

Influence of the Initiator on the Grafting of Polyvinyl Polymers

G. SMETS, J. ROOVERS, and W. VAN HUMBEEK

Laboratoire de Chimie Macromoléculaire, Université de Louvain, Louvain, Belgium

The preparation of graft and block copolymers is very often carried out with chain transfer initiation; by this method a polymer of one kind is dissolved in the presence of a monomer of another kind, and the mixture is subjected to polymerization conditions.

Initially it was admitted that the production of a macroradical resulted from a chain transfer reaction between a growing chain and the polymer present in the solution. An analogous reaction between the polymer and a primary radical originating directly in the decomposition of the initiator was considered to be unlikely; indeed, on the basis of the fact that the activation energy for the transfer reaction is higher than that for the propagation step, it was assumed that the addition of vinyl monomer onto a primary radical proceeds much more easily than the abstraction of an atom from a polymer molecule.¹

In the present paper some experiments are reported which were carried out more recently; these have shown that for some polymer-monomer systems the success of grafting depends on the nature of the initiator and consequently, on the nature of the primary radicals, whereas some other systems are insensitive to this influence. Three different systems were used, for which the grafting in the presence of benzoyl peroxide has been described previously: polystyrene-methyl methacrylate, polymethyl methacrylate-vinyl acetate, and polyethyl α -chloroacrylate-vinyl acetate.^{2,3} In these new experiments benzoyl peroxide, (B_2O_2) azobisisobutyronitrile (AIBN), di-*tert*-butyl peroxide and (DTBP), and *tert*-butyl hydroperoxide (TBHP) were used as initiators.

EXPERIMENTAL

A. Polystyrene-Methyl Methacrylate

The polystyrene was prepared at 85°C. in 30% benzene solution in the presence of benzoyl peroxide (0.5% with respect to the monomer). Poly-

styrene (2 g.) was dissolved in 6 g. methyl methacrylate and heated to and kept at 110°C. for 5 hr. in the presence of 30 mg. of initiator. After reaction the polymer mixture was diluted with butanone and precipitated in methanol-water (1:1). The fractionation was carried out by precipitation from a chloroform solution upon addition of methanol; the corresponding fractionation curves are given in Figure 1, in which the weight percentage of precipitate is plotted against the volume fraction of the precipitant (γ). The values indicated along the curves are the weight percentages of polystyrene in the different fractions; these were determined by infrared analysis of 5% dioxane solutions (14.30 μ ; Perkin-Elmer Model 112C).

B. Polymethyl Methacrylate-Vinyl Acetate

Methyl methacrylate was polymerized at 70°C. in 30% benzene solution in the presence of benzoyl peroxide (0.5% with respect to the monomer) over a 5-hr. period ($[\eta]_{\text{benzene}}^{26} = 0.32$).

Polymer (3 g.) dissolved in 11 g. of vinyl acetate (VAc) was heated at 95°C. for 6½ hr. in the presence of 0.25 mmole of initiator (B_2O_2 , AIBN, or DTBP). After reaction the polymer mixture was dissolved in 300 ml. of acetone, and methanol was added up to a γ value of 0.7. Unreacted polymethyl methacrylate precipitated (Fr I), while the graft copolymer remained in solution together with some homopolymer. After the acetone was distilled off and the methanolic solution was cooled, the graft copolymer precipitated; this was purified of any unreacted polymethyl methacrylate by dissolving it again in acetone and precipitating with methanol ($\gamma = 0.7$; Fr II). The graft copolymer which remained in solution was freeze-dried from its benzene solution (Fr III). The mother solution, from which Fr I had precipitated on cooling, contained much free polyvinyl acetate and eventually some soluble graft copolymer; these polymers were isolated by freeze-drying from benzene (Fr IV). The results of these fractionations are summarized

TABLE I
Fractionation of Graft Copolymers: Polymethyl Methacrylate-Vinyl Acetate Systems

Fraction	Bz ₂ O ₂ -initiated copolymerization		AIBN-initiated copolymerization		DTBP initiated copolymerization		
	Weight, g.	VAc, %	Weight, g.	VAc, %	Weight, g.	VAc, %	[η], ^a dl./g.
I	0.856	4	0.870	4	0.982	4	
II	0.704	9	0.680	9	0.796	11	0.36
III	0.715	55	0.739	50	0.66	60	0.53
IV	6.642	87	6.89	87	6.275	89	—

^a In benzene at 25°C.

in Table I. The percentages of vinyl acetate were determined by infrared analysis of chloroform solutions; the analytical bands were at 1150 and 1016 cm.⁻¹ for polymethyl methacrylate and polyvinyl acetate, respectively.

C. Polyethyl α -Chloroacrylate-Vinyl Acetate

Ethyl chloroacrylate was polymerized at 60°C. in 30% benzene solution in the presence of azobisisobutyronitrile (AIBN) (0.5% with respect to the monomer) over a period of 6½ hr. ($[\eta] = 0.48$ in benzene at 25°C.).

A 1.5-g. portion of polyethyl α -chloroacrylate (PCA), dissolved in 4.5 g. vinyl acetate, was heated at 90°C. in the presence of AIBN (0.9 wt.-% with respect to the monomer). After reaction and dilution with acetone the polymer was precipitated in a 1:1 methanol-water mixture. PCA and polyvinyl acetate (PVAc) can easily be separated from each

other on the basis of the solubility of PVAc in ethanol, while PCA precipitates from acetone solution after addition of ethanol up to γ -value of 0.218 to 0.333. After grafting, however, precipitation occurred only at γ values of 0.41 to 0.5, which indicated solubilization of the PCA. The graft copolymer was redissolved in methyl ethyl ketone and precipitated in a 1:1 methanol-water mixture (Fr I). On further addition of ethanol no more polymer could be isolated. By distilling off the acetone while keeping the volume constant by continuous addition of ethanol, and after cooling at 4°C., we obtained an appreciable precipitate (Fr II). On concentrating the filtrate we isolated a small third fraction (Fr III). Fractions II and III were both redissolved in toluene and reprecipitated in heptane. The composition of the polymers was determined from chlorine analysis by the method of Wurzschnitt.⁴ The system PCA-PVAc was graft copolymerized in the presence of benzoyl peroxide also. The experimental results are given in Table II.

Experiments with *tert*-butyl hydroperoxide (TBHP) and di-*tert*-butyl peroxide (DTBP) were carried out at the same concentrations but at several temperatures. The products were only partially soluble; they were extracted several times with acetone and separated into two main fractions (soluble and insoluble) which were analyzed by chlorine determination (see Table III).

DISCUSSION OF RESULTS

It can be seen from Figure 1 that the polymerization of methyl methacrylate in the presence of polystyrene gives appreciable amounts of graft copolymer if the reaction is initiated with benzoyl peroxide (BzO₂); indeed, 13.1 wt.-% polymer precipitates at intermediate γ values (0.436–0.65), and the branching fraction,⁵ i.e., the ratio of new polymer bound to the substrate to total new polymer, is equal to 0.13. Moreover, the methyl methacrylate

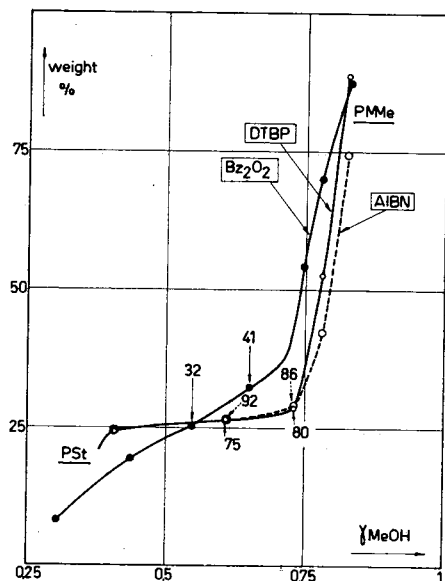


Fig. 1. Fractionation curves of polystyrene-methyl methacrylate graft copolymerized with the use of different initiators: (●), Bz₂O₂, (○) DTBP, (○) AIBN.

TABLE II
Fractionation of Graft Copolymers: Polyethyl α -Chloroacrylate-Vinyl Acetate Systems

Grafting conditions			Fr I		Fr II		Fr III	
Initiator	Time, hr.	Temp., °C.	Wt.-%	PVAc in fraction, %	Wt.-%	PVAc in fraction, %	Wt.-%	PVAc in fraction, %
BzO ₂ ^a	6	85	—	—	82	49	18	86
BzO ₂ ^a	5	110	—	—	88	40	12	82
AIBN	2.75	90	11	28	75	59	4.6	70

^a See Reference 3.

TABLE III
Fractionation of Graft Copolymers: Polyethyl α -Chloroacrylate-Vinyl Acetate Systems

Grafting conditions			Acetone-soluble polymer			Crosslinked polymer	
Initiator	Time, hr.	Temp., °C.	Wt.-%	PVAc, %	$[\eta]$, dl./g.	Wt.-%	PVAc, %
TBHP	2 ³ / ₄	90	34	42	0.7	66	78
TBHP	5 ¹ / ₂	90	56 ^a	67	0.75	44	63
TBHP	11 ¹ / ₂	90	24	81	0.67	76	71
DTBP	4 ¹ / ₂	100	(40)	59	0.78	(60)	88
DTBP	11 ¹ / ₂	100	26	68	0.58	74	76

^a This soluble fraction was separated into two fractions: fraction A was obtained by addition of methanol to the acetone solution up to a γ value of 0.75, while fraction B was obtained after evaporation by pouring into water and freeze-drying. Subfraction A represented 18 wt.-%, and contained 45% PVAc; subfraction B (74 wt.-%) contained 77% PVOAc.

content of the graft copolymer is very considerable (68 and 59%).

The diagrams for AIBN- and DTBP-initiated polymerizations are much more horizontal and similar to those of mixtures of both homopolymers;² in both cases only 4.5 and 4.8 wt.-% of the polymer, respectively, precipitated between γ values of 0.407 and 0.73, while the branching fraction was only about 0.01. Not only were the quantities of graft copolymer much smaller, but the degree of grafting was far less important (DTBP), and even insignificant (AIBN). These results stress markedly the dependence of grafting on the nature of the initiator in the methyl methacrylate-polystyrene system; they confirm the inferior capacity of the resonance-stabilized isobutyronitrile radicals $\text{Me}_2\text{C}=\dot{\text{C}}-\text{CN}$, in comparison with the $\text{C}_6\text{H}_5\cdot$ and $\text{C}_6\text{H}_5\text{COO}\cdot$ radicals, to engage in chain transfer reaction. Similar results were reported for the grafting of polydienes, where also grafting occurs only with benzoyl peroxide as initiator.⁶⁻⁹

In contrast, the polymerization of vinyl acetate in the presence of polymethyl methacrylate gives appreciable amounts of pure graft polymers, independently of the nature of the initiator; the degree of grafting with all initiators is about equally important (see Table I). Consequently, this system must be considered insensitive to the nature of the initiator.

For the system polyethyl α -chloroacrylate-vinyl acetate, the results with benzoyl peroxide and azobisisobutyronitrile are similar, showing no appreciable differences; the amounts of graft copolymer are very important, and practically the total polychloroacrylate is solubilized by combination with vinyl acetate. This must be related to the high sensitivity of the polychloroacrylate molecule towards a radical attack, as is confirmed by the experiments with butyl hydroperoxide and di-*tert*-butyl peroxide, in which again the degree of grafting is very high; a large production of crosslinked products indicates a particularly high reactivity of the tertiary butoxy radicals toward the polychloroacrylate; this effect, however, makes the comparison more difficult.

CONCLUSION

The amount and degree of grafting by chain transfer initiation depend strongly on the nature of the initiator for the system polystyrene-methyl methacrylate, azobisisobutyronitrile being much less efficient than benzoyl peroxide. In contrast, no appreciable differences could be attributed to the use of different initiators in the systems containing vinyl acetate, namely, polymethyl methacrylate-vinyl acetate and polyethyl α -chloroacrylate-vinyl acetate.

The authors are indebted to the Fonds National de la Recherche Scientifique (F.N.R.S.) for financial support given to the laboratory, and to the Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture (I.R.S.I.A.) for fellowships to two of them (J. R. and W. v. H.).

References

1. Gregg, R. A., and F. R. Mayo, *Discussions Faraday Soc.*, **2**, 328 (1947).
2. Smets, G., and M. Claesen, *J. Polymer Sci.*, **8**, 289 (1952).
3. Smets, G., L. Convent, and X. Van der Borgh, *Makromol. Chem.*, **23**, 171 (1957).
4. Wurzschnitt, B., *Microchim. Acta*, **35-36**, 769 (1951).
5. Voeks, J. F., *J. Polymer Sci.*, **18**, 123 (1955).
6. Merrett, F. M., *Trans. Faraday Soc.*, **50**, 759 (1954).
7. Minoura, Y., Y. Mori, and M. Imoto, *Makromol. Chem.*, **25**, 1 (1957).
8. Swift, P. M., *J. Appl. Chem.*, **8**, 803 (1958).
9. Allen, P. W., G. Ayery, C. G. Poore, and J. Scanlan, *J. Polymer Sci.*, **36**, 55 (1959).

Synopsis

The dependence of grafting on the type of initiator has been examined in the case of three polymer-monomer systems: polystyrene-methyl methacrylate, polymethyl methacrylate-vinyl acetate, and polyethyl α -chloroacrylate-vinyl acetate. The different initiators used in these experiments were benzoyl peroxide (Bz_2O_2), azobisisobutyronitrile (AIBN), di-*tert*-butyl peroxide (DTBP), and *tert*-butyl hydroperoxide (TBHP). In each case the graft copolymers were separated from the homopolymers by fractional precipitation or by extraction. In the case of the system polystyrene-methyl methacrylate, an appreciable degree of grafting as well as formation of graft copolymer occur in the presence of Bz_2O_2 ; in contrast, the grafting is low with DTBP and doubtful with AIBN. For the other two systems no noticeable differences occurred as function of the initiator. In the case of polyethyl α -chloroacrylate the amount of graft copolymer is exceptionally high owing to the sensitivity of this polymer to a radical attack; this sensitivity results in the partial insolubility of the graft copolymers in the presence of TBHP and DTBP, but not in the presence of AIBN.

Résumé

La dépendance des réactions de greffage en fonction de la nature de l'initiateur a été étudiée sur trois systèmes polymère-monomère, à savoir le polystyrène-méthacrylate de méthyle, le polyméthacrylate de méthyle-acétate de vinyle et le poly- α -chloroacrylate d'éthyle-acétate de vinyle. Les différents initiateurs utilisés étaient le peroxyde de benzoyle (Bz_2O_2), l'azobisisobutyronitrile (AIBN), le peroxyde de di-*tert* butyle et l'hydroperoxyde de *tert* butyle. Dans chacun des cas les copolymères greffés ont été séparés des homopolymères soit par précipitation fractionnée soit par extraction. Dans le cas du système polystyrène-méthacrylate de méthyle, le taux de greffage de même que la quantité de polymères greffés sont appréciables en présence de Bz_2O_2 ; ils sont par contre faible dans le cas du DTBP, voire douteux avec AIBN. Pour les deux autres systèmes il n'y a pas de différences notables en fonction de la nature de l'initiateur. Dans le cas du poly- α -chloroacrylate d'éthyle les quantités de polymères greffés sont particulièrement élevées par suite de la sensibilité de ce polymère à une attaque radicalaire; cette sensibilité entraîne d'ailleurs une insolubilisation partielle en présence de TBHP et DTBP, mais non en présence de AIBN.

Zusammenfassung

Die Abhängigkeit der Aufpfropfung von der Natur des Starters wurde für drei Polymer-Monomer-Systeme untersucht, nämlich Polystyrol-Methylmethacrylat, Polymethylmethacrylat-Vinylacetat und Polyäthyl- α -chloroacrylat-Vinylacetat. Die verschiedenen, bei diesen Versuchen benützten Starter waren: Benzoylperoxyd (Bz_2O_2), Azobisisobutyronitril (AIBN), Di-*tert*-butylperoxyd (DTBP) und *tert*-Butylhydroperoxyd (TBHP). In jedem Fall wurden die Pfcopolymeren von den Homopolymeren durch fraktionierte Fällung oder Extraktion getrennt. Im Falle des Systems Polystyrol-Methylmethacrylat sind in Gegenwart von Bz_2O_2 sowohl der Pfcopfcopolymeren beträchtlich; dagegen sind sie mit DTBP niedrig und mit AIBN zweifelhaft. Für die beiden anderen Systeme konnten keine nennenswerten Unterschiede bei den verschiedenen Startern festgestellt werden. Im Falle des Polyäthyl- α -chloroacrylats ist die Menge von Graftcopolymerem wegen der Empfindlichkeit dieses Polymeren gegen Radikalangriff ausnehmend hoch; diese Empfindlichkeit hat die teilweise Unlöslichkeit des Graftcopolymeren in Gegenwart von TBHP und DTBP, nicht aber in Gegenwart von AIBN, zur Folge.

Received April 28, 1960