GRAFTING EFFICIENCY

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INTRODUCTION

Up to now, very few data have been published concerning the kinetics of graft and block polymerization[1-3]. The problem is an attractive one because it makes possible a deeper understanding of the reaction mechanism, and particularly a comparison of the relative reactivities of the polymeric and low molecular weight radicals. It is the purpose of this paper to report and correlate some kinetic data we have obtained recently in our laboratory, and to discuss the significance of these results.

It must be pointed out that an evaluation of the importance of grafting compared with homopolymerization requires first of all very careful fractionation experiments on the reaction products. Indeed, the graft or block copolymer will usually be mixed with one or two corresponding homopolymers, from which it must be separated quantitatively. In the experiments on which we will report here, the separation was always carried out by fractional precipitation, unless otherwise indicated. A copolymer was considered as a graft- or a block-copolymer if it precipitated at a volume fraction of the precipitant (γ-value), which is *different* from (usually intermediate between) those of both corresponding homopolymers, and remains *constant* on reprecipitation of the polymer. This second criterion must also be fulfilled, because the fractionation assures a separation not only on the basis of the chemical composition, but also partially on the basis of the molecular weight.

After fractionation, the weight R_g of the second monomer bonded as graft or block can be determined taking due account of the composition of the latter, and the weight R_h of the second homopolymer can be determined. The ratio R_g/R_h has been taken as a measure of the grafting efficiency. The fact that the formation of graft or block copolymer also depends on the chain termination mechanism must, however, be taken into account. Indeed, in the ideal case for a monomer system terminating by a disproportionation mechanism between two growing radicals, if both radicals have the same efficiencies for chain initiation and propagation, the ratio R_g/R_h would be expected to be equal to unity; if, on the other hand, the chain termination proceeds by a radical combination reaction, so that a growing homopolymer chain can terminate with a growing graft chain by addition, an increase of the R_g/R_h ratio must be expected from unity to three, at least in the ideal case.

In the several systems which will be considered in the present paper, polymers carrying different reaction sites were used for initiating the polymerization of a second monomer. The decomposition of the labile

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groups was carried out either thermally or photochemically; this homolytic cleavage of the active groups always affords polymeric and low molecular weight radicals, whose efficiencies will becom pared. We will consider, in turn, initiation by the decomposition of terminal peroxides, terminal and side-chain peresters, peranhydride side-chains, and photosensitive terminal groups and side-chains.

RESULTS

Block polymerization with t-butyl-peroxide end groups[4]

Polystyrene carrying peroxy-t-butyl end groups has been prepared by polymerization of styrene in the presence of a t-butyl-hydroperoxide–copper octoate initiating system. This peroxy-t-butyl-polystyrene was used as initiator for the second-step polymerization of methyl methacrylate and vinyl acetate; the reactions were carried out at 97° using 3 g polymer/20 ml. The second-step polymerization behaves normally from the kinetic point of view, i.e. it obeys the square root law relationship with respect to the initiator, and it is a first order reaction with respect to the monomer. For the evaluation of the ratio R_g/R_h, one must take into account that, in the case of methyl methacrylate, some thermal polymerization occurs at 97°; this amount of thermal poly(methyl methacrylate) (R_{th}) must be subtracted from the R_h value. In order to evaluate its importance, methyl methacrylate was polymerized at the same temperature, but in the presence of inert polystyrene in order to make the solution isoviscous. In the case of vinyl acetate, any thermal polymerization may be neglected. The results are summarized in Table 1.

Table 1(a). Block copolymerization of methyl methacrylate with peroxy-t-butyl-polystyrene (initial concentration = 4·86 mmoles/l.) at 97°, using benzene as solvent

Monomer concentration (mole/l.)	$R_{tot} \times 10^5$ (mole l.$^{-1}$ sec^{-1})	Polymerized methyl methacrylate (%)	Methyl methacrylate as block (%)	Thermal poly (methyl methacrylate) (%)	Homo-polymer (%)	R_g/R_h
1·872	2·3	17	37·4	30·5	32·1	1·17
2·802	3·9	20	39·3	32·1	28·6	1·35
3·744	5·3	12·7	38·7	26·4	34·9	1·11

Table 1(b). Block copolymerization of vinyl acetate with peroxy-t-butyl-polystyrene (initial concentration = 15 mmoles/l.) at 97°, using benzene as solvent

Monomer concentration (mole/l.)	Polymerized vinyl acetate (%)	Vinyl acetate as block (%)	Homopolymer (%)	R_g/R_h
3·25	30·4	20·8	79·2	0·263
4·42	22	21·7	78·3	0·274
5·86	15·5	19·5	80·5	0·244

In the case of methyl methacrylate, the R_g/R_h ratio has a mean value of about $1 \cdot 2$; this must be interpreted on the basis of a termination reaction mainly by disproportionation, in agreement with the data of Bevington, Melville and Taylor[5]. It corresponds to about 1 addition to every 15 disproportionations. On this basis, the efficiency of both radicals is admitted to be equal, and consequently independent of their size.

For vinyl acetate, the mean value of $0 \cdot 26$ is much too low if one considers only the chain termination by disproportionation. It can be interpreted as being due to chain-transfer reaction between a block copolymer growing chain and a monomer or solvent molecule, as a result of which the block copolymer loses its capacity for further growth, while new homopolymer chains are started in the same kinetic chain. In the case of vinyl acetate, the value of R_g/R_h is not, therefore, a measure of the relative efficiency, but only a consequence of chain-transfer reactions.

Block copolymerization with terminal perester groups[6]

Polystyrene with terminal carboxylic acid groups has been polymerized with azo*bis*cyanopentanoic acid[7]. The end groups were transformed into acid chloride and t-butyl-perester groups by reaction with t-butyl-hydroperoxide. It was used for the polymerization of methyl methacrylate at 100° in benzene solution. The rate of polymerization was first order with respect to the monomer (2 g polymer/10 ml). The results are summarized in *Table 2*.
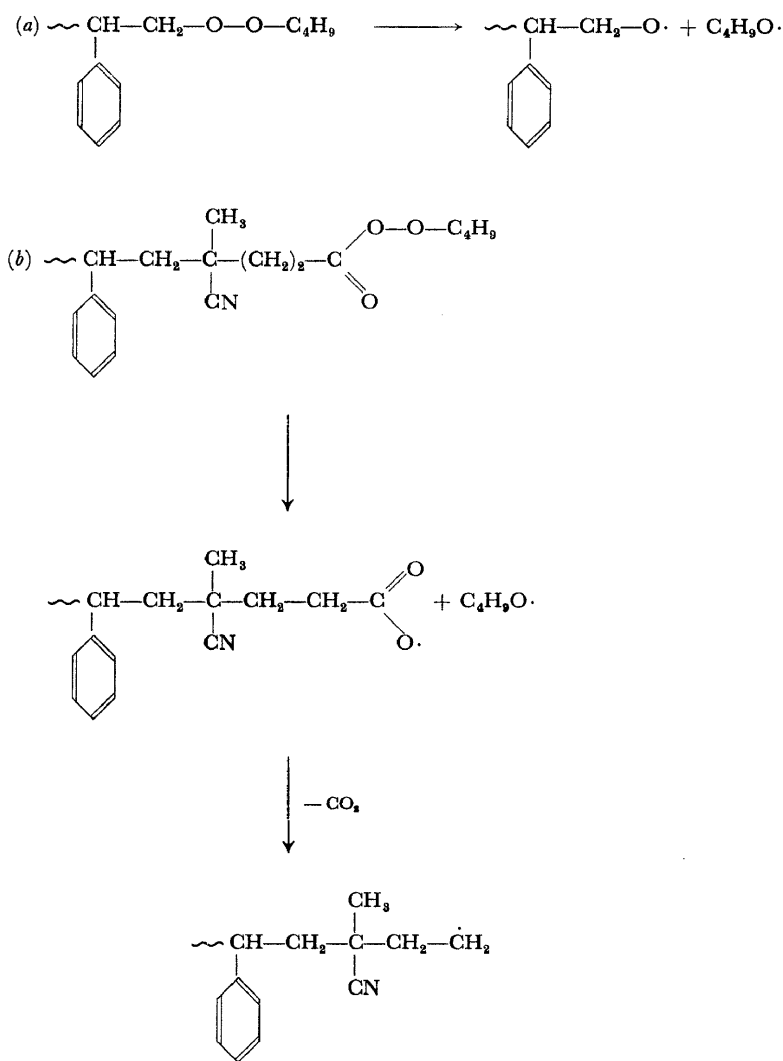
Table 2. Block copolymerization of methyl methacrylate with terminal t-butyl-peresterpolystyrene (initial concentration = $4 \cdot 86$ mmole/l.) at 100°, using benzene as solvent

Monomer concentration (mole/l.)	$R_{tot} \times 10^5$ (mole l.$^{-1}$ sec^{-1})	Polymerized methyl methacrylate (%)	Methyl methacrylate as block (%)	Thermal poly (methyl methacrylate) (%)	Homo-polymer (%)	R_g/R_h
$1 \cdot 869$	$7 \cdot 1$	$35 \cdot 6$	$12 \cdot 8$	$24 \cdot 6$	$62 \cdot 6$	$0 \cdot 205$
$2 \cdot 337$	$10 \cdot 4$	$29 \cdot 4$	$13 \cdot 9$	$19 \cdot 5$	$66 \cdot 6$	$0 \cdot 209$
$2 \cdot 805$	$13 \cdot 2$	$25 \cdot 4$	$12 \cdot 9$	$25 \cdot 5$	$61 \cdot 6$	$0 \cdot 209$
$3 \cdot 739$	$18 \cdot 0$	$31 \cdot 8$	$12 \cdot 5$	$27 \cdot 2$	$60 \cdot 3$	$0 \cdot 207$

When these data are compared with those of the preceding series, the most striking point is the low R_g/R_h-value, which is only $0 \cdot 2$–$0 \cdot 21$ instead of $1 \cdot 2$ for the same monomer. Considering the homolytic cleavage of both end groups, two very different radicals are produced, as shown in *Scheme 1*.

One is a very reactive β-phenylethoxide radical, the other a γ-cyanocarboxylate radical. The former is converted to a block copolymer on further addition of monomer, whereas the latter will decarboxylate at a suitable reaction temperature. By rearrangement and hydrogen transfer, the radical so formed will give both block copolymer and homopolymer. The R_g/R_h ratio will decrease as the transfer reaction becomes increasingly important.

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(a) $\sim$ CH—CH$_2$—O—O—C$_4$H$_9$ $\longrightarrow$ $\sim$ CH—CH$_2$—O· + C$_4$H$_9$O·

(b) $\sim$ CH—CH$_2$—C—(CH$_2$)$_2$—C with CH$_3$ and CN substituents, and O—O—C$_4$H$_9$, O

$\sim$ CH—CH$_2$—C—CH$_2$—CH$_2$—C with CH$_3$ and CN substituents, O, O· + C$_4$H$_9$O·

— CO$_2$

$\sim$ CH—CH$_2$—C—CH$_2$—ĊH$_2$ with CH$_3$ and CN substituents

Scheme 1

Graft polymerization with t-butyl-perester side groups[8,9]

Methyl acrylate and methyl methacrylate copolymers A and B containing t-butyl-perester groups were synthesized by copolymerization of acrylyl chloride with methyl methacrylate and reaction of the acrylyl chloride copolymer with t-butyl-hydroperoxide. Both copolymers A and B were used for initiating the grafting of styrene. In each case, the total rate of polymerization was first order with respect to the styrene concentration, while the square root dependence on the initiator concentration was observed. Some data obtained with copolymer A are summarized in *Table 3*.

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Table 3. Dependence of rate of grafting on styrene concentration with acrylic t-butyl-perester copolymer; series A: perester content, 1·2 moles per cent; [init] = 3% by weight; series B: perester content, 31·6 moles per cent; [init] = 5% by weight

Series	Monomer concentration $[M]$ mole/l.	Total rate $R_p \times 10^5$ mole l.$^{-1}$ sec^{-1}	Grafting rate $R_g \times 10^5$ mole l.$^{-1}$ sec^{-1}	R_g/R_h
A	2·62	1·46	0·73	1·0
	3·49	2·28	1·15	1·02
	4·37	2·22	1·11	1·0
	5·24	4·30	1·43	0·5
	6·11	4·32	1·37	0·46
B	2·62	9·64	8·2	5·7
	4·37	15·46	9·53	1·6
	5·24	19·9	10·4	1·1

In the case of copolymer A, for an initiating system of low perester content (series A), both the total rate and the grafting rate are virtually first order with respect to the monomer in dilute solution, and R_g/R_h is approximately equal to unity. At higher monomer concentration, however, the grafting rate remains constant while the rate of homopolymerization increases markedly. For the initiating system of high perester content (series B) at lower styrene concentration, grafting is favoured more than homopolymerization; again, at higher monomer concentration, the rate of grafting changes only slightly while the rate of homopolymerization increases markedly.

The rôle of the concentration of the initiating polymer in the graft reaction is apparent from *Table 4.*

Table 4. Effect of peracrylate copolymer concentration on grafting efficiency: monomer concentration [M] = 2·62 moles/l.; solvent = dioxan

No. of experiment	Temperature (°C)	Initial concentration (% by weight)	Perester content (% by weight)	$R_h \times 10^5$ (moles/l.)	$R_g \times 10^5$ (moles/l.)	R_g/R_h
1	74·5	1·0	18·9	1·73	0·60	0·34
2a	75	1·0	11·1	0·52	1·50	2·9
3	77	3·0	2·0	0·73	0·73	1·0
4	75	4·0	11·1	0·69	3·40	4·9
5	75	5·0	11·1	0·75	3·95	5·3
6	74	5·0	43·0	1·46	8·20	5·6

In experiment 2a, 4 per cent by weight of pure poly(methyl acrylate) was added to the system; here the influence of the viscosity of the system on the grafting efficiency is demonstrated. The same conclusion is reached from a comparison of experiments 1 and 3, which show that the initiator concentration is much more important than the perester content of the initiator itself. As in methyl acrylate, the ratio R_g/R_h decreases in more

concentrated monomeric solutions of the methyl methacrylate copolymer (B); however, grafting predominates over homopolymerization to a lesser degree, except at high dilution. Here again the concentration of the active polymer exerts an influence on the grafting efficiency, though to a much lesser extent than with copolymer A (*Table 5*).

Table 5. Effect of the initiator concentration on the grafting efficiency: monomer concentration [M] = 1·75 moles/l.; solvent = dioxan; temperature = 85°; perester content = 5·6 moles per cent

No. of experiment	Initial concentration (% by weight)	Total rate $R_p \times 10^5$ (mole l.$^{-1}$ sec^{-1})	R_g/R_h
a	1·6	2·20	0·41
b	3·0	2·94	0·42
c	5·0	3·40	0·53
d	1·6	2·29	1·06

In experiment d, 4·0 per cent by weight of polystyrene was added to the polymerizing system, and, as before, the efficiency of grafting increases markedly with increase in viscosity, although the over-all reaction rate remains unchanged.
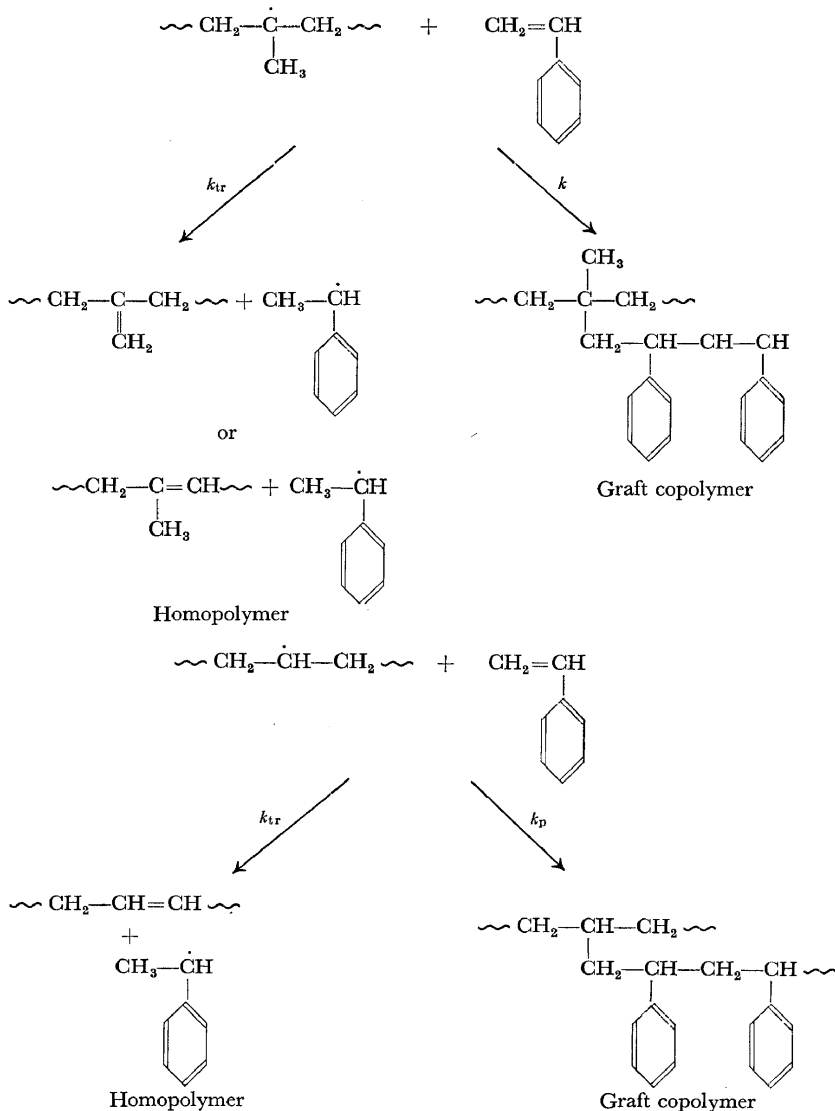
In all these experiments of grafting styrene monomer on to polymeric peresters, ideally both radicals have the same efficiency and a ratio R_g/R_h equal to three would be expected. This ratio is, in fact, greatly influenced by the monomer concentration, and its relative decrease with increasing monomer concentration may be attributed to either the occurrence of chain-transfer to the monomer, or to an increased efficiency of the t-butyloxy radical in more concentrated solution, or by assuming a limiting chain-length of the grafted chain, above which the grafts may be broken off, and so become homopolymer[10]. The grafting efficiency is also strongly increased by increasing the viscosity of the solution, e.g. by using a high macro-initiator concentration or by adding foreign inert polymer. Although the possibility of a chain-transfer to the polymer by a growing chain cannot be excluded, it seems more likely that the viscous medium has some influence on the efficiency of the $C_4H_9O \cdot$ radical. A decrease in the mobility of this radical would favour a transfer reaction to its parent copolymer, thus affording a new grafting site instead of producing a homopolymer.

The perester content of the initiating copolymer has much less influence over the R_g/R_h values than this viscosity effect. In a polymer of high perester content, there may be some recombination between radicals in the same chain, or a disproportionation reaction with double-bond formation. In both cases, macroradicals disappear without production of graft copolymers.

The ratio R_g/R_h has much lower values in the methacrylic perester series than in the acrylic series. This may be attributed to stronger steric hindrance in the former, which is due to tertiary substitution of the carboxylic carbon atom, and to the immediate environment of the perester group. However, the temperature of both reactions was different (85° for the methacrylic and

about 75° for the acrylic series), and it is common knowledge that temperature plays a very important part in the decarboxylation of the carboxylate radicals. Decarboxylation not only produces a much more stable radical in the methacrylic series than in the acrylic one, on account of increased hyperconjugation, but also one which can transfer a hydrogen atom to the monomer much more easily, as shown in *Scheme 2*.

$$\sim CH_2-\overset{\centerdot}{C}-CH_2\sim \quad + \quad CH_2=CH$$
$$\underset{CH_3}{|}$$

k_{tr} k

$$\sim CH_2-\underset{\overset{||}{CH_2}}{C}-CH_2\sim + CH_3-\overset{\centerdot}{C}H \qquad \sim CH_2-\underset{|}{\overset{CH_3}{C}}-CH_2\sim$$
$$CH_2-CH-CH-CH$$

or   Graft copolymer

$$\sim CH_2-\underset{CH_3}{\overset{|}{C}}=CH\sim + CH_3-\overset{\centerdot}{C}H$$

Homopolymer

$$\sim CH_2-\overset{\centerdot}{C}H-CH_2\sim \quad + \quad CH_2=CH$$

k_{tr} k_p

$$\sim CH_2-CH=CH\sim$$
$$+$$
$$CH_3-\overset{\centerdot}{C}H \qquad\qquad \sim CH_2-\underset{|}{CH}-CH_2\sim$$
$$CH_2-CH-CH_2-CH\sim$$

Homopolymer   Graft copolymer

Scheme 2

Graft polymerization with side peranhydride groups[11, 1]

Methyl methacrylate and acrylyl chloride were copolymerized, and the reaction products were treated with perbenzoic acid. After hydrolysis of

the unreacted acid chloride units, and treatment with diazomethane, the copolymer composition was, *e.g.* about 40 per cent methyl methacrylate, 10 per cent peranhydride and 50 per cent methyl acrylate. The peranhydride copolymer was used for initiating the second step polymerization of styrene, and again the R_g/R_h values were determined at constant polymer concentration for different monomer concentrations, and for different peranhydride contents. Some of the data are given in *Table 6*.

Table 6. Efficiency of grafting with peranhydride copolymer: solvent = toluene; temperature = 80°

Peranhydride content (% by weight)	Initial concentration (% by weight)	R_g/R_h values at styrene concentrations				
		2·614 (moles/l.)	3·485 (moles/l.)	4·356 (moles/l.)	5·227 (moles/l.)	6·099 (moles/l.)
5·35	5	0·48	0·52	0·53	0·59	0·62
9·25	5	0·35	0·33	0·42	0·41	0·45
	3	0·23	0·23	0·25	0·28	0·30
20·2	5	—	0·43	0·49	0·51	0·51
	3	—	0·38	0·44	0·47	0·47

The graft copolymers contained 40–60 per cent styrene, and their solubilities were much lower than that of the initiating copolymer. Considerations analogous to those in the preceding section on grafting with perester copolymers, can be developed on the basis of *Table 6*. The influence of the peranhydride content of the initiating copolymer is not as important as the concentration of the initiator polymer itself, *i.e.* than the viscosity of the solution. In this series, however, the R_g/R_h ratio increases slowly with increase in monomer concentration. The R_g/R_h values are about the same as those of the methacrylic perester copolymer, although the peranhydride units possess an acrylic structure. This indicates the importance of steric hindrance by neighbouring units, which must be considered responsible for the low degree of grafting. No definite conclusion about the relative grafting efficiency of peranhydride and perester groups, R—CO—O—O—CO—⟨◯⟩ and R—CO—O—O—C₄H₉, can be drawn from these results.

Photochemical graft and block polymerization with polymers containing eosin[12]

The polymerization of vinyl compounds by visible light in the presence of dye-reducing agent–oxygen systems has been described by Oster and coworkers. We were able to show with the aid of spectroscopic data that the dye molecules become incorporated into the polymer as leuco-derivatives during these photopolymerizations. On this basis, *N*-eosinpolyvinylamine and ω-*N*-eosinpoly(methyl methacrylate) were synthesized and used for the preparation of graft copolymers with acrylamide, acrylic acid, acrylonitrile and styrene, and the preparation of block copolymers with styrene and acrylamide. The grafts and blocks of the second monomer are bonded to the stem polymer through a leuco-dye group, as shown in *Scheme 3*.
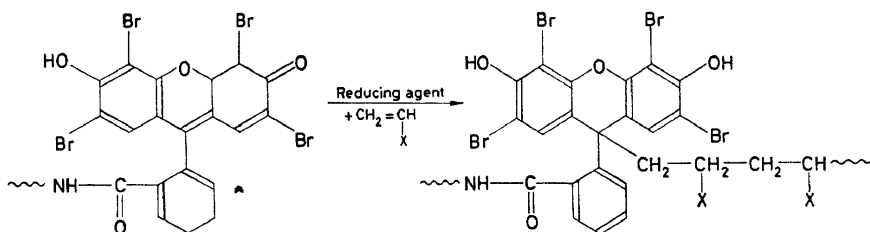
Scheme 3

The results are summarized in *Table 7*.

Table 7. Graft polymerization with N-eosinpoly(vinylamine hydrochloride) and ascorbic acid

Monomer (g%)	Solvent	Polymer (% by weight)	R_g/R_h
Acrylamide, 2·4	Water	1·0	∞
Acrylic acid, 4	Water	1·2	∞
Acrylonitrile, 5	Water	1·2	0·84
Styrene, 12	Acetic acid	2·4	1·44

No second homopolymer could be isolated for acrylamide and acrylic acid; the total weight increase corresponds to that on grafting and the R_g/R_h ratios are infinite. However, some homopolymers of acrylonitrile and styrene were isolated.

The very high yield obtained on grafting with acrylic acid led to experiments in double-grafting. A graft polymer, N-eosinpoly(vinylamine hydrochloride)–polyacrylamide (60/40), was used for initiating the polymerization of acrylic acid. The " ter-graft copolymer " contained 67 per cent acrylic acid, 19·8 per cent poly(vinylamine hydrochloride) and 13·2 per cent acrylamide.

Similar experiments with ω-N-eosinpoly(methyl methacrylate) are reported in *Table 8*.

Table 8.—Block copolymerization with ω-N-eosinpoly(methyl methacrylate) and thiourea; solvent = acetic acid

Monomer	Polymer (% by weight)	Time (h)	R_g/R_h
Styrene (20%)	4	3·5	1·86
Styrene (20%)	4	4	1·04
Styrene (20%)	4	7	0·87
Acrylamide (10%)	2·7	14	∞

Again, no homopolymer of acrylamide was isolated, and the grafting ratio is infinite, in spite of the relative low monomer concentration. In the case of styrene, the amount of homopolystyrene increases with the duration of irradiation, while the composition of the block copolymers remains practically constant at about 60 per cent poly(methyl methacrylate).

CONCLUSIONS

The synthesis of block copolymers of methyl methacrylate and poly-styrenes with t-butyl peroxide end groups gives a yield which indicates that ⟨benzene⟩—CH—CH₂—O· and Me₃C—O· radicals are equally efficient, as
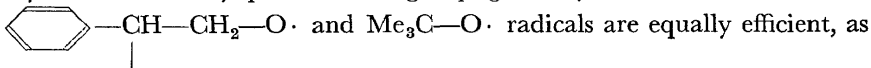
expected from their chemical structure.

However, the formation of blocks of methyl methacrylate with terminal t-butyl perester groups is much more difficult; this may be due to the fact that the reactivity of the carboxylate radicals is much lower than that of the t-butyloxy radicals.

Similarly, the synthesis of graft polymers, using t-butyl peresters or peranhydrides as active sites, gives a very low grafting yield with styrene, as there are great differences in the stabilities of the radicals and considerable steric hindrance, particularly in the methacrylic series. In these experiments, it can be seen that the viscosity of the solution has a marked effect on the grafting efficiency. This is probably due to chain-transfer between the small radical and the parent polymer, resulting in the formation of new graft sites.

Finally, the synthesis of graft and block copolymers with photosensitizing groups is of interest. Good yields are obtained by this method, and a second homopolymer is not always formed. The efficiencies of these reactions are, nevertheless, dependent on the nature of the second monomer; for example, they are especially high in the case of acrylamide and of acrylic acid.

Summary

Several polymers containing reactive side or end groups have been synthesized and used for the initiation of a second-step polymerization in order to obtain graft or block copolymers.

The relative efficiency of both radicals produced by the decomposition of these reactive sites has been evaluated on the basis of the amounts and the composition of the graft and homopolymer which were formed. Different systems initiating the reactions of polymer with monomer have been examined and compared with one another. The influence of the nature of the reactive site was considered by comparing the relative efficiencies of perester, peranhydride and peroxidic groups towards the same monomer, while the influence of the location of the reactive group (as side or as end group) on the efficiency was also examined in the case of perester groups and photosensitive groups.

The influence of the viscosity of the reaction medium was also taken into account.

The nature of the chain-termination reaction (addition or disproportionation), and the relative importance of the chain-transfer constant, are all-important for interpreting these efficiencies.

The author is indebted to the Centre des Hauts Polymères I.R.S.I.A., Belgium, for supporting this research.

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