

Photografting of Acrylic Monomers on Polystyrene Support

A. AJAYAGHOSH and S. DAS*

Photochemistry Research Unit, Regional Research Laboratory (CSIR), Trivandrum 695 019, India

SYNOPSIS

Polystyrene xanthates, prepared through the reaction of chloromethylated polystyrene resins with potassium O-ethyl xanthate, have been used for the photografting of acrylic monomers. Monomers such as acrylamide, acrylic acid, methacrylic acid, and methyl methacrylate were grafted onto the xanthate polymers on irradiation with a 450 W medium-pressure mercury lamp (Hanovia). Among these monomers, the maximum graft efficiency was obtained for methyl methacrylate. The effect of cross-link density of the xanthate polymer on the percentage graft yield was also studied. Scanning electron microscopic studies have shown that appreciable grafting has taken place on the surface of the polymer in a uniform manner. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Photoinduced grafting of vinyl monomers onto polymers has received a great deal of attention in recent years.¹⁻⁵ Grafting is a highly efficient method of imparting specific surface properties to a polymer, without affecting its bulk characteristics. Further, it is possible to introduce a wide variety of functional groups onto a polymer surface through grafting. Recently, surface modification of polymers by photografting of vinyl monomers has been reported for the immobilization of UV stabilizers onto polymer films.⁶ Photografting of vinyl monomers has also been employed for the preparation of polymeric catalysts.⁷ Improved catalytic activity and chemical yields have been achieved by the introduction of grafted chains as spacers between the insoluble matrix and the reactive sites. Otsu et al. reported the use of the *N,N*-diethyldithiocarbamate group for the photoinduced graft polymerization of vinyl monomers.⁸ Also, surface photografting of hydrophilic vinyl monomers onto polydimethylsiloxane containing a photosensitive diethyldithiocarbamate group has been described by Inoue and Kohama.⁹

Recently, successful attempts have been made for grafting acrylic monomers onto polystyrene beads by thermal and group transfer polymerizations.^{10,11}

However, not much work has been reported on the photoinduced grafting of acrylic monomers onto chloromethyl polystyrene resins, which is the most widely used polymeric support in organic reactions.

In this paper, we report the photoinduced grafting of acrylic monomers onto a polystyrene resin, containing photoactive xanthate pendant groups. The growing importance of cross-linked polystyrene resins for preparing polymeric reagents and the surface modification of polymers by graft polymerization prompted us to investigate the potential application of the xanthate chromophore for photoinduced grafting of acrylic monomers.

EXPERIMENTAL

Materials and Methods

Potassium O-ethyl xanthate¹² and polystyrene-*co*-divinylbenzene beads¹³ (2, 5, and 10% divinylbenzene cross-linked) were prepared as per reported procedures. All the acrylic monomers, except acrylamide, were purified under vacuum distillation, whereas acrylamide was recrystallized from benzene. Freshly distilled solvents were used throughout. IR spectra were recorded on a Perkin-Elmer Model 882 spectrophotometer, and the SEM pictures were taken on a JEOL JSM-35C scanning electron microscope. Photografting was performed in Pyrex tubes (20 × 1.3 cm) placed around a 450 W medium-

* To whom correspondence should be addressed.

pressure mercury lamp (Hanovia), housed in an efficient water-cooling jacket. The distance between the samples and source of light was approximately 4 cm.

Chloromethylation of Cross-Linked Polystyrene Resin

In a typical reaction, the polystyrene resin (10 g, 2% divinylbenzene cross-linked) was thoroughly extracted with chloroform for 2 h and the resin was then suspended in chloroform (50 mL), containing chloromethyl ethyl ether (16.4 mL, 180 mmol). Anhydrous stannic chloride (10.5 mL, 90 mmol) was slowly added to the polymer beads at 0–5°C with stirring. After the addition, the temperature of the reaction mixture was slowly raised and maintained at 10°C for 6 h with stirring. The polymer was then collected by filtration and washed thoroughly with aqueous dioxane (50%), with aqueous dioxane containing 10% HCl, water, and dioxane, and, finally, with methanol. The product was extracted with chloroform in a Soxhlet Extractor for 12 h and then dried under vacuum at 50°C to give 11.4 g of **2**. IR (KBr): 1270 and 680 cm^{-1} .

ANAL: Cl, 4.0 mmol/g.

Preparation of Polystyrene Xanthate **3**

To a stirred suspension of the chloromethyl polystyrene resin **2** (10 g, 40 mmol Cl) in DMF (50 mL) was added potassium O-ethyl xanthate (19.2 g, 120 mmol) at 28°C in small portions, with constant stirring. After 18 h, the polymer beads were collected by filtration and washed with DMF, water, and, finally, methanol. After drying under vacuum, 13.1 g of the polymer **3** was obtained. The residual chlorine analysis of **3** showed a 98% functional group conversion. Resins with 5% and 10% cross-linkings were also functionalized by the same procedure. IR (KBr): 1220 (C=S); 1050 cm^{-1} (C—O).

Photografting of Acrylamide on **3**

The xanthate polymer **3** (1 g) was suspended in a solution of acrylamide (3.98 g, 56 mmol) in water (10 mL) and degassed three times by a freeze-thaw technique. The reaction tube was sealed off and then irradiated under a 450 W medium-pressure mercury lamp for 6 h at 32°C. The grafted polymer, along with the homopolymer, was suspended in a sufficient amount of water and filtered through a sintered glass funnel. The filtrate was poured into excess methanol to give 0.91 g of the precipitated homopolymer. The grafted polymer was extracted with water in a Soxhlet Extractor for 18 h and then dried under vacuum at 60°C to give 1.96 g of the product. IR (KBr): 1670 cm^{-1} (CONH₂). Details of the graft yield and graft efficiency are given in Table I.

Photografting of Acrylic Acid on **3**

A mixture of acrylic acid (4.03 g, 56 mmol) and the resin **3** (1 g) in benzene (6 mL) was deaerated and photolyzed for 6 h as in the earlier case. The polymer beads were removed by filtration and extracted with water (Soxhlet, 24 h) to give 2.19 g of the grafted polymer. IR (KBr): 3400 (OH), 1700 cm^{-1} (C=O). Workup of the aqueous filtrate by precipitation with methanol gave 0.8 g of the homopolymer. The graft yield and graft efficiency are given in Table I.

Photografting of Methacrylic Acid on **3**

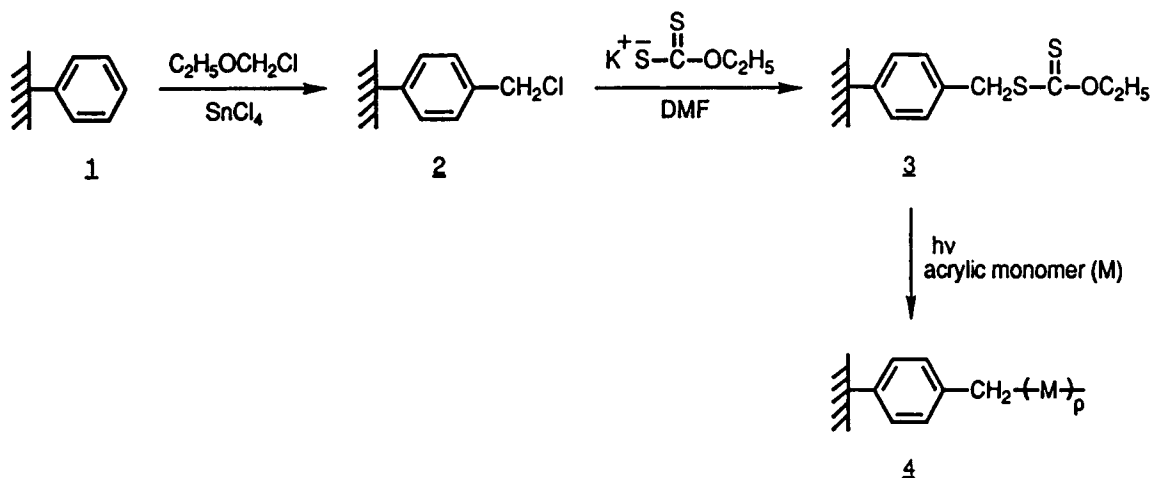
To a suspension of the polystyrene xanthate **3** (1 g) in benzene (6 mL) was added 4.82 g (56 mmol) of methacrylic acid and the mixture was photolyzed for 6 h after deaeration, as in the earlier cases. The polystyrene beads were washed with benzene and workup of the filtrate by the addition of methanol gave 0.81 g of the homopolymer. The beads, on extraction with benzene (Soxhlet, 24 h) and drying under vacuum, gave 2.21 g of the grafted polymer.

Table I Photografting of Different Acrylic Monomers on **3**^a

Monomer ^b	Homopolymer wt. (g)	Total Conversion (%)	Graft Yield (%)	Efficiency of Grafting (%)
Acrylamide	0.91	46.9	96	51.3
Acrylic acid	0.8	49.3	119	59.8
Methacrylic acid	0.81	41.9	121	59.9
Methyl methacrylate (MMA)	0.71	38.8	148	67.5

^a Xanthate polymer **3**, 1.0 g.

^b Monomer: 0.056M in 6 mL solvent; irradiation time, 6 h; temperature, 32°C.



Scheme 1

IR (KBr): 3400 (OH); 1700 cm^{-1} (C=O). Details of the graft yield and graft efficiency are given in Table I.

Photografting of Methyl Methacrylate on 3

A mixture of methyl methacrylate (MMA) (5.65 g, 56 mmol) and **3** (1 g) in benzene (6 mL) was deaerated and photolyzed for 6 h, as in the earlier cases. The mixture was diluted with benzene and filtered to give 2.48 g of the grafted polymer beads after extraction with chloroform (Soxhlet, 12 h) and drying under vacuum. IR (KBr): 1740 cm^{-1} (C=O). Workup of the benzene filtrate by precipitation with methanol gave 0.71 g of the homopolymer. The graft yield and graft efficiency are given in Table I.

RESULTS AND DISCUSSION

Polystyrene xanthates **3** were prepared from divinylbenzene cross-linked polystyrene resins **1** through the pathways shown in Scheme 1. Polystyrene resins **1** of different cross-linking ratios were prepared and they were chloromethylated with chloromethyl ethyl ether in the presence of anhydrous stannic chloride as per a reported procedure.¹⁴ The chlorine content of each resin was estimated by a modified Volhard titration method.¹⁵ The chloromethyl polystyrene resin **2** was then treated with potassium O-ethyl xanthate in dimethylformamide (DMF) to give the xanthate polymer **3**. The IR spectrum of **3** showed absorption bands at 1220 and 1050 cm^{-1} , corresponding to C=S and C—O

groups, respectively. Also, the absorption bands at 1270 and 680 cm^{-1} characteristic of the C—Cl group were absent in **3**, indicating thereby that a nearly quantitative conversion had taken place in the case of the 2% divinylbenzene cross-linked polymer. The degree of functionalization was assessed through the estimation of the residual chlorine in **3** and it was found to be 98%, after 18 h of reaction time. It has been observed that as the cross-link density of the polymer increased, the degree of substitution by the xanthate nucleophile decreased, and this may be attributed to the poor swelling of the resin in the solvent.

Photografting of Acrylic Monomers onto Polymer 3

Photografting of the acrylic monomers onto polymer **3** was achieved by the irradiation of the suspended polymers in monomer solutions at 32°C using a 450 W medium-pressure mercury lamp. During photolysis, the C—S bond of the xanthate polymer undergoes homolytic bond scission, thereby generating a macroradical on the polymer support and a xanthate radical in solution. These radicals initiate the graft polymerization of the acrylic monomer onto the polymer surface. A considerable amount of homopolymer was also formed during photolysis. After irradiation for a given length of time, the homopolymer was separated from the grafted polymer beads by Soxhlet extraction with suitable solvents.

The graft polymerization of acrylamide with the polymer **3** was carried out in water. After irradiation for 4 h, followed by extraction of the homopolymer

Table II Photografting of MMA^a on 3 at Different Intervals

Time (h)	Homopolymer wt. (g)	Total Conversion (%)	Graft Yield (%)
1	0.16	10.4	43
2	0.32	19.1	76
4	0.55	31.2	121
6	0.71	38.8	148
8	0.84	41.4	150

^a MMA, 5.6 g in 6 mL of benzene at 32°C.

with water, the weight of the grafted polymer beads was found to be approximately double the initial weight. The spherical shape of the polymer was retained in the grafted beads, although several monomer units were incorporated in the form of grafted chains. The IR spectrum of the grafted polymer showed an absorption band at 1670 cm⁻¹, characteristic of the CONH group of the grafted acrylamide chains.

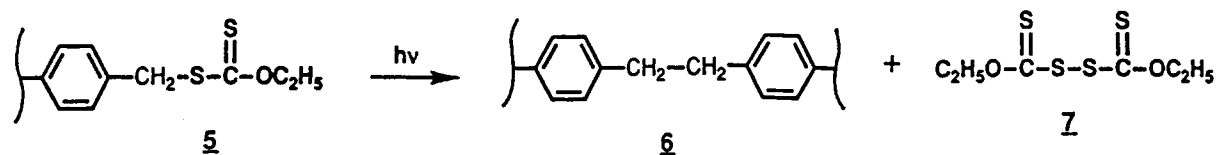
In the case of both acrylic acid and methacrylic acid, the grafting was done either with the neat monomer or with solutions of the monomer in benzene or water. When the grafting was performed in benzene, increased graft efficiency was noted, whereas in water, the efficiency was slightly decreased. This is attributed to the poor swelling of the hydrophobic polystyrene beads in water, thereby decreasing the surface area of the polymer beads. Therefore, the photografting of acrylic acid and methacrylic acid might have been restricted mostly to the surface of the polymer beads. The percentage yield of grafting for acrylic acid and methacrylic acid were found to be 119 and 121, respectively (Table I). The IR spectrum of the product resin, in each case, showed characteristic absorption peaks of the monomer used for grafting, indicating thereby the presence of the grafted polymeric chains. Similarly, the photografting of MMA on polymer 3 was carried out in benzene. After 6 h of irradiation at 32°C, the homopolymer was removed by Soxhlet extraction

with chloroform. The weight increase of the grafted polymer beads has been found to be 148%, after drying under vacuum. The IR spectrum of the polymer beads showed an absorption band at 1740 cm⁻¹, characteristic of the ester carbonyl of the grafted (poly)methyl methacrylate (PMMA).

Among the different monomers used, the maximum graft efficiency was obtained for MMA. The percentage graft yield for all the monomers increased with increasing irradiation time. The results of the photografting of MMA onto the xanthate polymer 3 at different irradiation times are given in Table II. The variation in the percentage graft yield was initially fast and a maximum of 150% was obtained after 8 h of irradiation. Variation in the percentage grafting was also observed as a function of the monomer concentration. The increase in the percentage graft yield with increasing monomer concentration is to be expected since the molecular weight of the graft polymer also increases with increasing monomer concentration. However, the percentage graft efficiency decreased with increasing monomer concentration, because a considerable amount of homopolymer is formed at higher monomer concentrations.

Mechanism of Photografting

Photochemistry of aroyl xanthates are well known in the literature.¹⁶ On photolysis, aroyl xanthates undergo homolytic bond fission resulting in the formation of aroyl and xanthate radicals, which subsequently dimerize to form benzil and the disulfide 7, respectively. It is believed that the polystyrene xanthate undergoes the same kind of photocleavage, generating benzyl radicals on the polymer, which initiate photografting. To confirm this mechanism, we have prepared a soluble polystyrene xanthate 5 by the reaction of potassium O-ethyl xanthate and poly(vinylbenzyl chloride) as described earlier. This polymer, on photolysis, gave a cross-linked polymer and the disulfide 7. The formation of the cross-linked polymer suggests the involvement of benzyl radicals, supported on the polymer chain (Scheme 2).



Scheme 2

Table III Photografting of MMA^a on 3 of Different Cross-Link Densities

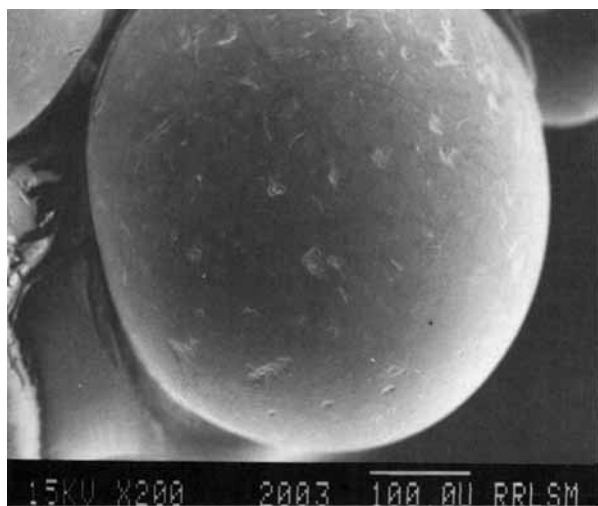
Resin	Cross-link Density (%)	Homopolymer Wt. (g)	Total Conversion (%)	Graft Yield (%)
3a	2	0.71	38.8	148
3b	5	0.76	35.1	122
3c	10	0.98	33.6	98

^a MMA, 5.64 g in 6 mL benzene at 32°C, 6 h.

Effect of the Cross-Linking of Polystyrene Resin on Graft Yield

We have examined the effect of the cross-linking density of the polystyrene beads on the grafting of various acrylic monomers and these results are pre-

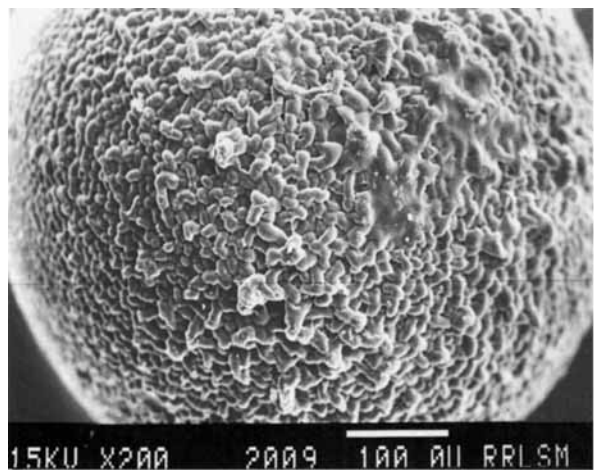
sented in Table III. For this purpose, chloromethyl polystyrene resins with different cross-link densities were prepared and these resins were converted to the corresponding xanthate polymers, as described earlier. Thus, polystyrene xanthates with 2, 5, and 10% cross-link densities, containing approximately



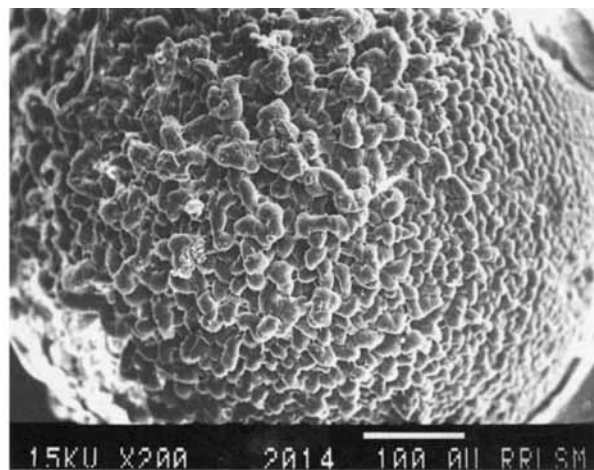
(a)



(b)



(c)



(d)

Figure 1 Scanning electron micrograph pictures: (a) of the ungrafted polystyrene bead at $\times 200$ magnification; (b) of the polymer bead, grafted with acrylamide; (c) of the polymer bead, grafted with acrylic acid; (d) of the polymer bead, grafted with MMA.

the same amount of xanthate groups, were obtained. In the present work, the degree of cross-linking is represented by the amount of divinylbenzene used for polymerization. On the photografting of the various monomers with these resins, we observed a slight decrease in the graft efficiency as the cross-link density increased (Table III). This has been attributed to the poor swelling of the highly cross-linked polymer in solvents, thereby decreasing the available surface area for grafting.

Scanning Electron Microscopic (SEM) Studies

Further confirmation of the grafting of various acrylic monomers onto the xanthate polymer was derived from the SEM studies of the grafted polymer beads. The scanning electron micrograph of an ungrafted polystyrene bead at $\times 200$ magnification is shown in Figure 1(a). It is evident from this micrograph that the surface of the unmodified polymer bead is nearly smooth. Figure 1(b), (c), and (d) are the SEM pictures of the surface of the polymer beads, grafted with acrylamide, acrylic acid, and MMA, respectively. These pictures clearly indicate the presence of large number of grafted chains on the surface of the polymer beads. It is also evident that the spherical shape of the polymer beads has been fully retained after grafting, indicating a highly uniform grafting over the polymer beads.

CONCLUSIONS

In the present studies, we have observed that various acrylic monomers can be grafted photochemically onto chloromethylated polystyrene beads by incorporating a photosensitive xanthate group. The xanthate chromophoric groups, immobilized on cross-linked polystyrene support, are capable of initiating polymerizations of monomers and their subsequent grafting. This type of reaction can be used effectively for introducing reactive functional groups onto a neutral polymer such as polystyrene, and this procedure has several potential applications in making

polymeric reagents, catalysts, ion-exchange resins, etc., with improved reactivity and specificity.

This work was supported by the Council of Scientific and Industrial Research, Government of India. This is document No. RRL-PRU-9 from the Photochemistry Research Unit of RRL, Trivandrum.

REFERENCES

1. G. Oster, G. K. Oster, and H. Moroson, *J. Polym. Sci. Polym. Symp.*, **34**, 671 (1959).
2. S. Tazuke, T. Matoba, H. Kimuri, and T. Okada, ACS Symp. Ser. 121, American Chemical Society, Washington, DC, 1980, p. 217.
3. B. Ranby, Z. M. Gao, A. Hutt, and P. Y. Zhang, ACS Symp. Ser. 364, American Chemical Society, Washington, DC, 1988, p. 168.
4. K. Allmer, A. Hult, and B. Ranby, *J. Polym. Sci. Polym. Chem.*, **27**, 1641 (1989).
5. A. K. Mohanty and B. C. Sing, *Polym. Plast. Technol. Eng.*, **27**, 435 (1988).
6. K. Allmer, A. Hult, and B. Ranby, *J. Polym. Sci. Polym. Chem.*, **27**, 3405 (1989).
7. K. Arai, *J. Appl. Polym. Sci.*, **38**, 969 (1989).
8. T. Otsu, K. Yamashita, and K. Tsuda, *Macromolecules*, **19**, 287 (1986). T. Otsu, T. Ogawa, and T. Yamamoto, *Macromolecules*, **19**, 2087 (1986).
9. H. Inoue and S. Kohama, *J. Appl. Polym. Sci.*, **29**, 877 (1984).
10. K. Inoue, H. Takemoto, and T. Tanigaki, *Makromol. Chem.*, **190**, 3127 (1989).
11. W. R. Hertler, D. Y. Sogah, and F. P. Boettcher, *Macromolecules*, **23**, 1264 (1990).
12. I. S. Shupe, *J. Assoc. Official Agr. Chem.*, **25**, 495 (1942).
13. J. A. Greig and D. C. Sherrington, *Eur. Polym. J.*, **15**, 867 (1979).
14. J. M. J. Frechet, M. D. de Smet, and M. J. Farrall, *J. Org. Chem.*, **44**, 1774 (1979).
15. R. S. Feinberg and R. B. Merrifield, *Tetrahedron*, **30**, 3209 (1974).
16. D. Weir, A. Ajayaghosh, M. Muneer, and M. V. George, *J. Photochem. Photobiol. A. Chem.*, **52**, 425 (1990).

Received March 1, 1991

Accepted October 10, 1991