

Graft Copolymerization with Perester Side Groups

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Various syntheses^{1,2} of graft copolymers have been described which involve the presence of suitable centers of reaction on the main chain of a preformed polymer. Most often these centers are reactive side groups, e.g., peroxides, hydroperoxides, or perester groups which can be introduced on the backbone polymer by autoxidation³⁻⁶, ozonization,⁷ direct chemical syntheses,⁸⁻¹⁰ or radiolysis in the presence of oxygen.^{11,12} These groups then give rise, on decomposition, to active macro free radicals.

Very few results have been given concerning the kinetics of this type of graft copolymerization, and in the present paper an attempt will be made to explain the data obtained for such a system. Because of its relatively high stability, the *tert*-butyl perester group seems highly attractive from a kinetic standpoint, and it was used in this work for the grafting of styrene onto methyl acrylate and methyl methacrylate copolymers containing this side group.

EXPERIMENTAL

1. Materials

Styrene (U.C.B.) stabilized by hydroquinone was washed twice in 10% caustic soda and again twice with distilled water. It was then dried for 24 hr. over anhydrous sodium sulfate and distilled under nitrogen at reduced pressure. *Methyl methacrylate* and *methyl acrylate* (U.C.B.) were treated in the same way. Their respective boiling points were 46°C. at 100 mm. and 80°C. at 760 mm. All monomers were stored at -5°C. until required.

The solvents *toluene* and *dioxane* (B.D.H.) were analytical grade materials and were kept over sodium wire before being distilled just prior to use. The dioxane was refluxed in the presence of sodium for 10 hr. to destroy any peroxides present.

Acrylyl chloride was prepared from acrylic acid and benzoyl chloride by the transesterification method described by Stempel et al.¹³ and was distilled twice under nitrogen (b.p. 74-76°C. at 740 mm).

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tert-Butyl hydroperoxide was prepared by the method of Milas and Sergenov¹⁴ and was dried before use over anhydrous magnesium sulfate. Analysis on the basis of hydroperoxide groups showed a purity of 94.6%.

2. Preparation and Composition of Copolymers

Methyl acrylate-*tert*-butyl peracrylate (MA-TBP) and methyl methacrylate-*tert*-butyl peracrylate (MMA-TBP) copolymers were synthesized. The synthesis of the perester-containing copolymers was effected in two stages. A 25% solution of the two monomers in dry toluene was polymerized at 45°C. for 3 hr. in the presence of 0.5% azobisisobutyronitrile as initiator. The copolymer was then twice precipitated in dry petroleum ether and dried under vacuum. The copolymer compositions were obtained from the combined analyses of the chloride groups present (Volhard method) and of those hydrolyzed during the preparation (titration in *N,N*-dimethylformamide with sodium methoxide in benzene, with thymol blue as indicator¹⁵). From these compositions the copolymerization parameters were calculated to be as given in Table I. In this table r_1 and r_2 are the reactivity ratios of the acrylyl chloride and the comonomer, respectively, and Q and e are the reactivity and polarity values.

TABLE I
Copolymerization of Acrylyl Chloride

Comonomer	r_1	r_2	Q	e
Methyl acrylate	2.3	0.345	0.57	+1.08
Methyl methacrylate	1.51	0.48	0.62	+0.98

To prepare the perester polymers,⁸ a copolymer was treated in dioxane solution with dry *tert*-butyl hydroperoxide in a stoichiometric ratio of 2:1 with respect to the chloride content, and the solution was left standing for 24 hr. It was then treated with a stoichiometric quantity of dry pyridine and shaken for several hours. The polymer was precipitated in petroleum ether, filtered, dried, and treated with water to hydrolyze the unreacted chloride groups. The *tert*-butyl peracrylate content was determined by iodometric titration according to the Silbert and Swern method,¹⁶ while the acrylic acid content was found by the titration described above.¹⁴

In order to eliminate the possibility of an effect of acidic groups on the stability of the perester-containing polymers (see Section A below), these active copolymers were dissolved, directly after isolation, in dry dioxane and treated with diazomethane. The methylated polymer was then precipitated in water, dried, dissolved in dioxane, and isolated by freeze drying. This treatment affords an acid-free copolymer containing *tert*-butyl perester groups which can be used as initiator for graft copolymerization.

It should be pointed out that it is much more difficult to synthesize the methacrylic than the acrylic series of these polyperesters, probably

because of high steric hindrance existing along the acid chloride groups. With an original copolymer containing 62 wt.-% acrylyl chloride, the maximum yield obtainable in peracrylate was 15.4 wt.-%. With a methyl methacrylate-methacrylyl chloride system the reaction is practically prohibited, since an SN_2 reaction cannot occur.

3. Graft Copolymerization

Graft copolymerization was carried out in sealed tubes in the temperature range 70–85°C. with dioxane as solvent. The concentration of the initiating polymer was varied between 0.5 and 5.0 wt.-%.

4. Fractionation and Isolation of Graft Copolymers

The fractionation was carried out at 25°C. by progressive precipitation on addition of methanol to a 2% polymer solution in chloroform. For both initiating systems, all fractions collected between γ -values (i.e., precipitant volume fractions) of 0.29 and 0.52 were practically pure polystyrene; less than 1 wt.-% was precipitated at γ -values in the range of 0.43–0.52, and it always consisted more than 90% of polystyrene.¹⁰

The remaining solution was concentrated to remove the chloroform, and graft copolymer so precipitated was filtered off, dissolved in dioxane, and isolated by lyophilization. As the initial copolymers are soluble in methanol there is little or no contamination of the graft copolymer fraction. The residual methanol solution was evaporated to dryness and the ester copolymer (free of polystyrene) was isolated.

Infrared analyses of the polymer fractions were carried out with a Perkin-Elmer Model 112 C double-beam infrared spectrometer with rock salt prisms. The amount of polystyrene in a polymer was determined by measuring the phenyl group absorption at 14.35 μ in dioxane.

RESULTS

A. Decomposition of Perester Copolymers

Perester-Ester Copolymers. The rates of decomposition of perester groups were measured at various temperatures for two copolymers of differing composition. The apparent first-order rate constants and the activation energies were evaluated, and the results are given in Table II. The differences between polymers I and III, viz., a higher rate of decomposition and a lower activation energy in the case of the latter, must be attributed primarily to their different molar compositions, the induced decomposition of peresters being favored by a high perester content. It is known that the induced decomposition due to radicals present in solution gives rise to a modification in the rate equation, i.e., the introduction of an additional term expressing the perester concentration to the 1.5 power.¹⁷ The rate is then written

$$-d[\text{Per}]/dt = k_1[\text{Per}] + k'[\text{Per}]^{1.5} \quad (1)$$

TABLE II
 Decomposition of Polymers Containing Perester Groups

Polymer	Composition, mole-%		Temp., °C.	$k_1 \times 10^5$	E_a	Concn. of polymer (solvent)
	<i>tert</i> - Butyl per- acrylate	Methyl acrylate				
I	12.19	87.81	75	0.7		
			85.5	2.5	29.6	2% (benzene)
			95	6.9		
III	32	68	(60)	(0.4)		1% (dioxane)
			73.7	1.2	26.8 \pm 0.5	
			95	11.7		

where $k' = k_3(k_1/k_4)^{0.5}$, in which k_1 , k_4 , and k_3 are the rate constants of the first-order decomposition, the recombination of radicals, and the induced decomposition, respectively. Integration of this equation gives

$$\ln \left(\frac{(k_1/k') + [\text{Per}]^{0.5}}{[\text{Per}]_0^{0.5}} \right) - \ln \left(\frac{(k_1/k') + [\text{Per}]_0^{0.5}}{[\text{Per}]_0^{0.5}} \right) = k_1 t \quad (2)$$

The value of the constant k' was determined by use of the method described by Bartlett and Nosaki. To find k' , two polymers of strongly different perester contents (5.1 and 30.6 mole-%) were decomposed at 76°C. in 1% solution in dioxane. Samples were taken at the same time intervals in the two runs; therefore, if $[\text{Per}]_1$ and $[\text{Per}]_2$ indicate the per ester concentrations at a given time, the rate equation may be written in the form

$$1/[\text{Per}]_1^{0.5} = \frac{C}{[\text{Per}]_2^{0.5}} + \frac{C-1}{[k_1/k']} \quad (3)$$

The graph of $[\text{Per}]_1^{-0.5}$ against $[\text{Per}]_2^{-0.5}$ is a linear plot whose slope and intercept on the y -axis give the values of C and $(C-1)/(k_1/k')$. By introducing (k_1/k') into eq. (2) the value of k_1 and consequently that of k' can be calculated. The experimental data are given in Table III. From these results, by using eqs. (2) and (3) one can calculate the values $C = 1.6$, $(k_1/k') = 0.46$, and $k_1 = 1.5 \times 10^{-5}$. The rate constant for the induced decomposition, k' , is then about twice the value of that for first-order decomposition.

It must always be kept in mind that these values of the decomposition rate constants, so determined, are influenced not only by the molar composition of the polymer but also by various other factors, such as the internal polymer structure (location of groups, tacticity of chains), the chain length, and the solution viscosity. These aspects will be considered in a future paper. The use of a variety of solvents in these experiments probably exerts an influence of secondary importance. In fact, *tert*-butyl per-

TABLE III
 Decomposition of Perester-Ester Copolymers^a

Polymer IV ^b			Polymer V ^c	
[a - x], mmoles/l.	[Per] ₁ ^{-0.5}	Time, min.	[a - x], mmoles/l. ^d	[Per] ₂ ^{-0.5}
57.5	4.17	0	295	1.84
55.5	4.24	68	267	1.94
49.5	4.50	120	244	2.02
46	4.66	180	222.5	2.12
43	4.82	240	197	2.25

^a 1% solution in dioxane, at 76°C.^b Perester/methyl acrylate molar ratio 5.1/94.9.^c Perester/methyl acrylate molar ratio 30.6/69.4.^d a = initial concentration perester, x = decomposed perester.

isobutyrate, when decomposed under constant experimental conditions in benzene and in dioxane has practically identical activation energies, viz., 31.6 and 31.4 kcal./mole, respectively.

Perester-Ester-Acid Copolymers. The decomposition of organic peresters incorporated in a polymer chain is very sensitive to the presence of acid groups in the polymer. In the presence of the latter it is found that there is a rapid decomposition step followed by a slower one. The activation energies are notably different, increasing from 15 kcal./mole for the rapid step to 25.6 kcal./mole for the slow step. Very remarkably, the degree of conversion reached during the rapid step is always slight, and varies with the polymer composition. Thus a copolymer containing 8 mole-% perester, 9 mole-% acid and 83 mole-% methyl acrylate reacted rapidly until 10% of the perester groups were decomposed; on the other hand, a copolymer containing 28.1 mole-% perester, 67 mole-% acid, and 4.9 mole-% unreacted acrylyl chloride, and whose preparation suggests a statistical distribution of groups along the chain, demonstrated a rapid

 TABLE IV
 Rate of Decomposition of Perester Groups in a Perester-Acid Copolymer^a

Temperature, °C.	$k_1 \times 10^5$, sec. ⁻¹	
	Slow step	Rapid step
100	51	
85	12.7	
74.7	4.1	
60	0.8	5.7
40		1.5
25		0.45
E_a , kcal./mole	25.6	15

^a The copolymer was composed of 28.1 mole-% perester, 67 mole-% acid, and 4.9 mole-% residual acid chloride groups.

step until the disappearance of 25–30% of the perester groups, after which the reaction slowed down.

The latter copolymer was subjected to a more quantitative study in which the decomposition was followed at different temperatures in a 1% dioxane solution. From the graph of the logarithm of the perester concentration versus time the first-order rate constants were calculated for the rapid step (at low temperatures) and the slow step (at higher temperatures). The results are assembled in Table IV.

We must therefore distinguish between two clearly different reactions, of which the much more rapid one is essentially responsible for the instability of polymers containing acid groups. On the other hand, the slow decomposition step has an energy of activation only slightly different from that of acid-free perester-ester copolymers, although the rate is about four times higher in the present case.

It must be noted not only that the presence of acid groups in the polymer gives rise to a rapid decomposition of part of the perester functions, but also that this decomposition is much faster than that brought about by the addition of external acid. Thus, when a polymer containing 25.2 mole-% perester is dissolved in glacial acetic acid, the rate constant is increased only to 1.5×10^{-5} and 2.3×10^{-5} sec.⁻¹ at 60° and 70°C. respectively, values much smaller than in the previous system, despite the high concentration of acetic acid.

B. Polymerization of Styrene Initiated by a TBP-MA Copolymer

To determine the dependence of the polymerization rate on the perester concentration, several experiments were carried out in the region of 75°C. on solutions of styrene in dioxane containing varying amounts of initiating copolymer. After some hours the reactions were stopped and the weight increases determined; the results are shown in Table V. The rates of conversion of styrene to polymer plotted logarithmically as a function of the perester concentration gave linear plots with slopes of approximately 0.5. Thus, the square root dependence on the perester concentration is valid even in the case of polymeric initiators. A similar result has been found by Hahn and Fischer⁸ for *tert*-butyl peracrylic ester as initiator in the bulk polymerization of methyl methacrylate.

The dependence of the rate of polymerization on the monomer concentration was determined at 74.5°C. in dioxane solution at a constant initiator concentration of 1.0 wt.-% of a polymer containing 12.2 mole-%/ester groups. The polymerization time was 310 min. The results are given in Table VI. These results demonstrate that a practically linear relationship exists (see Fig. 1) from which it may be concluded that the total rate is first order with respect to the monomer concentration under these experimental conditions of low perester content initiators and dilute polymer solutions. Considering that the homolytic cleavage of the perester O—O link in a polymer produces *tert*-butoxy radicals and macroradicals, both homopolystyrene and graft copolymer will be produced in quantities depending

TABLE V
Dependence of Styrene Polymerization Rate on Perester Concentration

Content of perester in initiating copolymer, mole-%	Temp., °C.	Polymeri- zation time, min.	Monomer concn., moles/l.	Perester concn. $\times 10^3$, mole/l.	$R_p \times 10^5$, mole/l.- sec.	$\log R_p / \log$ [Per]
1.2	75	360	4.365	0.69	1.62	0.49
				1.39	2.25	
				2.07	2.78	
				2.78	3.0	
				3.47	3.43	
14.2	77	420	4.365	0.69	1.86	0.48
				1.39	2.38	
				2.07	2.73	
				2.78	3.24	
				4.17	4.0	
25.2	70	420	2.619	3.75	3.57	0.50
				5.0	4.1	
				6.25	4.7	
				7.5	5.1	

TABLE VI
Dependence of Rate on Monomer Concentration in Styrene Polymerization

Monomer concn., moles/l.	Overall rate $R_p \times 10^5$, mole/l.-sec.	Homopolymeriza- tion rate $R_h \times 10^5$, mole/l.-sec.
2.62	2.32	1.73
3.49	2.83	2.08
4.36	3.52	2.70
5.24	3.91	3.40
6.11	4.97	4.13

TABLE VII
Dependence of Rate of Grafting on Monomer Concentration in Styrene Polymerization

Series	Monomer concn., moles/l.	Total rate $R_p \times 10^5$, mole/l.-sec.	Grafting rate $R_g \times 10^5$, mole/l.-sec.	Styrene in graft copolymer, wt.-%
A ^a	2.62	1.46	0.73	53.8
	3.49	2.28	1.15	—
	4.37	2.22	1.11	61.0
	5.24	4.30	1.43	—
	6.11	4.32	1.37	75.3
B ^b	2.62	9.64	8.2	—
	4.37	15.46	9.53	—
	5.24	19.9	10.4	—

^a Perester content in initiator 1.2 mole-%; [Init], 3 wt.-%.

^b Perester content in initiator 31.6 mole-%; [Init], 5 wt.-%.

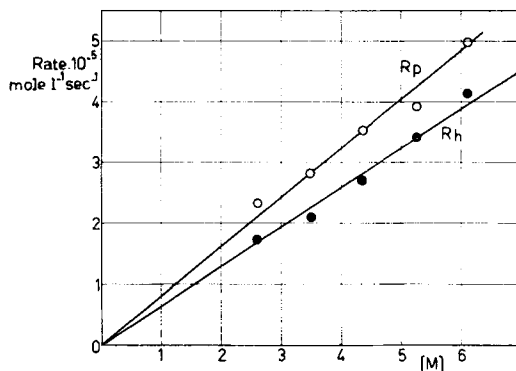


Fig. 1. Dependence of rate on monomer (styrene) concentration with *tert*-butyl peracrylate-methyl acrylate copolymer as initiator.

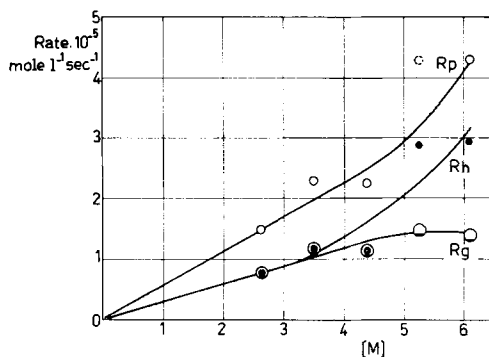


Fig. 2. Rate of polymerization of styrene at 74°C. in a 3% solution of polymer in dioxane (perester content 1.2 mole-%).

on the relative efficiencies of the two radical types. In Table VI the rate of homopolymerization is given for various monomer concentrations, and, as shown in Figure 1, this rate is also sensibly first order with respect to the styrene concentration, under these experimental conditions. Experiments were next carried out to compare the importance of the graft reaction in such polymerizations, and results are given in Table VII for two such series. The rates were calculated as follows: R_p from the total weight increase after polymerization, R_h from the weight of homopolystyrene after fractionation, and R_g from the weight of the isolated graft copolymers taking due account of the styrene content of the latter.

Table VII shows an increase in the styrene content of the graft copolymer with increasing monomer concentration. The effects of monomer concentration and of perester content of the backbone polymer are shown in Figures 2 and 3. Figure 2 shows that for an initiating system of low perester content (1.2 mole-%) both the total rate and the grafting rate are sensibly first order with respect to monomer in reasonably dilute solutions,

where the ratio R_g/R_h has a value of unity. At higher styrene concentrations, however, the grafting rate remains fairly constant while there is a marked increase in the rate of homopolymerization. In Figure 3 where the perester content is much higher (31.6 mole-%), as is the concentration of the polymeric initiator, a first-order relationship is still valid for the total rate, but at low styrene concentration grafting is greatly favored over the homopolymerization reaction. An increase in the monomer concentration, however, is again found to change the rate of grafting only slightly while giving a corresponding marked increase in the homopolymerization rate.

A comparison of Figures 2 and 3 suggests that the concentration of the initiating polymer may play an important role in the graft copolymerization, and from a study of this influence it is found that the grafting efficiency is much improved with a high concentration of perester copolymer. The results of several experiments are shown in Table VIII.

TABLE VIII
Effect of Peracrylate Copolymer Concentration on Grafting Efficiency

Expt. no.	Temp., °C.	[Init], wt.-%	Perester content, wt.-%	$R_h \times 10^5$, mole/l.-sec.	$R_g \times 10^5$, mole/l.-sec.	R_g/R_h
A1 ^a	74.5	1.0	18.9	1.73	0.60	0.34
A2a	75	1.0	11.1	0.52	1.50	2.9
A3	77	3.0	2.0	0.73	0.73	1.0
A4	75	4.0	11.1	0.69	3.40	4.9
A5	75	5.0	11.1	0.75	3.95	5.3
A6	74	5.0	43.6	1.46	8.20	5.6
B1 ^b	74.5	1.0	18.9	2.60	0.80	0.31
B2	75	3.0	2.0	2.80	1.43	0.51
B3	74	5.0	43.6	9.46	10.43	1.1

^a Series A: $[M] = 2.62$ mole/l. in dioxane.

^b Series B: $[M] = 5.24$ mole/l. in dioxane.

In experiment A2a 4% by weight of pure polymethyl acrylate was added to the polymerizing system and, as can be seen from the data, R_g/R_h was greatly increased. This provided evidence of the importance of the viscosity of the system to the grafting efficiency. This conclusion is confirmed by comparing experiments A1 with A3 and B1 with B2. These results also demonstrate the much more important influence on the grafting reaction of the initiator concentration as opposed to the perester content of the initiator. The significance of these and other results will be discussed in a later section of the paper.

C. Polymerization of Styrene Initiated by a TBP-MA-MMA Copolymer

As previously noted, it proved more difficult to prepare peresters from a methyl methacrylate-methyl acrylate copolymer, and, as a result, a high concentration of chloride groups was necessary to produce copolymer initiators sufficiently rich in perester groups. In each experiment reported

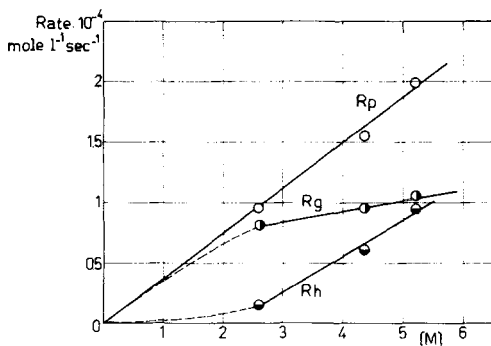


Fig. 3. Rate of polymerization of styrene at 74°C. in a 5% solution of polymer in dioxane (perester content 31.6 mole-%).

here the methyl methacrylate content of the copolymer was kept sensibly constant (viz., 38 units per hundred) whereas the contents of methyl acrylate and *tert*-butyl peracrylate were varied.

As found in the experiments of Section B, the total rate of polymerization is first order with respect to the styrene concentration (see Fig. 4), and the square root dependence on the initiator concentration is demonstrated—i.e., termination is by a reaction involving two growing radicals. The data for this is given in Table IX. As shown in Figure 4 the rate of grafting in this series is not first order unless perhaps at very low monomer concentrations, even with an initiating polymer of low perester content. In fact, the

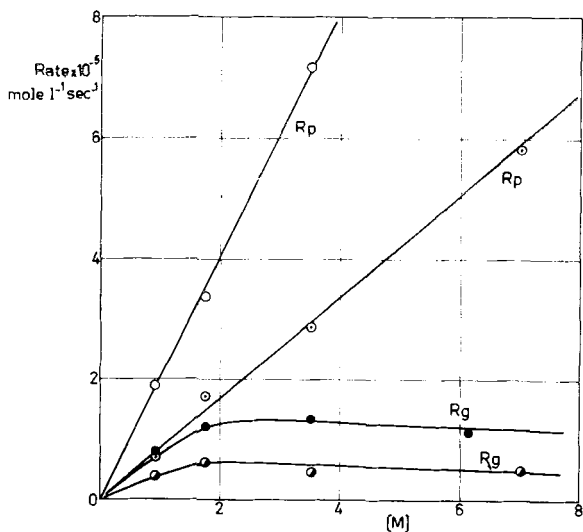


Fig. 4. Effect of monomer concentration on R_p and R_g in dioxane at 85°C.: (O, ●) 5% solution of polymer (perester content 5.6 mole-%); (○, ⊙) 1.6% solution of polymer (perester content 10.7 mole-%).

TABLE IX
Dependence of Rate on Initiator Concentration in Styrene Polymerization^a
 $\log R_p / \log [\text{Init}] = 0.46$

[Init], wt.-%	$R_p \times 10^5$, mole/l.-sec.
1.6	2.20
3.0	2.94
5.0	3.40

^a [M], 1.75 moles/l. in dioxane; perester content 5.6 mole-%; polymerization temp. 85°C.

rate of grafting becomes practically independent of styrene concentration (cf. Fig. 2).

As with methyl acrylate copolymer, the ratio R_g/R_h is again found to decrease in more concentrated monomer solutions (see Fig. 5), although the relative importance of grafting over homopolymerization in this system is considerably less than in the previous case, except at high dilution. Table X shows the effect of the perester content on the R_g/R_h ratios and gives the amount of polystyrene included in the graft copolymers. The viscosities of the solutions in these experiments were shown to be all of the same order of magnitude.

It has also been found that the concentration of the reactive polymer exerts an influence on the efficiency of grafting, though to a much lesser extent than in the first series (see Table VIII, experiments in series A). The results are given in Table XI.

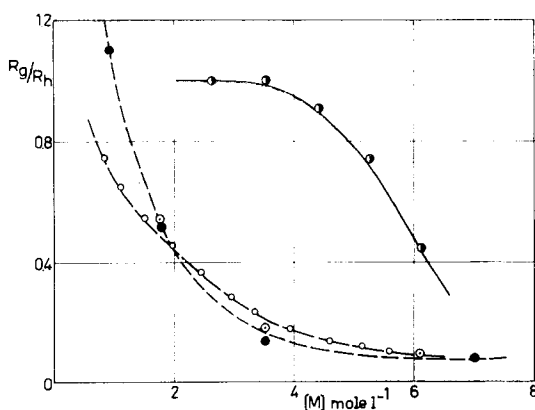


Fig. 5. Effect of monomer (styrene) concentration on R_g/R_h with methyl methacrylate-methyl acrylate-*tert*-butyl peracrylate as initiator in dioxane at 85°C.: (●) 1.6% solution of polymer (perester content 10.7 mole-%), (○) 5.0% solution of polymer (perester content 5.6 mole-%); and methyl acrylate-*tert*-butyl peracrylate as initiator in dioxane at 77°C.: (●) 3% solution of polymer (perester content 1.2 mole-%; values extrapolated from Figure 2).

TABLE X
 Effect of Perester Content on Grafting Efficiency^a

Perester content, mole-%	R_g/R_h	Polystyrene in graft copolymer, wt.-%
10.7	0.51	72.0
5.6	0.41	67.2
2.7	0.34	52.4

^a [M] = 1.75 mole/l. in dioxane; [Init] = 1.6 wt.-%; polymerization temperature 85°C.

 TABLE XI
 Effect of Initiator Concentration on Grafting Efficiency^a

[Init] wt.-%	Total rate $R_p \times 10^5$, mole/l.-sec.	R_g/R_h	Polystyrene in graft copolymer, wt.-%
1.6	2.20	0.41	67.2
3.0	2.94	0.42	66.7
5.0	3.40	0.53	65.0
1.6 ^b	2.29	1.06	84.3

^a [M], 1.75 moles/l. in dioxane; perester content 5.6 mole-%; polymerization temperature 85°C.

^b 4.0 wt.-% polystyrene was added to the polymerizing system.

In the experiment in which polystyrene was added to the system, the increase in viscosity markedly increased the efficiency of the grafting reaction, as was found before. As is seen from Table XI this added polymer had no effect on the total reaction rate.

DISCUSSION

In the polymerization of styrene initiated by the thermal decomposition of polymeric peresters, the dependences of the total reaction rate are found to be the same as for low molecular weight peroxides, i.e., the rate is first order with respect to the monomer concentration and proportional to the square root of the initiator concentration. The relative importance of grafting over homopolymerization is much more complicated, however. In the ideal case, for a monomer system terminating by a disproportionation mechanism between two growing radicals, and where the polymer carboxylate radical, $-\text{COO}\cdot$, and the *tert*-butoxy radical, $\text{C}_4\text{H}_9\text{O}\cdot$, have the same efficiencies for chain propagation, a value of R_g/R_h of unity would be expected. In the present case of styrene, however, termination is by a radical combination reaction so that a growing homopolystyrene chain can terminate with a growing graft chain by addition, the result of which should lead to an increase in R_g/R_h from 1 to 3 in the ideal case.

Since the R_g and R_h values are obtained from the weights of polystyrene isolated as grafted polymer and homopolymer, respectively, these values are

not true indications of the efficiencies of the respective radical species. An explanation is sought, however, for the very high (e.g., 5.0) and very low values of R_g/R_h found under different experimental conditions. This ratio is found to be greatly influenced by the monomer concentration. The relative decrease in the grafting reaction with increasing monomer concentration may be explained by the occurrence of chain transfer to monomer. Such a reaction will lead to an increase in the amount of homopolystyrene, since transfer by a growing chain, whether homo or graft, leads to the production of a polystyrene radical and the loss of a grafting site. Alternatively, the decrease in the R_g/R_h ratio may be due to an increased efficiency of the *tert*-butoxy radical in concentrated monomer solutions. For example, if the $C_4H_9O\cdot$ radical could be rendered inactive by an association with the solvent (dioxane) molecules, this could explain the manifestation of the graft reaction in dilute solutions, since a decrease in the dioxane concentration would lead to the release of $C_4H_9O\cdot$ radicals for homopolymerization. There is, however, no experimental evidence for such an association. A third explanation has been proposed by Banderet¹⁸ on the assumption of a limiting chain length for the graft. Solubility limitations, for instance, may place such a limit on the length of the grafted chains, and it is not unreasonable to expect that certain highly grafted copolymers in a concentrated solution will be in a highly swollen state, and that parts of the grafts may be broken off and so enter the solution as homopolymer. An increase in monomer concentration will thus favor the homopolymerization rate as measured gravimetrically. This interpretation was proposed by Banderet in order to explain data concerning the grafting of acrylonitrile on polystyrene. In the present system with styrene as monomer such a physical explanation does not seem acceptable, since styrene monomer is a good solvent for polystyrene and a monomer transfer reaction is preferred.

The "grafting efficiency," i.e., R_g/R_h , is also strongly affected by the initiator concentration, the higher the latter the greater being the value of this ratio (see Table VIII). This effect could be due to the increase in the viscosity of the polymerizing system brought about by a high macro-initiator concentration. It was found, in fact, that in both series the addition of unreactive polymer also increased the relative amount of grafted polymer, especially with the acrylic system where the added polymer was polymethyl acrylate. This increase in R_g/R_h must be attributed to the advent of chain transfer to polymer, i.e., the abstraction of an α -hydrogen atom from the backbone polymer by the $C_4H_9O\cdot$ radical, giving a new grafting site and *tert*-butyl alcohol. The correspondingly higher values of R_g/R_h with the pure acrylic system (see Section B) are then explained by the greater availability of α -hydrogens on the methyl acrylate units. At the same time, R_g/R_h is increased by the addition of polystyrene (Section C). Here there can be no increase in the transfer to polymer so that there must be some influence of the viscous medium on the efficiency of the small $C_4H_9O\cdot$ radical species. A decrease in the mobility of this radical would favor a transfer reaction to its parent copolymer. This transfer to polymer reaction or the partial trapping of $C_4H_9O\cdot$ radicals seems more plausible

as an explanation for the very high R_o/R_h values found in Section B than an explanation based on the chemical inefficiency of the *tert*-butoxy radical. It must be remembered that this radical readily decomposes to give acetone and a methyl radical.

Compared with the initiator concentration, the perester content of the copolymer has a much less important influence on the R_o/R_h values (see Tables VIII and X). In fact, it may be that in a polymer of high perester content all the perester groups are not effective reaction sites and that there occurs to some extent a recombination between radicals along the same chain, or double-bond formation (disproportionation). In either case macroradicals are consumed and disappear from the system without the production of graft copolymer. Of course the possibility of such interactions exists only when the number of perester groups per chain is sufficiently high.

Similar kinetic studies are in progress, in which an analogous backbone polymer containing other reactive side groups (peroxides, peranhydrides) is also used for the grafting of various monomers. The main difference lies in the nature of the small radical; the relative efficiencies of graft- and homopolymerization will be reported later.

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Synopsis

The kinetics of the graft copolymerization of styrene onto methyl acrylate (MA) and methyl methacrylate copolymers (MMA) containing *tert*-butyl perester groups have been studied. The synthesis of these perester copolymers was carried out in two steps: (1) copolymerization of acrylyl chloride with methyl (meth)acrylate, and (2) reaction of the acrylyl chloride copolymer with *tert*-butyl hydroperoxide. Further, these perester copolymers were usually treated with diazomethane in order to methylate any carboxylic group which might be present. The graft copolymers were separated from both homopolymers by progressive precipitation on addition of methanol to the chloroform solution of the copolymers. The stability of these perester copolymers has been considered and found to depend on whether there are acid groups in the copolymer. The first-order rate constants and the activation energy of decomposition in the absence of acid groups have been evaluated. These values depend on the molar composition of the copolymer; an induced decomposition of peresters is favored by a high perester content, which is responsible for a decrease in E_a (26.8 instead of 29.6 kcal./mole). In the presence of free carboxylic groups, some of the perester groups decompose very rapidly, the energy of activation of their decomposition being only 15 instead of 25.6 kcal./mole for the slow step. The degree of conversion attained during the rapid step is a function of the stereochemical structure of the copolymer, and the rate of decomposition is much higher than that produced by the addition of external acid. With the MA perester the rate of grafting is proportional to the square root of the perester concentration while it is first order with respect to the monomer concentration. These dependences were found to hold also for the overall rate of polymerization (from the total weight increase) as well as for the grafting rate (from the isolated graft copolymer and its styrene content). The styrene content of the graft copolymer increases with monomer concentration (e.g., 53.8 and 75.3 for monomer concentrations of 2.6 and 6.1 moles/l., respectively). At low monomer concentration, grafting is greatly favored over homopolymerization; it is also enhanced by the viscosity of the solution. With the MMA perester also, the grafting rate obeys the square root law for the perester concentration and the first-order dependence on monomer. However, the rate of grafting is practically independent of the styrene concentration over a large range. The relative importance of grafting over homopolymerization is in this case much less than with MA-TBP, except at high dilution. Different interpretations are suggested in order to explain the very high and sometimes very low values of R_g/R_h , the ratio of the rate of grafting to the rate of homopolymerization. The different behaviors of the MA and MMA peresters are discussed.

Résumé

On a étudié la cinétique de la copolymérisation greffée du styrène à des copolymères d'acrylate et de méthacrylate de méthyle contenant des groupes peresters tertio-butyliques. La synthèse de ces copolymères de peresters a été effectuée en deux étapes: la première consiste dans la copolymérisation du chlorure d'acryloyle avec l'acrylate (ou méthacrylate) de méthyle, la seconde dans la réaction du copolymère de chlorure d'acryloyle avec l'hydroperoxyde tertio-butylique. De plus, ces copolymères peresters étaient d'ordinaire traités au diazométhane de façon à méthyler les groupes carboxyliques éventuellement présents. Les copolymères greffés ont été séparés des deux homopolymères par précipitation progressive en additionnant du méthanol à une solution chloroformique des copolymères. On a également envisagé le problème de la stabilité de ces copolymères peresters; elle est fonction de la présence de groupes acides dans le copolymère. En absence de groupes acides on a évalué les constantes de vitesse de premier ordre et l'énergie d'activation de décomposition. Ces valeurs dépendent de la composition molaire du copolymère; une décomposition induite des peresters est favorisée par une teneur élevée en perester, et est responsable d'une diminution de E_a (26.8 au lieu de 29.6 Kcal/mole). En présence de groupes acides carboxyliques, une partie des

groupes peresters se décompose très rapidement, l'énergie d'activation de leur décomposition étant uniquement de 15 Kcal au lieu de 25.6 Kcal mole pour l'étape lente. Le degré de conversion atteint au cours de l'étape rapide est fonction de la structure stéréochimique du copolymère, et la vitesse de décomposition est beaucoup plus élevée que celle produite par l'addition d'une quantité équivalente d'acide externe. Avec le MA la vitesse de polymérisation greffée est proportionnelle à la racine carrée de la concentration en perester; par rapport à la concentration en monomère, la vitesse de polymérisation greffée aussi bien que la vitesse de polymérisation totale sont toutes deux du premier ordre. La première de ces deux vitesses est obtenue au départ de la quantité de copolymère greffé isolé et de sa teneur en styrène, la seconde au départ de l'augmentation de poids total. La teneur en styrène du copolymère greffé croît avec la concentration en monomère (par exemple croît de 53.8 à 75.3 pour une concentration molaire de 2.6 et 6.1 respectivement). A basses concentrations en monomère, la réaction de greffage est nettement favorisée si on la compare à la homopolymérisation; elle est également favorisée par une augmentation de viscosité de la solution. Avec le MMA la loi de la racine carrée de la concentration en initiateur de même que le premier ordre par rapport à la concentration en monomère sont également obéies. La vitesse de greffage est toutefois pratiquement indépendante de la concentration en styrène sur un large domaine des concentrations. L'importance relative du greffage comparé à la homopolymérisation est dans ce cas-ci beaucoup moins prononcée que dans le cas précédent avec le MA, sauf aux fortes dilutions. Plusieurs interprétations ont été suggérées en vue d'expliquer les valeurs très élevées et parfois très basses du rapport R_g/R_h , rapport des vitesses de greffage à celle de homopolymérisation. Les comportements différents des MA and MMA ont également été discutés.

Zusammenfassung

Die Kinetik der Pfropfcopolymerisation von Styrol auf Methylacrylat- und Methylmethacrylatcopolymeren (Cop A und Cop M) mit einem Gehalt an *tert*-Butylperestergruppen wurde untersucht. Die Synthese dieser Perestercopolymeren wurde in zwei Stufen ausgeführt. Die erste besteht in der Copolymerisation von Acrylylchlorid mit Methylmethacrylat, die zweite in der Reaktion des Acrylylchloridcopolymeren mit *tert*-Butylhydroperoxyd. Ausserdem wurden diese Perestercopolymeren zur Methylierung eventuell vorhandener Carboxylgruppen gewöhnlich mit Diazomethan behandelt. Die Pfropfcopolymeren wurden von den beiden Homopolymeren durch fraktionierte Fällung mit Methanol aus Chloroformlösung getrennt. Die Stabilität dieser Perestercopolymeren hängt von der Gegenwart von Säuregruppen im Copolymeren ab. Für die Zersetzung in Abwesenheit solcher Gruppen wurden die Geschwindigkeitskonstanten erster Ordnung und die Aktivierungsenergie ermittelt. Die Werte hängen von der molaren Zusammensetzung des Copolymeren ab; eine induzierte Zersetzung der Perester wird durch einen hohen Gehalt an Perester begünstigt und ist für eine Erniedrigung von E_a (26,8 anstatt 29,6 kcal Mol⁻¹) verantwortlich. Bei Anwesenheit freier Carboxylgruppen zersetzt sich ein Teil der Perestergruppen sehr rasch, wobei die Aktivierungsenergie der Zersetzung nur 15 kcal, anstelle von 25,6 bei der langsamen Reaktion, beträgt. Der während der raschen Zersetzung erreichte Umsetzungsgrad ist eine Funktion der stereochemischen Struktur des Copolymeren; die Zersetzungsgeschwindigkeit ist viel höher als die durch Zusatz fremder Säure hervorgerufene. Beim Perester-Cop-A ist die Pfropfungsgeschwindigkeit der Quadratwurzel aus der Peresterkonzentration proportional, während sie in bezug auf die Monomerkonzentration sowohl bei der Bruttopolymerisationsgeschwindigkeit (aus der Gesamtgewichtszunahme) als auch bei der Pfropfgeschwindigkeit (aus dem isolierten Pfropfcopolymeren und seinem Styrolgehalt) von erster Ordnung ist. Der Styrolgehalt des Pfropfcopolymeren nimmt mit der Monomerkonzentration zu (z.B. 53,8 bzw. 75,3 für eine Monomerkonzentration von 2,6 bzw. 6,1 Mol l⁻¹). Bei niedriger Monomerkonzentration ist die Pfropfung gegenüber der Homopolymerisation stark begünstigt; sie wird auch durch die

Viskosität der Lösung erhöht. Beim Perester-Cop-M gilt ebenfalls das Quadratwurzelgesetz für die Peresterkonzentration und die erste Ordnung in bezug auf das Monomere. Die Pfropfungsgeschwindigkeit ist jedoch von der Styrolkonzentration in einem grossen Bereich unabhängig. Die Bedeutung der Pfropfung relativ zur Homopolymerisation tritt in diesem Fall, mit Ausnahme hoher Verdünnung, viel weniger hervor als beim Cop A. Verschiedene Deutungen wurden zur Erklärung der sehr hohen und manchmal sehr niedrigen Werte des Verhältnisses R_g/R_h , Pfropfungsgeschwindigkeit durch Homopolymerisationsgeschwindigkeit, vorgeschlagen. Das verschiedene Verhalten von Cop A und Cop M wurde diskutiert.

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