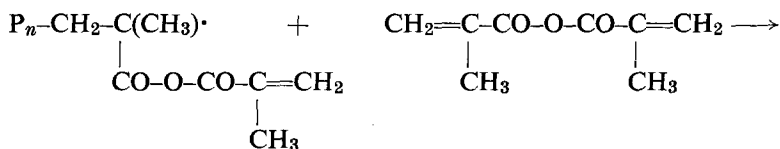
occurs very readily. This feature is considered in this paper as part of a more general examination of the behaviour of the monomer in radical polymerization. There is another distinct interest in this monomer in that its polymer can be converted to polymethyl methacrylate; cyclopolymerization leads to a polymer having a micro-structure unachievable by direct polymerization of monomeric methyl methacrylate⁶.

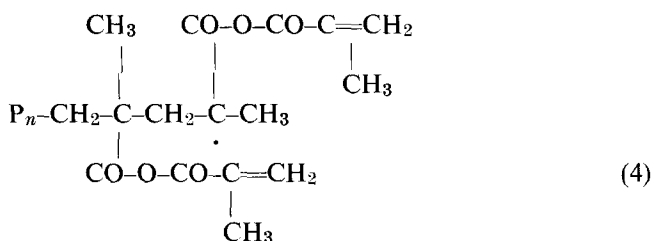
Part of the work involving MAA concerned an examination of its reactivity towards reference radicals. For examination of the benzoyloxy radical, samples of ¹⁴C-benzoyl peroxide were used to initiate polymerizations⁷; the resulting polymers were analyzed for benzoate and phenyl end-groups to permit study of the competition between the reactions



and evaluation of k_3/k_2 . For investigation of the reactivity of MAA towards polymer radicals, monomer reactivity ratios were determined by an isotopic method for copolymerizations with styrene, methyl methacrylate and methyl acrylate. In a binary copolymerization with this monomer, it may be necessary to consider three types of polymer radical and six types of growth reaction in addition to reaction scheme (1). It has been shown⁸ that the two radicals in reaction scheme (1) behave so similarly in copolymerization that it is possible to apply the usual treatments for binary copolymerizations without penultimate group effects. A value of e for MAA has been deduced and has been correlated with the reactivity of the monomer towards the benzoyloxy radical.

Smets *et al*³ considered a competition between the intramolecular process (1) and the growth reaction





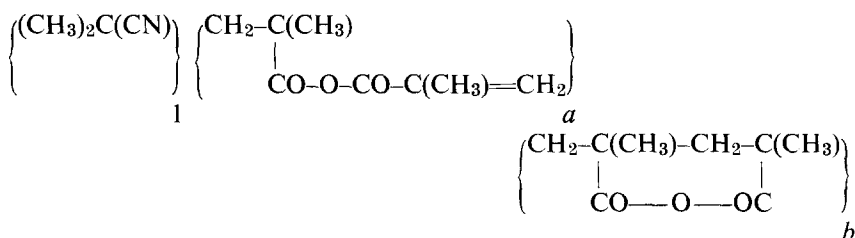
in the homopolymerization of MAA. According to a simple kinetic analysis, the molar fraction (f_c) of cyclized units is related to the concentration of monomer (m) thus

$$\frac{1}{f_c} = 1 + \frac{2k_4m}{k_3} \quad (5)$$

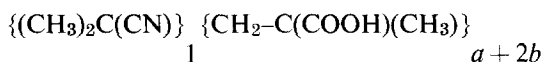
To find ($1/f_c$), the pendant double bonds in a polymer were determined by bromometry. Equation (5) was not fully satisfied in that the extrapolated value of f_c for zero concentration of monomer was significantly less than unity. This result was attributed in part to experimental errors and in part to the occurrence of reactions, in addition to scheme (4), leading to carbon-carbon double bonds in the polymer. Similar results were obtained by application of the same procedure to copolymers of MAA⁸.

Alternative methods have now been devised and tested for determination of f_c for homopolymers and copolymers of MAA. In general, the methods involve tracer studies of the changes in polymers brought about by hydrolysis.

Suppose that a homopolymer of MAA has labelled end-groups which are stable to hydrolysis, e.g. $(\text{CH}_3)_2\text{C}(\text{CN})$ groups derived from ^{14}C -azoisobutyronitrile used as initiator. If the original polymer is represented as



then the polymer after complete reaction can be represented as



Hydrolysis must cause the specific activity of the polymer to rise because of the detachment of methacrylic units from uncyclized monomer units. If materials are assayed by gas counting, it is necessary only to consider their carbon contents so that

$$\frac{\text{counting rate of polymer before hydrolysis}}{\text{counting rate of polymer after hydrolysis}} = \frac{a + 2b}{2(a + b)} \quad (6)$$

neglecting the very small contribution of the labelled end-groups to the total carbon content of the polymer. The value of f_c , equal to $b/(a+b)$, can therefore be found.

A similar procedure can be applied to a copolymer of MAA with ^{14}C -styrene. If such a copolymer is represented as $(\text{C}_8\text{H}_8)_1(\text{C}_8\text{H}_{10}\text{O}_3)_{a+b}$ where a and b are respectively the relative numbers of uncyclized and cyclized MAA units

$$\frac{\text{counting rate for copolymer}}{\text{counting rate for monomeric styrene}} = \frac{1}{1+a+b} \quad (7)$$

After complete hydrolysis, the copolymer can be taken as

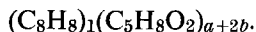


so that

$$\frac{\text{counting rate for copolymer before hydrolysis}}{\text{counting rate for copolymer after hydrolysis}} = \frac{2+(a+2b)}{2+2(a+b)} \quad (8)$$

From equations (7) and (8), a and b can be calculated so that f_c can be found.

If a hydrolyzed copolymer of styrene and MAA were methylated with ^{14}C -diazomethane, it would be converted to a copolymer of styrene and ^{14}C -methyl methacrylate; the specific activity of this product would depend upon that of the diazomethane, the composition of the original copolymer and the relative numbers of cyclized and uncyclized MAA units. Taking the original copolymer, as before, as $(\text{C}_8\text{H}_8)_1(\text{C}_8\text{H}_{10}\text{O}_3)_{a+b}$, the final copolymer of styrene and methyl methacrylate can be represented as



For gas counting

$$\frac{\text{counting rate of final product}}{\text{counting rate of diazomethane}} = \frac{a+2b}{8+5(a+2b)} \quad (9)$$

The value of $(a+b)$ can be deduced from data on the copolymerization of styrene and MAA; then equation (9) can be used to find a , b and f_c .

EXPERIMENTAL

Materials

Preparations of labelled initiators have been described^{9, 10}. ^{14}C -methyl methacrylate and ^{14}C -methyl acrylate were made by exchange between the unlabelled monomers and ^{14}C -methanol. ^{14}C -styrene was made by destructive distillation of ^{14}C -cinnamic acid prepared from ^{14}C -benzaldehyde by the Perkin reaction. Monomeric MAA was a commercial product (Kodak Ltd). All monomers and solvents were purified by standard procedures; monomers were distilled in high vacuum immediately before use.

For preparation of ^{14}C -diazomethane, labelled methylamine was first converted to nitrosomethylurea which was then decomposed basically to give a solution of diazomethane in benzene. For assay, ^{14}C -diazomethane

was converted to ^{14}C -methyl- β -naphthoate by reaction with a suspension of β -naphthoic acid in ether; allowance was made for the substantial dilution of the active carbon.

Preparation of polymers

Polymerizations were performed in sealed dilatometers in the complete absence of air; conversions did not exceed 5%. For MAA at 60°C, 20.7% contraction was taken as equivalent to 100% polymerization; for homopolymerizations, concentrations of monomer up to 3.22 mol/l could be used without pronounced auto-acceleration.

Polymers were recovered by precipitation in methanol; after filtration almost to dryness, they were dissolved in benzene, reprecipitated in methanol, filtered off and dried in vacuum at room temperature. Filtration to dryness caused polymers containing MAA to become insoluble in benzene. Test separations established that the procedures led to complete removal from polymers of uncombined labelled monomer or labelled initiator.

Chemical treatment of polymers

Polymers were subjected to alkaline hydrolysis¹¹. Samples of poly MAA (about 100 mg) were refluxed with water (75 ml) and sodium hydroxide pellets (250 mg) until the polymers dissolved. The solutions were then heated on a steam bath and concentrated hydrochloric acid was added to precipitate poly(methacrylic acid) which was filtered off and dried in vacuum (recovery, about 80%). For hydrolysis of copolymers of styrene with MAA, a little benzene was added to the system to swell the copolymers.

The method of Katchalsky and Eisenberg¹² was used for esterification of polymethacrylic acid and its copolymers with styrene. Materials were treated with ^{14}C -diazomethane in benzene until the polymer dissolved and the yellow colour persisted. The excess diazomethane was removed on a rotary evaporator. The solution of polymer was filtered through sintered glass; benzene washings of the undissolved material on the sinter were added to the filtrate which was then added slowly to excess methanol. The precipitated polymer was recovered and dried in vacuum.

Assay of labelled materials

Gas counting of carbon dioxide was used. Samples were oxidised by wet oxidation. Counting rates refer to counts per minute (corrected for lost counts and background) for a standard mass of carbon dioxide; a counting rate of 9000 corresponds to a specific activity of about 1 microcurie per g of carbon.

Polymerizations with ^{14}C -benzoyl peroxide

MAA was polymerized at 60°C in benzene with benzoyl peroxide at 1 g/l. At each concentration of monomer, one polymer was prepared with peroxide labelled in the rings (R-peroxide) and another with peroxide labelled at the

carboxyl carbon atoms (C-peroxide). There were indications of auto-acceleration in the later stages of the polymerizations but the parallel experiments gave very similar conversion/time plots. Values of rate of initiation and k_t/k_p^2 were calculated from the results referring to R-peroxide. From the counting rates of corresponding polymers and those of the peroxides, values of the fraction x were calculated by equation (10).

$$x = \frac{\text{no. of benzoate end-groups}}{\text{sum of nos. of benzoate and phenyl end-groups}}$$

$$= \frac{\text{counting rate of C-polymer}}{\text{counting rate of R-polymer}} \times \frac{\text{counting rate of R-peroxide}}{\text{counting rate of C-peroxide}} \quad (10)$$

Results are shown in *Table 1* and *Figure 1* which gives k_2/k_1 as 0.49 l/mol.

For comparisons of the reactivities of monomers towards the benzoyloxy radical, methyl methacrylate ($k_2/k_1 = 0.33$ l/mol) has been used as standard¹³,

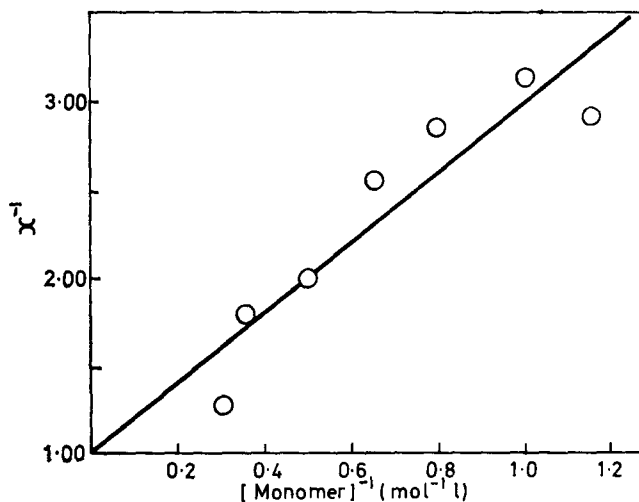


Figure 1 Nature of end-groups in poly(methacrylic anhydride) prepared at 60°C with benzoyl peroxide as initiator and benzene as diluent.

$$x = (\text{no. of benzoate end-groups}) / (\text{sum of nos. of benzoate and phenyl end-groups})$$

so that the relative reactivity of MAA is 1.48. The molecule of MAA, however, contains two identical carbon-carbon double bonds and so the relative reactivity of one such bond can be taken as 0.74; this correction may not be completely justified since, in a dilute solution of MAA, the double bonds are not distributed uniformly but occur in pairs.

Table 1 Polymerizations with labelled benzoyl peroxides

Concn. of MAA (mol l ⁻¹)	10 ⁵ (rate of polym.) (mol l ⁻¹ s ⁻¹)		Counting rate of polymer		10 ⁸ (rate of init.) (mol l ⁻¹ s ⁻¹)	k_t/k_p^2 (mol l ⁻¹)	x
	R-per- oxide	C-per- oxide	R-per- oxide	C-per- oxide			
0.87	2.20	2.56	194	63	1.88	12.3	0.34
1.00	2.74	2.77	186	56	2.10	13.8	0.32
1.25	3.13	3.50	156	49	2.11	14.9	0.35
1.50	3.90	4.06	127	47	2.05	16.9	0.39
2.00	5.72	5.47	102	48	2.30	14.8	0.50
2.75	8.13	7.80	64	34	2.06	12.4	0.56
3.22	9.84	9.80	47	35	1.88	10.1	0.79

Counting rates for R- and C-peroxide = 281 000 and 266 000, respectively

Polymerizations with ¹⁴C-azoisobutyronitrile

Table 2 shows results for polymerizations of MAA at 60°C in benzene with ¹⁴C-azoisobutyronitrile at 0.3 g/l; there were no induction periods and only slight indications of auto-acceleration.

Table 2 Polymerizations with labelled azoisobutyronitrile

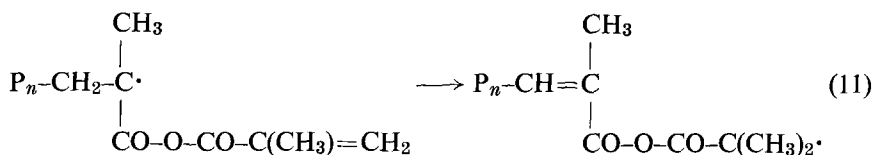
Concn. of MAA (mol l ⁻¹)	10 ⁵ (rate of polym.) (mol l ⁻¹ s ⁻¹)	Counting rate of polymer		10 ⁸ (rate of init.) (mol l ⁻¹ s ⁻¹)	k_t/k_p^2 (mol l ⁻¹)
		before hydrolysis	after hydrolysis		
0.50	1.13	752	833	1.63	16.0
1.00	3.27	468	516	2.94	13.8
1.50	5.24	296	328	2.98	12.2
2.00	6.91	224	251	2.98	12.5
2.50	8.71	186	—	3.12	12.8

Counting rate for initiator = 1 040 000

Except at the lowest concentration of monomer, the rates of initiation correspond to those observed under similar conditions with styrene¹⁴. The order with respect to monomer is about 1.08, in agreement with the results shown in Table 1; the values of k_t/k_p^2 are similar for the two sets of experiments.

Using (6), the values of f_c were calculated from the counting rates of polymers before and after hydrolysis. Figure 2 shows these results and those of Smets *et al*³ which refer to polymerization in cyclohexanone at 36.6°C. It is confirmed that a high proportion of MAA units are cyclized. The intercepts are clearly greater than unity; in the tracer experiments, this means

that the increases in specific activity accompanying hydrolysis are larger than might have been expected. Possible failings in the experimental procedures (such as loss of labelled end-groups, incomplete hydrolysis, and failure to remove contaminants from hydrolyzed polymers) would lead to the opposite effect. The results can be explained on the basis of the isomerization scheme (11) which was proposed by



Smets *et al*³ and which might be regarded as a type of 'back-biting' in competition with cyclization. If the product of scheme (11) engages in further growth, an anhydride linkage becomes incorporated in the main polymer chain; breakage of this linkage during hydrolysis would cause a section of the polymer chain to be detached leaving a residue comparatively rich in the end-groups derived from the labelled initiator.

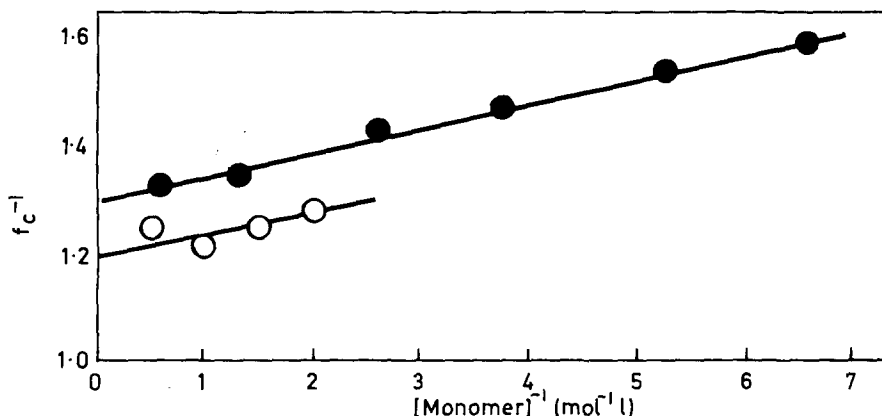


Figure 2 Dependence of fractional number (f_c) of cyclized methacrylic anhydride units upon concentration of monomer during polymerization.

○, This work; polymerization at 60°C with benzene as diluent;

●, Work of Smets *et al*³; polymerization at 36.6°C with cyclohexanone as diluent

Copolymerizations involving methacrylic anhydride

Binary copolymerizations of MAA with labelled samples of styrene, methyl methacrylate and methyl acrylate were performed at 60° in benzene with benzoyl peroxide at 1g/l. Contraction/time plots for systems including methyl acrylate were linear but many of those for the other comonomers showed auto-acceleration and formation of gel in the later stages.

For gas counting, a high polymer derived from MAA (C₈H₁₀O₃) and a

^{14}C -monomer containing n carbon atoms per molecule can be represented as $(\text{C}_8)_a(\text{C}_n)_{1-a}$ so that

$$\frac{\text{counting rate of copolymer}}{\text{counting rate of labelled monomer}} = r = \frac{n(1-a)}{8a + n(1-a)}$$

$$\text{and mole fraction of MAA in copolymer} = a = \frac{n(1-r)}{n(1-r) + 8r} \quad (12)$$

Typical results are shown in Table 3. Monomer reactivity ratios from Fineman-Ross plots are as follows (monomer-1 taken as MAA):

with styrene: $r_1 = 0.33 \pm 0.03$, $r_2 = 0.10 \pm 0.01$

with methyl methacrylate: $r_1 = 1.70 \pm 0.07$, $r_2 = 0.22 \pm 0.02$

with methyl acrylate: $r_1 = 4.75 \pm 0.15$, $r_2 = 0.16 \pm 0.02$

For styrene at 36.6°C , Smets *et al*⁸ gave $r_1 = 0.26$ and $r_2 = 0.12$.

Table 3 Copolymerizations of ^{14}C -methyl methacrylate and methacrylic anhydride

Mole fraction methyl methacrylate in monomer mixture	Counting rate of copolymer	Mole fraction methyl methacrylate in copolymer
0.20	298	0.13
0.40	594	0.25
0.50	787, 740*, 771†	0.32, 0.30*, 0.31†
0.60	1005	0.39
0.70	1268	0.48
0.80	1657	0.59
0.90	2058	0.70
0.965	2809	0.87

Counting rate for monomeric methyl methacrylate = 3476; reaction mixtures contained 60% benzene by volume, except * (50%) and † (70%)

From the three values of r_1r_2 and taking the values of e for styrene, methyl methacrylate and methyl acrylate as -0.8 , 0.4 and 0.6 respectively, e for MAA is found to be about 1.2 ; Smets *et al*⁸ gave 1.1 . It has been shown that the reactivities of monomers towards the benzoyloxy radical decrease as the values of e become more positive¹³; previous results suggest that a reactivity towards the benzoyloxy radical of 0.74 (that of methyl methacrylate taken as unity) might correspond to a value of about $+1$ for e , in fair agreement with the experimental result for MAA.

For comparisons of the reactivities of reference polymer radicals towards monomers, it is necessary to correct values of r_1 and r_2 and to make due allowance for the presence of two identical carbon-carbon double bonds in the molecule of MAA. To compare reactivities of monomers towards the poly(MAA) radical, the quoted values of r_1 should be halved; for comparison of the reactivity of MAA towards other polymer radicals, the values of r_2 should be doubled. These considerations do not affect calculations of e since they involve the products r_1r_2 .

Reactions of polymers and copolymers of methacrylic anhydride

Copolymers of MAA with ^{14}C -styrene were assayed before and after hydrolysis (see Table 4). Equations (7) and (8) were then used to calculate values for the ratio of the numbers of cyclized and uncyclized MAA units. Table 4 includes a column showing the counting rate after hydrolysis calculated on the assumption that all MAA units were uncyclized. Only small changes in counting rates were caused by hydrolysis; in two cases, the counting rates were reduced so that the only conclusion to be drawn is that most of the MAA units in the copolymers were cyclized.

Table 4 Hydrolysis of copolymers of methacrylic anhydride with ^{14}C -styrene

Counting rate of polymer before hydrolysis	Counting rate of polymer after hydrolysis	(a + b)	Calc. max. counting rate for hydrolyzed copolymer	$\frac{b}{a + b}$
1186	1282	3.72	1960	0.8
2161	2124	1.59	3120	—
2492	2370	1.25	3450	—
2871	3018	0.95	3800	0.8

Copolymer represented as $(\text{C}_8\text{H}_8)_a(\text{C}_8\text{H}_7\text{O}_2)_b$ where a and b refer to uncyclized and cyclized units respectively

Counting rate for monomeric styrene = 5608

Three unlabelled homopolymers of MAA were hydrolyzed; the products were methylated with ^{14}C -diazomethane and assayed. The counting rate calculated for complete reaction was 4280; the observed values were 4130, 4116 and 4172 indicating that reaction was very nearly complete. Preliminary experiments of the same type were performed on unlabelled copolymers of MAA with styrene but the observed counting rates of the products were less than the minimum possible values calculated from (9) assuming that all MAA units were uncyclized (see Table 5). It can only be concluded that hydrolyses of the original copolymers were incomplete because of the heterogeneous nature of the system.

Table 5 Treatment with ^{14}C -diazomethane of hydrolyzed copolymers of methacrylic anhydride with styrene

(a + b) in copolymer	Calc. counting rate for product assume a = 0	assume b = 0	obs. counting rate for product
3.76	3530	3060	2960
1.25	2610	1880	2110
0.71	2010	1320	1260

See footnotes to Table 4

Counting rate for diazomethane = 21400

CONCLUSIONS

- (1) For radical copolymerizations at 60°C involving methacrylic anhydride (monomer-1), monomer reactivity ratios are as follows:

with styrene	$r_1 = 0.33 \pm 0.03$
	$r_2 = 0.10 \pm 0.01$

with methyl methacrylate	$r_1 = 1.70 \pm 0.07$
	$r_2 = 0.22 \pm 0.02$

with methyl acrylate	$r_1 = 4.75 \pm 0.15$
	$r_2 = 0.16 \pm 0.02$

These results lead to a value of e of about 1.2 in agreement with Smets *et al*⁸.

- (2) Monomeric methacrylic anhydride is at 60°C less reactive than methyl methacrylate towards the benzoyloxy radical. Its low reactivity towards this reference radical can be correlated with the comparatively large value of e .
- (3) In homopolymers of methacrylic anhydride and in its copolymers with styrene, there is a high proportion of cyclized monomer units. The results do not completely satisfy a simple reaction scheme in that the proportions of cyclized units are unexpectedly high in homopolymers prepared using low concentrations of monomer. This effect has also been reported³ from studies involving different experimental methods.

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