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Graft Efficiency

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Dedicated to Prof Dr. W. KERN on the occasion of his 60th birthday

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SUMMARY:

Polystyrenes carrying *tert.*butyl peracrylic side groups have been synthesized by copolymerization of styrene with acrylyl chloride, partial esterification of the acid chloride units with *tert.*butyl hydroperoxide, and, finally, methylation of the remaining free carboxylic groups. The weight percent of perester units varied from 0.9 to 3.4, that of methyl acrylate between 14 and 18%. These copolymers were used at 75 °C. in benzene solution for initiating the polymerization of methyl methacrylate; this second step polymerization obeys the square-root law with respect to the initiator concentration, and is proportional to the monomer concentration. The graft efficiency, *i.e.* the ratio of the amount methyl methacrylate bonded as grafts to that of homopolymer, has been determined by carrying out fractionation of the several reaction products, using the precipitation method with chloroform as solvent and methanol as precipitant. The graft efficiency decreases from 1.52 to 0.77 when the monomer concentration increases from 1.91 to 7.54 mole $\cdot l^{-1}$; it is however unsensitive to the macroinitiator concentration, unsensitive to the bulk viscosity of the reaction medium as well as to the presence of non-solvent (methanol) in this medium.

The perester-content of the macroinitiator exerces a slight influence, the efficiency being higher when this content increases.

The temperature affects strongly the efficiency ratio; this ratio increases from 0.53 to 1.11 when the temperature rises from 55 ° to 75 °C.; this effect stresses the strong influence of the nature of the radical with respect to their ability of monomer addition.

ZUSAMMENFASSUNG:

Polystyrol mit seitenständigen Acrylsäure-*tert.*-butylhydroperoxidestergruppen wurde durch Copolymerisation von Styrol mit Acrylsäurechlorid erhalten, wonach die Acrylsäurechloridbausteine teils mit *tert.*-Butylhydroperoxid und die unversehrten Säurebausteine teils zum Methylester umgesetzt wurden. Der Perestergehalt lag im Bereich von 0,9 bis 3,4%, der des Acrylsäuremethylesters von 14 bis 18%. Diese Polymere dienten bei 75 °C in Benzol zur Auslösung der Polymerisation von Methacrylsäuremethylester. Die Polymerisation in zweiter Stufe folgt dem Quadratwurzelgesetz hinsichtlich der Initiatorkonzentration und ist proportional der Monomerkonzentration. Der Pfropfwirkgrad, das ist das Verhältnis der Menge an aufgezweigtem Methacrylsäuremethylester zur Menge des

Stammpolymers, wurde durch Fraktionierung der Reaktionsprodukte bestimmt. Hierbei war Chloroform Lösungs- und Methanol Fällungsmittel. Der Pfropfwirkgrad fällt von 1,52 auf 0,77, wenn die Monomerkonzentration von 1,91 auf 7,54 Mol·l^{-1} steigt. Er ist indessen unbeeinflußt von der Konzentration des Makroinitiators, der Viskosität des Reaktionsmediums wie auch von der Anwesenheit eines Nichtlösers wie Methanol in diesem Medium.

Der Perestergehalt des Makroinitiators übt einen geringen Einfluß aus; der Grad ist größer, wenn der Gehalt zunimmt.

Die Temperatur hat eine starke Wirkung auf das Wirkverhältnis der verschiedenen Radikale; dieses Verhältnis wächst von 0,53 auf 1,11, wenn die Temperatur von 55 auf 75 °C steigt. Dieser Befund unterstreicht den starken Einfluß auf die Leichtigkeit der Monomeranlagerung, die von der Struktur des Radikals abhängt.

Introduction

The kinetics of graft polymerization of styrene onto polymethyl acrylate and polymethyl methacrylate carrying tert.butyl peroxide side groups, have been described previously[1].

It has been found that the grafting efficiency, *i.e.* the ratio of the amount of styrene bonded as grafted side chains to that of homo-polystyrene, was dependent from the monomer concentration, the composition of the macro-initiator, the bulk viscosity of the reaction medium and the reaction temperature. Analogous results were obtained with similar polymers containing side peranhydride groups[2].

It seems therefore interesting to examine the reverse situation, in which the initiating system would be a polystyrene carrying *tert.*butyl peroxide side groups, and the second monomer would be methyl methacrylate. It is well known indeed that a polystyrene back-bone is much less sensitive to a radical attack as those of the polyacrylic or polymethacrylic polymers, and consequently a pronounced difference in behavior could be expected.

It is the purpose of the present paper to present these new results and to compare them with those of the previous polymer-monomer systems.

1. *Experimentals*

a) *Copolymerization of acrylyl chloride and styrene*

Copolymers were prepared in 20% monomer solution in dry benzene at 67 °C. in the presence of 0.5% azobisisobutyronitrile with respect to the total weight of monomers. Previously monomers, solvent and precipitant were carefully dried before use; the copoly-

mers were precipitated in heptane and dried *i.vac.* at 60 °C. The yields were always kept between 5 and 10%. The copolymer composition was determinated on the basis of the chlorine content[3]; the data are given in Table 1.

Table 1. Copolymerization of acrylyl chloride (M_1) and styrene (M_2)

Molar concentration		Molar fraction of acrylyl chloride	
(M_1)	(M_2)	Monomer mixture	Copolymer
0.018	1.858	0.009	0.16
0.035	1.840	0.020	0.19
0.090	1.783	0.048	0.30
0.361	1.497	0.198	0.43
0.534	1.270	0.295	0.44
0.889	0.909	0.494	0.475
1.036	0.731	0.587	0.49
1.448	0.374	0.795	0.52
1.698	0.094	0.948	0.54

The copolymerization parameters r_1 and r_2 are equal to $r_1 = 0.03 \pm 0.01$; $r_2 = 0.10 \pm 0.01$.

Consequently the copolymers show a strong alternating structure. On the basis of the Q and e schema of ALFREY and PRICE[4,5] the reactivity Q and polarity e of acrylyl chloride are equal to 0.8 and +1.6 respectively (for styrene $Q_2 = 1.0$ and $e_2 = -0.8$).

b) *Co(styrene-methylacrylate–tert.butyl peracrylate)*

To a solution of a styrene-acrylyl chloride copolymers in dry dioxane, *tert.*butyl hydroperoxide and pyridine were added under stirring in an inert atmosphere. After reaction the mixture is poured into methanol/water (5/1); the unreacted acid chloride units are thus transformed to methyl ester and free carboxylic acid.

In order to prevent the acid decomposition of the *tert.*butyl peracrylate groups[6], these carboxylic acid units are esterified by dissolving the copolymer in dioxane and treated with diazomethane until the solution becomes coloured yellowish. The copolymer is then precipitated again in methanol/water and dried *i.vac.* The perester content was determined by the iodometric method as described by SILBERT and SWERN[7].

The transformation of acid chloride into *tert.*butyl perester proceeds only slowly and with low yield. In order to obtain an initiator containing between 1 and 3.5% perester unit, it is therefore necessary to start with a copolymer containing 15% acrylyl chloride.

Table 2. Composition of polymeric ester initiators

Polymer	Weight per cent			Molecular weight
	Perester	Me-acrylate	Styrene	$\overline{M}_n$ (osmot.)
PIn_1	1.4	14.2	83.5	81,000
PIn_2	3.4	14.0	82.4	92,000
PIn_3	1.0	17.6	81.4	89,000
PIn_4	0.9	18.1	81.0	115,000

For the purpose of the present study, copolymers with high styrene content are necessary for making possible the separation of graft- and homopolymers. The composition and the molecular weight of the initiators are given in Table 2.

c) *Graft polymerization and fractionation*

Grafting experiments were carried out in benzene solution under nitrogen atmosphere at 75 °C.; at this temperature the thermal polymerization of methyl methacrylate can be neglected as well as the degradation and depolymerization of the macroradicals which are formed. After reaction the copolymers were precipitated by pouring the solution in heptane and dried *i.vac.* at 40 °C. The copolymer mixture was fractionated at 25 °C. by the precipitation method[8] using chloroform as the solvent and methanol as precipitant.

The fractionation method has been standardized by using mixtures of polymethyl methacrylate homopolymer and a (styrene-methyl acrylate) copolymer of the same overall composition as the macroinitiator (styrene 82%) (except the perester group). As can be seen from Fig. 1, both polymers can be separated satisfactorily. In order to make the separation even sharper, the macroinitiator itself has been fractionated before use, and the small fractions precipitating at γ-value above 0.45 were discarded; on this way, the initiating copolymer (mainly polystyrene) precipitated between $\gamma = 0.3$ and 0.45, while homo-polymethyl methacrylate above $\gamma = 0.75$.

Table 3. Fractionation of a mixture*) of a co(styrene 82/methyl acrylate 18) polymer ($\overline{M}_n$ = 43,400) and polymethyl methacrylate ($\overline{M}_n$ = 56,000)

Volume fraction MeOH, γ	Wt. of fraction (mg.)	(%)	PStyr. content (%)	PStyr. recuperated (%)
0.40	970.2	32.3	88.7	73.2
0.45	250.1	8.4	83.7	17.2
0.49	83.6	2.8	74.9	5.3
0.54	62.4	2.1	59.8	3.2
0.60	37.2	1.2		
0.675	33.4	1.1		
0.785	701.7	23.4		
Residue (dryness)	830.2	27.6		
Total	2968.8	98.9		99.6

*) 1.382 g. co(styrene 82/methyl acrylate 18) polymer and 1.618 g. polymethyl methacrylate in 150 ml. $CHCl_3$.

Using this fractionation method, the graft copolymer precipitated between $\gamma = 0.55$ and 0.73. In fact from $\gamma = 0.55$ and 0.60 the solution becomes cloudy without floculation of the copolymer; apparently the side graft chains remain solvated in the medium and prevent the precipitation of the copolymer. Further additions of methanol causes the desolvatation of the side grafts, and consequently the precipitation of the copolymer. The different fractions were isolated by centrifugation, redissolved in butanon and precipitated again in a mixture methanol/water. Only the residual fraction (γ = 0.78 to 1.00) was obtained by

evaporation of the solution. When the amount of graft polymer is very large, coprecipitation with some polymethyl methacrylate homopolymer occurs; these large fractions were therefore refractionated, and the compositions of the grafts determined after purification.

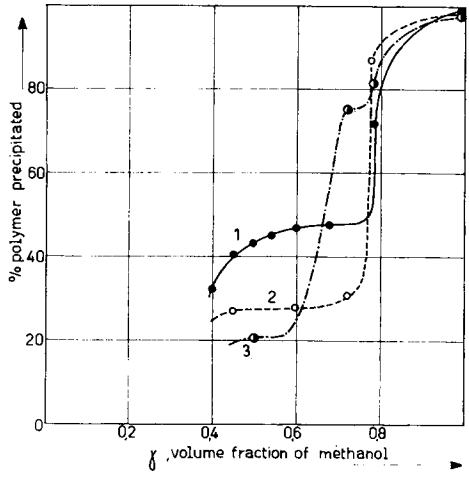

Fig. 1. Fractionation of polymer mixtures and grafted polymer systems. Solvent: Chloroform, precipitant: methanol, t°: 25 °C. Curve 1: ● mixture co(styrene 82/methyl acrylate 18) polymer and polymethyl methacrylate (Table 3). Curve 2: ○ polymer obtained from methyl methacrylate, polymerized with *tert.*butylperoxide as initiator in the presence of co(styrene 82/methyl acrylate 18) polymer (Table 4). Curve 3: ◑ graft reaction product of methyl methacrylate onto perester containing polymer

In Table 4 an example is given of the fractionation of a graft reaction product, obtained in benzene solution at 75 °C. in the presence of 2% PIn_3 as initiator (*i.e.* perester concentration equal to 1.39 mmole·l^{-1}); the concentration of monomer was 4.774 mole l^{-1}.

It has also been verified that in the course of the side chain grafting due to the perester groups of the macroinitiator, practically no grafting occurs simultaneously, by chain transfer to polymer, either in the presence of added di-*tert.*butylperoxide, either in the absence of any initiator.

Therefore 2 g. of a co(styrene 82/methyl acrylate 18) polymer ($\overline{M}_n$ = 103,000) have been dissolved in 25 ml. benzene in the presence of 9.36 g. methyl methacrylate and 50 mg. di-*tert.*butyl peroxide. The solution has been heated up at 100 °C. during 315 min.; after reaction the polymers were precipitated. A weight increase of 4.278 g. polymethyl methacrylate was obtained, *i.e.* a degree of conversion of 46%. 2.5 g. of the polymer mixture was then fractionated; the results are given in Table 5 (Fig. 1, curve 1).

As can be seen from these data, the amount of grafted methyl methacrylate by transfer is very low and represents only 2% of the total polymerized methyl methacrylate, although the reaction conditions were more favorable for an eventual grafting in this experiment, than in the usual graft experiments.

Table 4. Fractionation of graft reaction product.
1.989 g. polymer dissolved in 150 ml. chloroform

Fract. No.	Vol. fract. MeOH, γ	Wt. of fraction mg. polymer exper.	correct	corrected*) (%)	PStyr. content (%)	PStyr. recuped. mg. (correct)*)	Remarks
1	0.37–0.50	750	774	38.9	82.5	638.5	—
2	0.50–0.71	43	44	2.2	40.7	18	graft
3	0.71–0.735	1013.5	1046	52.6	14.3	149.5	refractionated
4	0.75–0.78	87.5	90	4.5	0	0	homo PMMA
5	residue	34	35	1.8	0	0	homo PMMA
Total		1928	1989	100		806	total recuped. polym. 96.9%
Refractionation of fraction No. 3 985.5 mg. dissolved in 100 ml. chloroform							
3a	0.43–0.72	41	45	2.3	38	17	graft
3b	0.72–0.73	251.5	275	13.8	18	49.5	graft
3c	0.745–1.0	664	726	36.5	9	65	refractionated
Total		956.5	1046	52.6		131.5	total recuped. polym. 97.05%
Refractionation of fraction No. 3c 616 mg. dissolved in 50 ml. chloroform							
3d	0.45–0.74	301	368	18.5	16	59	graft
3e	0.74–0.76	101	123	6.2	0	0	homo PMMA
3f	0.78–1.0	192	235	11.8	0	0	homo PMMA
Total		594	726	36.5			total recuped. polym. 96.4%

*) Corrected values are thoses calculated for 100% recuperated polymer.

It is also worthwhile to mention that a similar chain transfer experiment carried out in the same experimental conditions with pure homopolystyrene instead of the styrene-methyl acrylate copolymer gives only 0.8% methyl methacrylate bonded to the polymer, *i.e.* about a third of the preceding case.

Consequently grafting by chain transfer reaction to polymer can be neglected during the graft experiments studied in the present paper.

Infrared spectra of the copolymers were recorded in dioxane solutions with a Perkin-Elmer 21 double beam spectrometer. The styrene content was determined with the mono-substituted phenyl group absorption at 696 cm^{-1}, that of methyl acrylate and of methyl methacrylate with the carbonyl absorptions at 1736 and 1732 cm^{-1}. The perester carbonyl group absorbs at 1768 cm^{-1}.

Table 5. Polymerization of methyl methacrylate in the presence of co(styrene 82/methyl acrylate 18) polymer, and of di-*tert.*butyl peroxide as initiator. Fractionation of reaction product

Vol. fract. MeOH, γ	Wt. of fraction (mg.)	Wt. of fraction (%)	PStyr content (%)	PStyr recuperated	PMMA recuperated (mg.)
0.45	696	27.8	82	584.5	—
0.60	18	0.7	66	12	4.5 graft
0.72	51.5	2.0	31.5	16.5	30 graft
0.78	1384	55.4	2.5	34.0	1381.5 homo
Residue ...	296.5	11.9	0	0	302 homo
Total	2446	97.8		647	1728

Molecular weights were determined osmometrically in benzene at 25 °C.; similarly viscometric measurements were carried out in benzene at 25 °C. in a modified UBBELOHDE dilution viscosimeter. The molecular weights of the graft copolymers varied from $\overline{M}_n$ = 250,000 to 600,000; those of homopolymethyl methacrylate were between 150,000 and 300,000.

2. *Experimental Results and Discussion*

a) *Kinetics of polymerization*

Before considering the efficiency of grafting, the overall kinetics of graft polymerization have been examined from the point of view of the order of reaction with respect to the macroinitiator and the monomer concentrations. In a first series of experiments carried out at 75 °C. in benzene solution in the presence of 20 volume percent of methyl methacrylate, different concentration of macroinitiator have been used. The solutions were made isoviscous by adding inert high molecular polystyrene (molecular weight: 10^6). After 170 min., the reactions were stopped by precipitation of the copolymer. The experimental data are given in Table 6.

By plotting in a logarithmic diagram the rate *versus* the perester concentration, one obtains a straight line, passing through the origin and with a slope equal to 0.5 (Fig. 2).

A similar result was already found previously for other macroinitiators[1,2,9,10].

Table 6. Rate dependance from the concentration of macroinitiator

PIn_1: 1.4% perester content PIn_2: 3.4% perester content		(MMA) = 1.87 mole·l^{-1} t° = 75 °C., solvent: C_6H_6
PIn g./25 ml. solution	(perester) 10^3 mole·l^{-1}	Rp·10^5 mole·l^{-1}·sec^{-1}
1.20 PIn_1	1.20	2.83
0.65 PIn_2	1.54	3.04
2.00 PIn_1	2.01	3.36
2.79 PIn_1	2.70	4.05
1.64 PIn_2	3.87	5.25

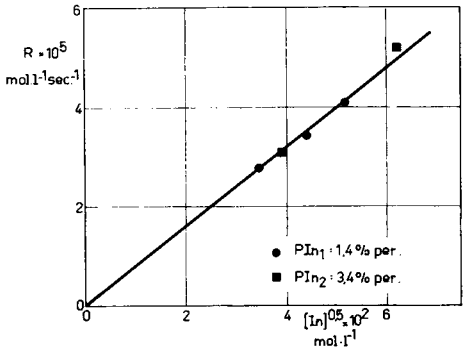

Fig. 2. Rate dependance on the macroinitiator concentration. t° = 75 °C. (MMA) = 1.87 mole·l^{-1}. PIn_1 ● = 1.4% perester; PIn_2 □ = 3.4% perester

Similar experiments were carried out at 75 °C. in benzene solution at constant initiator concentration (2 weight-%) but different monomer concentrations. The times of reaction varied between 30 and 100 min. (Table 7), the degree of conversion being kept below 10 %.

By plotting the rate of polymerization *vs.* the monomer concentration, a linear line is obtained, indicating a first order reaction with respect to the monomer, except at low concentration where it may be higher than the unity (Fig. 3).

From these data it may again be concluded that the second step polymerization initiated with a macroinitiator, behaves similarly to that of the usual polymerization with low molecular weight initiator.

Table 7. Rate dependance on the monomer concentration

PIn_3 = 1.0% perester (perester) = $1.39 \cdot 10^{-3}$ mole·l^{-1}	t° = 75 °C. solvent: C_6H_6
(MMA) mole·l^{-1}	$Rp \cdot 10^5$ in mole·l^{-1}·sec^{-1}
1.913	2.7
2.886	4.83
3.818	5.4
4.774	7.24
5.7	8.94
7.545	11.85

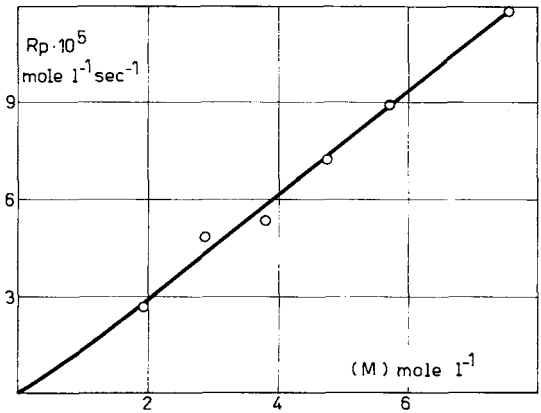

Fig. 3. Rate of polymerization of methyl methacrylate with macroinitiator. Influence of monomer concentration. (Perester) = $1.39 \cdot 10^{-3}$ mole·l^{-1}; solvent: benzene

b) *Grafting efficiency*

When the perester side groups of the macroinitiator decompose, two different radicals are produced, a carboxylate macroradical and a *tert.*-butyloxide radical. The carboxylate radical will lose its carbon dioxide at least partially, while the *tert.*butyloxide radical on dismutation gives acetone and a methyl radical.

It is evident that the relative reactivity of these radicals with respect to methyl methacrylate may be very different; it can however be evaluated easily by fractionation of the reaction products and further analysis. The ratio of the amount of methyl methacrylate bonded as grafted side

chains to that of homo-polymethyl methacrylate originating from the *tert.*butyloxy radical is considered as a measure of their relative reactivity, *i.e.* of their grafting efficiency, if the degree of conversion is kept sufficiently low. This efficiency must be equal to the unity, if both radicals have the same reactivity and if the chain termination proceeds mainly by disproportionation. Moreover, it has been shown that grafting by chain transfer reaction between a growing chain and the polystyrene macroinitiator is negligible (see experimentals), so that this effect must not be taken into account.

In this section the influence of the different kinetic parameters on this efficiency ratio will be examined; therefore we will consider successively the influence of the initiator and monomer concentrations, the influence of the viscosity of the reaction medium and of the temperature, and finally the influence of the presence of a non-solvent in the reaction medium.

With respect to the monomer concentration, a series of graft experiments have been carried out in the presence of a constant perester-copolymer concentration at 75 °C. in benzene solution. The degrees of conversion were always between 2 and 10 %. The results are given in Table 8.

Table 8. Graft efficiency in the presence of a constant perester-copolymer concentration at 75 °C. in benzene solution

Influence of the concentration of methyl methacrylate
2.00 % PIn_3 (1.0 % perester) [In] = $1.39 \cdot 10^{-3}$ mole·l^{-1} Solvent: benzene, t^0 = 75 °C.

[MMA] mole·l^{-1}	Time (min.)	mg. PMMA in 50 ml. solution			$R \cdot 10^5$ mole·l^{-1}·sec^{-1}			$\frac{R_g}{R_h}$
		total	grafted	homo	R_p	R_g	R_h	
7.545	29	1034	451	583	11.85	5.17	6.68	0.77
5.700	38	1020	491	529	8.94	4.30	4.63	0.96
4.774	50	1087	581	506	7.24	3.87	3.37	1.15
3.818	60	967	539	428	5.37	2.99	2.38	1.26
2.886	105	1524	882	642	4.83	2.80	2.03	1.37
1.913	105	847	511	336	2.69	1.62	1.07	1.52

Fig. 4 shows a linear relationship between the total rate of polymerization and the monomer concentration; contrarily the diagrams of the rates of grafting and of homopolymerization *vs.* monomer are curved and intercept each other at (M) = 5.4 mole·l^{-1}. In the upper diagram the Rg/Rh ratio *i.e.* the efficiency decreases linearly with an increasing mono-

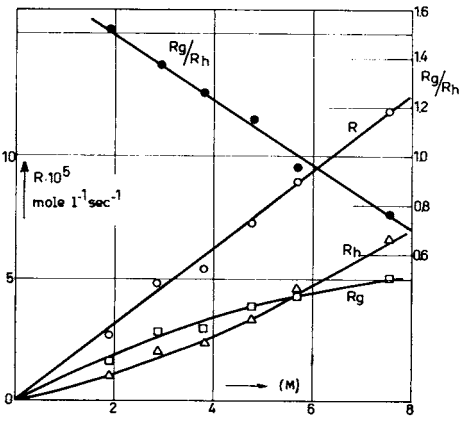

Fig. 4. Influence of the methyl methacrylate concentration on the grafting efficiency. Grafting at 75 °C. in benzene solution with 2 % PIn_3 (1 % perester). [In] = $1.39 \cdot 10^{-3}$ mole·l^{-1}

mer concentration. This effect can be attributed to an increasing contribution of the chain transfer reactions when the monomer concentration increases. Indeed, the chain transfer constant of methyl methacrylate monomer C_M has been found equal to $1 \cdot 10^{-5}$ at 60 °C.[11] and $8 \cdot 10^{-5}$ at 70 °C.[12] while that of benzene equals $0.75 \cdot 10^{-5}$ at 80 °C.[13]. Consequently the relative importance of the homopolymerization increases with increasing monomer concentration. This behavior was also found previously for acrylic-methacrylic copolymers containing perester groups[1], which were used for grafting of styrene; contrarily with peranhydride containing polymers, the efficiency increased slowly with the monomer concentration[2]. This effect may therefore not be explained only on the basis of chain transfer with monomer, but should be also a function of the nature of the small radicals which are produced.

With respect to the concentration of *tert.*butyl peracrylate concentration, the situation is more complex, because an increase of initiator concentration necessarily increases the viscosity of the solution, and this viscosity increase can affect as well the initiator efficiency as the graft efficiency ratio. Indeed, the apparent first order rate constant of decomposition at 75 °C. of initiator PIn_4 dissolved in benzene-methyl methacrylate (9 vol./1 vol.) decreases from $1.1 \cdot 10^{-5}$ to $0.9 \cdot 10^{-5}$ sec^{-1} when this decomposition is carried out in the presence of 2 weight-% high molecular weight polystyrene ($\overline{M}_w$ 10^6). Similar results will be reported later with respect to the photopolymerization of styrene[14]. This decrease

of efficiency of the initiator due to the recombination of primary radicals should however not affect the graft efficiency ratio, in so far as macroradicals and *tert.*butyloxide (or methyl) radicals recombine with each other before adding monomer. It was however observed previously in the case of perester containing polyacrylate that a change of viscosity of the medium increases markedly the graft efficiency ratio of styrene[1)], and this increase was attributed to the advent of chain transfer to polymer, *i.e.* the abstraction of an α-hydrogen atom from the backbone polymer by the $C_4H_9O\bullet$ radical, giving a new site of grafting. Therefore reactions have been carried out in presence or absence of inert high molecular weight polystyrene; the degree of conversion varied between 23 and 34 % and the results are reported in Table 9.

Table 9. Grafting efficiency in presence or absence of inert high molecular weight polystyrene

Influence of the initiator and of the viscosity of the medium. Solvent: benzene (25 ml.) t°: 65 °C.

Initiator	PIn (%)	(In) 10^3 mole $\cdot l^{-1}$	(MMA) mole $\cdot l^{-1}$	PST added (mg.)	PST added (%)	η_{sp} at 25 °C.	Time (min.)	mg. PMMA in 25 ml. solution total	grafted	homo	$\frac{R_g}{R_h}$
PIn_1	2.00	2.00	1.87	45	0.18	1.8	170	858	521	337	1.54
14 % perester	2.70	2.70	1.87	0	0	1.8	170	1075	658.5	416.5	1.58
	2.70	2.70	1.87	300	1.2	6.3	170	1280	769	511	1.52
PIn_3	2.00	1.39	1.913	0	0	–	105	423.5	255.5	168	1.52
1 % perester											
PIn_2	2.00	4.73	3.74	0	0	1.0	180	3236	2071	1165	1.78
3.4 % perester	2.00	4.73	3.74	324	1.3	5.0	170	3063	1968	1095	1.80
	2.00	4.73	3.74	629	2.5	13.1	160	2695	1769	926	1.91

As can been seen from these data the grafting efficiency of methyl methacrylate onto polystyrene containing peracrylate units remains about constant for one series of experiments (with initiators of similar composition); moreover it is practically not affected by an increase of viscosity of the reaction medium. This corresponds to the much higher stability of the polystyrene backbone with respect to a radical attack, than the polyacrylic chain.

Another factor which influences the graft ratio consists in the composition of the polymeric initiator itself; indeed the PIn_2 initiator containing

3.4 % perester shows always a higher efficiency than PIn_1 (1.4 % perester) and PIn_2 (1 % perester), although the higher monomer concentration at which the experiments were carried out would have rather caused a decrease of it (see above).

In all these experiments the graft efficiency is relatively high, although the chain termination reaction of methyl methacrylate proceeds mainly by disproportionation; it must however been pointed out that a graft ratio to 3 should be expected if termination proceeds by addition, so that the occurrence of both termination processes interprete easily the present values of 1.5 to 1.8.

The influence of the temperature on the graft efficiency may result from an increasing importance of the induced decomposition of the perester groups, from the percent decarboxylation of the macroradical[15] and from the relative importance of the dismutation of the *tert.*butyloxide radicals with respect to an hydrogen-abstraction reaction with the reaction medium[16-19].

The decarboxylation of the macroradical (Ea = 5–10 Kcal.) as well as the dismutation of the *tert.*butoxide radicals (Ea between 11 and 17 Kcal.) increase both although differently with increasing temperature[20,21].

On account of these changes in the initiating radical species, a modification of grafting ratio can reasonably be expected by variation of the reaction temperature. Indeed, as can be seen from Table 10, the ratio

Table 10. Graft efficiency. Influence of the temperature

2.00 % PIn_4 (0.9 % perester) (In) = $1.25 \cdot 10^{-3}$ mole·l^{-1} MMA = 3.97 mole·l^{-1}
Solvent: benzene

t °C.	Time min.	mg. PMMA in 50 ml. solution			$R \cdot 10^5$ mole·l^{-1}·sec^{-1} *)		R_g/R_h
		total	grafted	homo	R_g	R_h	
55	480	370	129	241	0.09	0.17	0.53
65	100	659	316	343	1.05	1.14	0.92
75	70	775	408	367	1.94	1.74	1.11

*) Degree of conversion: 2 to 4 %.

varies from 0.53 to 1.11 between 55 ° and 75 °C.; although the relative importance of the addition termination increases with a decrease of temperature, nevertheless the graft ratio is much less at lower temperature; it suggests a higher initiation efficiency of the decarboxylated macroradical than that of the carboxylate one.

Some experiments were also carried out in the presence of a non-solvent, namely methanol. Indeed it was found previously that the grafting of styrene onto perester side groups[2] as well as the bulk polymerization of methyl methacrylate onto ω-perester polystyrene[10] are lowered when the reactions were carried out in the presence of 40–50 % methanol, and this effect was interpreted by a decrease of accessibility of the primary macroradicals, due to the coiling up of the macromolecules in the reaction medium. Contrarily, ODIAN, ROSSI, and TRACHTENBERG[22] observed an appreciable increase of grafting of styrene onto polyethylene film when the initiation by γ-rays was carried out in the presence of methanol, a maximum of rate of grafting being observed at 50 % methanol. It was therefore interesting to examine the influence of the presence of 20 volume percent of methanol on the grafting efficiency; at this γ-value although the macroinitiator remains soluble, the macromolecule is coiled up as was observed by an appreciable decrease of specific viscosity of the corresponding solution.

The data are summarized in Table 11.

Table 11. Grafting efficiency. Influence of non-solvent: methanol

2.0 % PIn_4 (0.9 % perester) (In) = $1.25 \cdot 10^{-3}$ mole·l^{-1} Solvent: benzene $t^0 = 75$ °C.

MMA mole·l^{-1}	γ-Value of MeOH	Time min.	Conv. (%)	mg. PMMA in 50 ml. sol. total	grafted	homo	$R \cdot 10^5$ mole·l^{-1}·sec^{-1} R_g	R_h	R_g/R_h
3.97	0.0	70	4	775	408	367	1.94	1.74	1.11
3.80	0.2	86	8	1556	794	762	3.08	2.95	1.04

As can be seen from these results, an increase of both rates of grafting and homopolymerization of methyl methacrylate was observed on account of a decrease of rate of termination. The grafting efficiency remains however practically unchanged, the termination of the grafted chains being equally affected than that of the homopolymer.

Conclusion

The graft efficiency of methyl methacrylate onto a *tert.*butyl peracrylate containing polystyrene is independent of the concentration of initiator. It is not affected by an increase of the overall viscosity of the

reaction medium nor by the presence of a non-solvent. It decreases however with an increase of monomer concentration as well as by a decrease of reaction temperature.

This behavior differs markedly from the previously described system, and stresses the importance of the nature of the polymer backbone as well as that of the second monomer.

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