

Accelerative Effects in Radiation-Induced Graft Polymerization

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In previous papers,¹⁻³ we have reported the acceleration of radiation-induced graft polymerization by solvents in the systems polyethylene-styrene and nylon-styrene. We wish now to report further results which complete our studies of this phenomenon. The present work has shown that the use of solvent additives can substantially increase the rate of grafting in the systems polypropylene-styrene, polyvinyl chloride-styrene, polyethylene-methyl acrylate, polypropylene-methyl acrylate, polyethylene-*tert*-butylaminoethyl methacrylate, nylon-methyl acrylate, and Teflon-methyl acrylate.

RESULTS AND DISCUSSION

The investigations carried out in this laboratory have been concerned with the study of the effects of solvents on radiation-induced graft polymerization. It has been found that the use of the proper solvent has a pronounced accelerative effect on the rate of grafting. A number of grafting systems have been investigated and, despite polymer-monomer-solvent differences, the accelerative effect was observed.

The Graft Polymerization of Styrene

It has been found that the rate of radiation-induced graft polymerization of styrene to the base polymers polyethylene, polypropylene, polyvinyl chloride, and nylon is substantially increased when the styrene monomer is diluted with methanol. The effect of methanol on the grafting rates of styrene to the various polymers can be seen in Tables I-IV. (The polyethylene and nylon data have been reported elsewhere,^{1,3} but are reproduced here for the sake of completeness.)

In the case of graft polymerization of styrene to polyethylene, polypropylene, and polyvinyl chloride, the mechanism of the increased rates observed on dilution of the styrene with methanol has been attributed to the incursion of a Trommsdorff type of effect brought about by the insolubility of the growing graft polystyrene chains in methanol. The mechanism of this effect in the polyethylene-styrene system has been studied in detail.²

TABLE I
Effect of Methanol on the Grafting of Styrene to Low-Density Polyethylene^a

Vol.-% styrene in monomer solution	% graft/hr.
100	4.3
90	7.1
70	6.9
50	8.2
30	11.9
10	6.1

^a Dose rate = 0.070 Mrads/hr.

TABLE II
Effect of Methanol on the Grafting of Styrene to Polypropylene^a

Vol.-% styrene in monomer solution	% graft/hr.
100	6.7
90	10.2
70	10.5
50	25.5
30	2.4
10	1.0

^a Dose rate = 0.080 Mrads/hr.

TABLE III
Effect of Methanol on the Grafting of Styrene to Polyvinyl Chloride^a

Vol.-% styrene in monomer solution	% graft/hr.
100	0
70	2.4
50	5.4
30	13.8

^a Dose rate = 0.041 Mrads/hr.

TABLE IV
Effect of Methanol on the Grafting of Styrene to Nylon^a

Vol.-% styrene in monomer solution	% graft/hr.
100	0
90	17.8
70	16.6
50	14.2
30	11.8
10	4.9

^a Dose rate = 0.071 Mrads/hr.

The acceleration observed in the nylon-styrene system was caused by the fact that dilution of styrene with methanol led to enhanced access of the monomer to the grafting sites in the nylon, and this in turn produced a greatly enhanced grafting rate. This has been shown by studying the phase equilibria in the various polymer-monomer-solvent systems.¹⁻⁴

The Graft Polymerization of Acrylates

The rates of the radiation-induced graft polymerizations of the polar functional monomers methyl acrylate and *tert*-butylaminoethyl methacrylate have also been shown to be sensitive to the effect of solvent additives. Acceleration in the rates of grafting of methyl acrylate to high-density polyethylene, polypropylene, nylon, and Teflon was obtained when the monomer was diluted with methanol. The rate of the graft polymerization of *tert*-butylaminoethyl methacrylate to low-density polyethylene was shown to be increased by the use of hexane. This work demonstrated

TABLE V
Effect of Methanol on the Grafting of Methyl Acrylate to High-Density Polyethylene*

Vol.-% methyl acrylate in monomer solution	% graft/hr.
100	5.1
50	4.8
30	7.6
10	1.4

* Dose rate = 0.061 Mrads/hr.

TABLE VI
Effect of Methanol on the Grafting of Methyl Acrylate to Polypropylene*

Vol.-% methyl acrylate in monomer solution	% graft/hr.
100	2.5
70	1.8
50	2.8
30	1.8

* Dose rate = 0.021 Mrads/hr.

TABLE VII
Effect of Methanol on the Grafting of Methyl Acrylate to Nylon*

Vol.-% methyl acrylate in monomer solution	% graft/hr.
100	0.47
90	6.9
70	16.9
50	12.3
30	7.6

* Dose rate = 0.070 Mrads/hr.

that it is possible to use solvent additives to increase the rates of graft polymerization of some polar monomers (the acrylates) as well as a nonpolar monomer (styrene). The effect of solvent dilution on the rates of graft polymerization of the acrylates can be seen in Tables V-IX.

TABLE VIII
Effect of Methanol on the Grafting of Methyl Acrylate to Teflon^a

Vol.-% methyl acrylate in monomer solution	% graft/hr.
100	2.5
90	2.3
70	2.1
30	5.8

^a Dose rate = 0.61 Mrads/hr.

TABLE IX
Effect of *n*-Hexane on the Grafting of *tert*-Butylaminoethyl Methacrylate to Low-Density Polyethylene^a

Vol.-% <i>tert</i> -butylaminoethyl methacrylate in monomer solution	% graft/hr.
100	6.1
90	10.3
70	22.0
50	14.5

^a Dose rate = 0.020 Mrads/hr.

The acceleration in the rates of graft polymerization of methyl acrylate to high-density polyethylene, polypropylene, and Teflon, that occurred on dilution of the monomer with methanol, was caused by the onset of the Trommsdorff effect. This effect was also responsible for the increase in the rate of the grafting of *tert*-butylaminoethyl methacrylate to low-density polyethylene that came about when the monomer was diluted with hexane.

The grafting of methyl acrylate to nylon with methanol was an interesting case. In this system the acceleration in the rate of graft polymerization on the addition of solvent was caused by both the Trommsdorff effect and the effect of solvent swelling on the polymer.

EXPERIMENTAL

Materials

The low-density polyethylene was Du Pont B301 3 mil film. The high-density polyethylene was Union Carbide's Visotherm 3 mil film. The polypropylene was Avisun 5 mil film. The TFE Teflon was Du Pont 3 mil film. The polyvinyl chloride was Bakelite QBAA-6304 1.5 mil cast film.

Styrene, stabilized with *p*-*tert*-butyl catechol, was washed with 10% sodium hydroxide, dried twice over magnesium sulfate, and distilled: b.p. 45°C. at 15 mm. Hg. Methyl acrylate (Rohm & Haas) inhibited with hydroquinone, was washed with a solution of 5% sodium hydroxide and 20% sodium chloride, dried over magnesium and calcium sulfates, and distilled: b.p. 44°C. at 210 mm. Hg. *tert*-Butylaminoethyl methacrylate (Rohm & Haas) inhibited with *N,N'*-diphenyl-*p*-phenylenediamine was distilled: b.p. 52°C./3 mm. Hg.

Methanol was dried over soda lime and distilled. *n*-Octane was dried over magnesium sulfate and distilled. *n*-Hexane was distilled before use.

Graft Polymerization Procedure

All the polymer films were washed in benzene and then dried under vacuum at 65°C. except the nylon which was dried at 85°C. The polymer films were added to the monomer-solvent solutions and the mixtures purged with nitrogen at room temperature for 15 min., except that the *tert*-butylaminoethyl methacrylate was nitrogen purged at -20°C. for 20 min. The mixtures were then equilibrated overnight. All experiments were carried out in ground-glass-stoppered test tubes. Irradiations were carried out at 25°C. with the RAI Co⁶⁰ source facility. To avoid post-irradiation effects, samples were worked up as soon as possible after irradiation. To remove homopolymer and monomer, the films were exhaustively washed with solvent, the styrene-grafted films with benzene, the methyl acrylate-grafted films with ethyl acetate, and the *tert*-butylaminoethyl methacrylate-grafted films with acetone. The films were then dried as described above under vacuum. The amount of graft was calculated as:

$$\% \text{ graft} = \frac{\text{Increase in wt.} \times 100}{\text{Original wt. of polymer}}$$

All grafting experiments were run in duplicate. With the styrene systems the reproducibility was very good, being at least of the order of $\pm 5\%$ in most of the experiments. The precision of duplicate acrylate experiments was lower, agreement being in many cases no better than to within $\pm 15\%$. Only semiquantitative significance should, therefore, be ascribed to most of the acrylate data. The scatter in duplicate grafting experiments with the acrylates was due most probably to small amounts of inhibitor and oxygen and the fact that these monomers were far more sensitive than styrene to radiation polymerization.

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References

1. Odian, G., A. Rossi, and E. N. Trachtenberg, *J. Polymer Sci.*, **42**, 575 (1960).
2. Odian, G., M. Sobel, A. Rossi, and R. Klein, *J. Polymer Sci.*, **55**, 663 (1961).
3. Odian, G., M. Sobel, A. Rossi, R. Klein, and T. Acker, *J. Polymer Sci.*, in press.
4. Odian, G., T. Acker, E. Ratchik, M. Sobel, and R. Klein, "Final Report on Contract AT(30-1)-2318 for the Division of Isotope Development," United States Atomic Energy Commission, *Report RAI* **301**, January 31, 1962.

Synopsis

It has been demonstrated that the use of solvent additives can substantially increase the rate of radiation-induced graft polymerization in the systems polyethylene-styrene, polypropylene-styrene, polyvinyl chloride-styrene, nylon-styrene, polyethylene-methyl acrylate, polypropylene-methyl acrylate, nylon-methyl acrylate, Teflon-methyl acrylate, and polyethylene-*tert*-butylaminoethyl methacrylate. Two different mechanisms have been shown to be responsible for the observed accelerative effects. One is the incursion of a Trommsdorff effect due to the insolubilization of the growing graft polymer chains in the solvent-monomer medium. The other mechanism is the enhancement in the degree of accessibility of monomer to grafting sites within the polymer brought about by the greater ability of the solvent additive to swell certain base polymers.

Résumé

On a montré que l'addition de solvants peut augmenter substantiellement la vitesse de polymérisation de greffage initiée par radiation dans les systèmes polyéthylène-styrène, polypropylène-styrène, chlorure de polyvinyle-styrène, nylon-styrène, polyéthylène-acrylate de méthyle, polypropylène-acrylate de méthyle, nylon-acrylate de méthyle, Teflon-acrylate de méthyle, et polyéthylène-méthacrylate de *t*-butylaminoéthyle. On a démontré deux mécanismes différents qui sont responsables des effets d'accélération observés. L'un de ceux-ci est l'intervention d'un effet Trommsdorff dû à l'insolubilisation de la chaîne de polymère greffé dans le milieu solvant-monomère. L'autre mécanisme est l'augmentation du degré d'accessibilité du monomère aux endroits de greffage sur le polymère, due à la plus grande aptitude du solvant à gonfler certains polymères de base.

Zusammenfassung

Es wurde gezeigt, dass die Verwendung von Lösungsmittelzusätzen die Geschwindigkeit der strahlungs-induzierten Pfropfpolymerisation in den Systemen Polyäthylen-Styrol, Polypropylen-Styrol, Polyvinylchlorid-Styrol, Nylon-Styrol, Polyäthylen-Methylacrylat, Polypropylen-Methylacrylat, Nylon-Methylacrylat, Teflon-Methylacrylat und Polyäthylen-*t*-Butylaminoäthylmethacrylat wesentlich erhöhen kann. Für die beobachteten Beschleunigungseffekte sind zwei verschiedene Mechanismen verantwortlich. Der eine besteht im Auftreten eines Trommsdorff-Effekts durch das Unlöslichwerden der wachsenden Pfropfpolymerketten im Lösungsmittel-Monomermedium. Den anderen Mechanismus bewirkt die bessere Zugänglichkeit der Aufpfropfungsstellen im Polymeren für das Monomere durch die grössere Fähigkeit der Lösungsmittelzusätze, eine Quellung gewisser Polymerer zu bewirken.

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