Eur. Polym. J. Vol. 29, No. 1, pp. 63–68, 1993
Printed in Great Britain. All rights reserved

0014-3057/93 \$5.00 + 0.00

POLYMER-BOUND *S*-BENZOYL *O*-ETHYL XANTHATE: A NEW HETEROGENEOUS PHOTOINITIATOR

A. Ajayaghosh,* R. Francis and S. Das
Photochemistry Research Unit, Regional Research Laboratory, Trivandrum 695019, India

(Received 6 May 1992)

Abstract—Ethyleneglycol dimethacrylate crosslinked poly(2-hydroxyethyl methacrylate) (PHEMA) has been prepared by a reported procedure. A photodissociable chromophore, *S*-benzoyl *O*-ethylxanthate has been synthesized on the crosslinked PHEMA beads and used as a heterogeneous photoinitiator. The photopolymerization efficiency of this photoinitiator has been compared with that of the corresponding soluble photoinitiator, *S*-benzoyl *O*-ethyl xanthate. The rate of photopolymerization, using the polymer-bound initiator is higher than that for the soluble photoinitiator for longer irradiation times. For shorter irradiation times, the rate of polymerization is lower for the polymer-bound initiator than for the soluble material. During photopolymerization of methyl methacrylate, a sharp increase in the rate is observed after an initial delay, whereas, for the soluble initiator, the rate of polymerization is constant with time. Comparison of the rate of homopolymerization and that of the accompanying graft polymerization reveals that the latter process is more efficient.

INTRODUCTION

Activities in the field of photopolymerization continue to expand in several directions because of the fundamental and technological importance of this topic [1–3]. Many photoinitiators have been reported and several of them are industrially important [4–6]. Most of these photoinitiators, on u.v. irradiation, undergo homolytic bond scission generating the benzoyl radical, which participates in the initiation of polymerization. Thus, it is important to construct a molecule which can easily generate benzoyl radicals on irradiation as a first approach to producing an improved photoinitiator. A recent report from this laboratory described the use of a sulphur-containing photoinitiator, viz. *S*-benzoyl *O*-ethyl xanthate, for the photopolymerization of methyl methacrylate (MMA) (Scheme 1) [7]. The excited state processes and the transients involved in the phototransformation of some of the aroyl xanthates have been examined recently using the nanosecond laser flash photolysis technique [8]. Laser flash photolysis of *S*-benzoyl *O*-ethyl xanthate reveals that the primary photoprocess in this case involves a C(=O)—S bond cleavage to generate both the benzoyl and ethoxythiocarbonyl thiyl radicals which initiate polymerization.

Industrial applications of many of the conventional photoinitiators have been rather limited for several reasons. Some of these problems are due to the poor storage stability, bad odour and noncompatability with monomers. A possible solution to these problems could arise from the use of polymeric photoinitiators and several such initiators have been reported [9–14]. However, not much is known on the use of a photoinitiator covalently linked to a crosslinked macromolecular support and its effect on the efficiency of photopolymerization. Polymer-bound reagents, catalysts and enzymes have already been reported for several uses [15].

The present study describes the synthesis of a polymer-bound analogue of *S*-benzoyl *O*-ethyl xanthate and its use as a heterogeneous photoinitiator for the polymerization of acrylic and vinylic monomers. The results of comparisons between the polymer-bound photoinitiator and its soluble analogue for the photopolymerization of MMA and styrene are presented.

EXPERIMENTAL PROCEDURES

Materials and methods

Solvents were dried and distilled before use. MMA and styrene were purified by washing with a 5% solution of NaOH, followed by distillation under reduced pressure. 2-Hydroxyethyl methcrylate (HEMA) and ethyleneglycol dimethacrylate (EGDM) were distilled under vacuum to remove inhibitors and stored in a refrigerator. AIBN was recrystallized twice from methanol. Anhydrous ethanol [16] and potassium *O*-ethyl xanthate [17] were prepared by reported procedures.

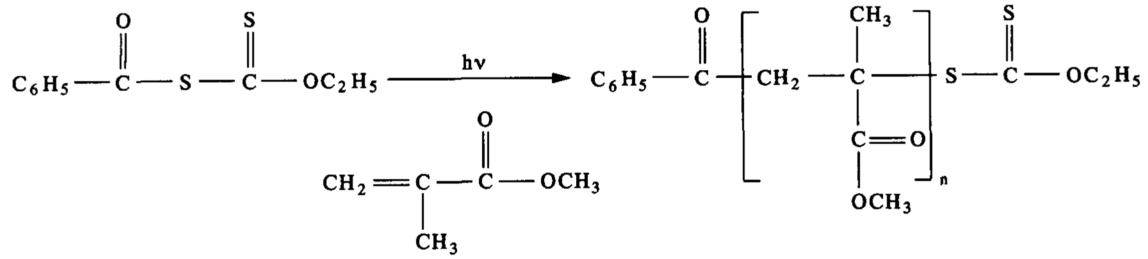
i.r. and u.v. spectra were recorded on Perkin–Elmer Model 882 and Shimadzu 2100-A spectrophotometers, respectively. ^{1}H-NMR spectra were recorded on a Varian EM-360 (60 MHz), instrument, using $CDCl_3$ as solvent and TMS as internal standard. Sulphur analyses were carried out by the Midwest Microlab (Indianapolis, U.S.A.). Photopolymerizations were carried out on an Oriel Optical Illuminator with a 500 W super high pressure Hg lamp (USHIO USH 508 SA). Light of 400 nm wavelength was selected using 345 nm long pass and 400 nm band pass filters and focussed through a slit of 2 cm width. All irradiations were done at 30 ± 1° The light intensity was maintained constant throughout the photopolymerizations.

Preparation of crosslinked 2-hydroxyethyl methacrylate beads (PHEMA) (1)

HEMA (12 ml), ethyleneglycol EGDM (0.6 ml), AIBN (90 mg) and benzyl alcohol (18 ml) were mixed in a 250 ml flask. A solution of NaCl (35%, 50 ml) and NaOH (1 M, 9 ml) containing $MgCl_2$, $6H_2O$ (0.51 g) were separately

---

*To whom all correspondence should be addressed.



Scheme 1

prepared and charged into the flask containing monomers. The contents were degassed with argon for 15 min and stirred at 500 rpm, at 70° on a water bath. After 3 hr, the flask was cooled to room temperature; the polymer beads were collected by filtration and washed thoroughly with methanol to remove benzyl alcohol completely. The polymer beads were then washed with dil. HCl to remove $Mg(OH)_2$ and finally with distilled water. The PHEMA beads after drying in vacuum at 60° weighed 11.7 g (90%). Fine beads in the range of 100–200 mesh were collected by sieving.

Preparation of poly(S-benzoyl O-ethylmethacrylate xanthate) resin (3)

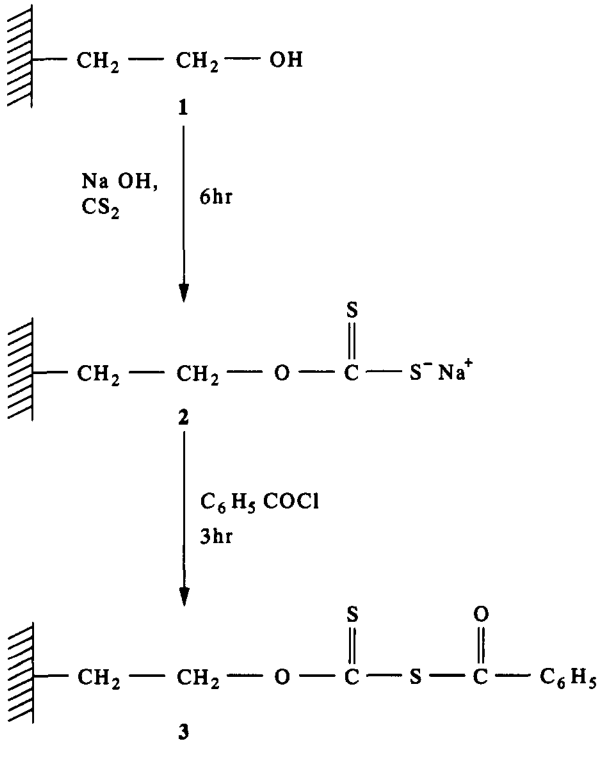
PHEMA (4 g) was suspended in NaOH solution (3 N, 50 ml) and stirred for 1 hr. To this suspension, CS_2 (18 ml, 0.15 mol) was added and the stirring was continued for an additional 5 hr. The reaction mixture was decanted and the polymer beads were washed thoroughly with water, methanol and chloroform. The sodium *O*-ethyl methacrylate xanthate resin (**2**) thus obtained was suspended in a mixture of chloroform and acetone (1:1, 20 ml), followed by the addition of benzoyl chloride (5 ml, excess). The reaction mixture was stirred in the dark for 4 hr. The resulting yellow resin was collected by filtration, washed several times with chloroform, acetone, water and methanol. The *S*-benzoyl *O*-ethyl methacrylate resin (**3**) thus obtained was dried in vacuum to give 6.2 g; anal. S, 6.7% (2.09 mmol S/g); i.r. (KBr): 1700 cm^{-1} ($C_6H_5C{=}O$), 1055 ($C{=}S$).

Determination of the xanthate group content in polymer (3)

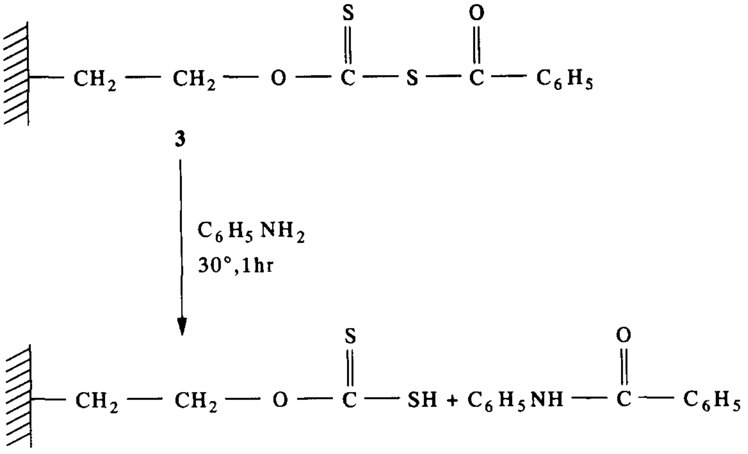
A small sample of the polymer (**3**) (100 mg) was stirred with aniline (0.5 ml) in a mixture of chloroform and acetone (1:1, 5 ml) for 1 hr. The yellow colour of the polymer totally disappeared during this period, indicating completion of the reaction. The polymer was filtered off, washed with chloroform and the solvent was removed from the filtrate under reduced pressure to yield 70 mg of benzanilide. From the amount of benzanilide obtained, the xanthate group content was found to be 1.78 mmol/g. The xanthate group content was also determined by elemental sulphur analysis and was found to be 2.09 mmol/g of polymer.

Photopolymerization of MMA and styrene using the polymer-bound photoinitiator (3)

All photopolymerizations were carried out in cylindrical reaction vessels of pyrex glass (2.5 cm × 2 cm). Suspensions of known amounts of the polymeric photoinitiator (**3**) in the monomer were degassed with pure argon for 10 min. The suspensions were then irradiated at 400 nm, selected from a



Scheme 2



Scheme 3

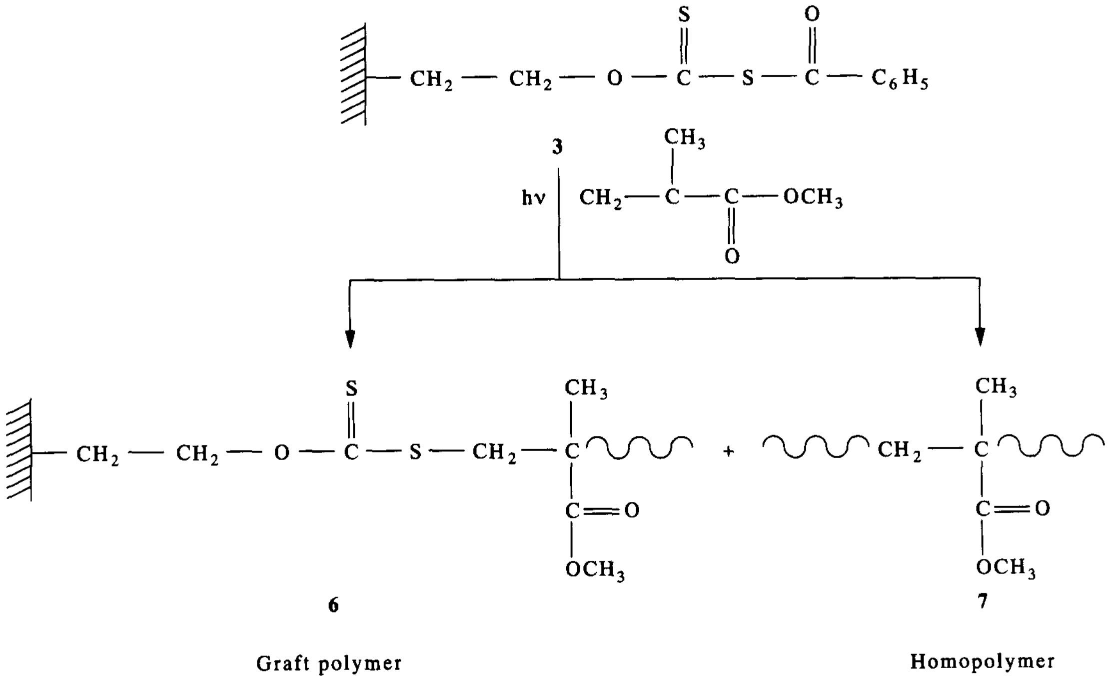
500 W high pressure Hg lamp housed on an Oriel Optical Rail, using 340 nm long pass and 400 nm band pass filters. After irradiation for known periods at 30 ± 1°, the contents of the tubes were filtered, washed several times with benzene, dried under vacuum and weighed. The filtrate was concentrated and poured into excess methanol. The polymer formed was collected, washed with methanol, dried and weighed. The conversion was calculated from the total weight of the homopolymer and the polymer grafted onto the polymer-bound photoinitiator. The rate of polymerization (R_p) was calculated from the total conversion.

Photopolymerization of MMA and styrene using soluble S-benzoyl O-ethyl xanthate

Photopolymerizations using the soluble photoinitiator were carried out under identical conditions as for the polymer-bound, photoinitiator. After irradiation for a known period, the contents were poured into excess methanol. The precipitated polymer was filtered off, washed several times with methanol and dried to constant weight. The rate of polymerization (R_p) was calculated.

RESULTS AND DISCUSSION

PHEMA beads (5% EGDM crosslinked, 100–200 mesh) were prepared by suspension polymerization of HEMA using AIBN as initiator [18]. This polymer was converted to the corresponding sodium xanthate (**2**) by treatment with equimolar amounts of NaOH and CS_2 (Scheme 2). Treatment of the resin (**2**) with excess benzoyl chloride afforded the corresponding yellow *S*-benzoyl xanthate resin (**3**) (Scheme 2). The i.r. spectrum of the *S*-benzoyl xanthate resin (**3**) shows characteristic peaks at 1700 ($C_6H_5C{=}O$) and 1055 cm^{-1} ($C{=}S$). The loading of benzoyl groups on the polymer (**3**) was determined by elemental analysis or by transferring the benzoyl group to an amine



Scheme 4

Table 1. Photopolymerization of MMA using polymer-bound initiator (3)*

Time (min)	Wt of homopolymer (g)	Wt of graft polymer (g)	Total conversion (g)	Conversion (%)	$R_p \times 10^3$ (M sec^{-1})
20	0.03	0.12	0.15	2.0	0.12
24	0.06	0.40	0.46	6.1	0.32
28	0.20	0.97	1.17	15.6	0.69
32	0.40	2.15	2.55	34.0	1.30
35	0.32	2.40	2.72	36.3	1.30
40	0.38	3.10	3.48	46.5	1.40

*MMA, 8 ml; initiator, 100 mg; temperature, 30°.

Table 2. Effect of MMA concentration on photopolymerization using polymer-bound initiator (3)*

MMA concentration [M]	Wt of homopolymer (g)	Wt of graft polymer (g)	Total conversion (g)	Conversion (%)	$R_p \times 10^4$ (M sec^{-1})
2	0	0.40	0.40	25	2.2
4	0.13	0.68	0.81	25	4.5
5	0.17	0.95	1.12	28	6.2
6	0.21	1.27	1.48	31	8.2
7	0.27	1.75	2.02	36	11.2

*Irradiation time, 30 min; initiator, 100 mg; temperature 30°.

(Scheme 3). From these analyses, an average capacity of 1.78 mmol of xanthate group/g of polymer was obtained. During photoirradiations, various parameters such as light intensity, distance from the source and temperature were kept constant. Photopolymerizations of MMA and styrene, using the polymeric photoinitiator were performed for various monomer and initiator concentrations. During photolysis the C(=O)—S bond of the photoinitiator undergoes cleavage, generating thiocarbonyl thiyl radicals on the polymer and benzoyl radicals in solution. These radicals initiate both graft and homopolymerization of the monomers (Scheme 4).

The results of the polymerization of MMA in bulk using the polymeric initiator (3) at various intervals are shown in Table 1. It is found that, unlike the soluble photoinitiator, the rate of polymerization (R_p) of MMA using the polymer-bound photoinitiator is not constant. A plot of monomer conversion against irradiation time indicates that the total conversion is very low during the initial stages; however, after 20 min there is a sudden increase in the conversion (Fig. 1). During the initial stages of polymerization, a linear relationship is obtained for both soluble and polymer-bound initiators, when the monomer conversion is plotted against irradiation time. However, for shorter irradiation times (< 25 min), the rate of polymerization is lower for the polymer-bound initiator than for the corresponding soluble initiator; for longer irradiation times (> 25 min), the rate of polymerization is higher for the polymer-bound initiator.

Increase in the rate of polymerization of MMA for the polymer-bound initiator at longer irradiation times could be explained by considering the difference in the swelling of the initiator in the monomer. Initially, the swelling of the bound initiator in the monomer is less and consequently the photodecomposition of the initiator is not very efficient. However, as the irradiation proceeds, some PMMA chains are grafted onto the polymeric initiator. This process may significantly influence the swelling characteristics of the initiator and, as a consequence, the surface area of the polymeric initiator increases, exposing

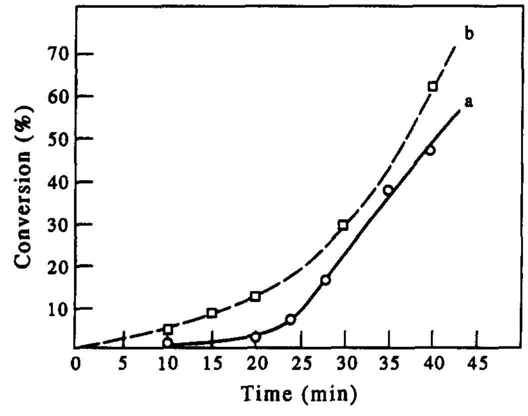


Fig. 1. Relation between percentage conversion and irradiation time for the photopolymerization of MMA using the polymer-bound initiator (3). (a) MMA (bulk); (b) MMA (5 M in benzene).

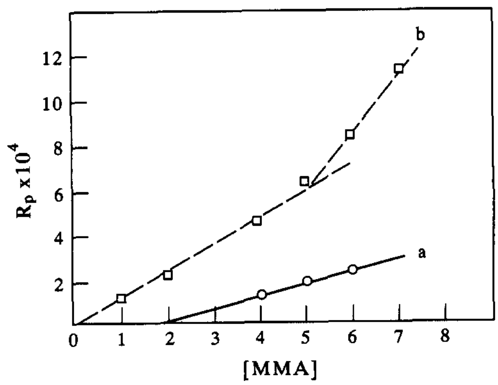


Fig. 2. Relation between the rate of polymerization (R_p) and monomer concentration for the photopolymerization of MMA. (a) Soluble initiator, (b) polymer-bound initiator.

Table 3. Photopolymerization of styrene using the polymer-bound initiator (3)*

Time (min)	Wt of homopolymer (g)	Wt of graft polymer (g)	Total conversion (g)	Conversion (%)	$R_p \times 10^5$ (M sec^{-1})
30	0.02	0.04	0.06	0.83	3.30
60	0.04	0.11	0.15	2.06	4.17
90	0.07	0.21	0.28	3.90	5.20

*Styrene, 8 ml; initiator, 100 mg; temperature, 30°.

Table 4. Effect of monomer concentration on the photopolymerization of styrene*

Conc. of styrene (M)	Wt of homopolymer (g)	Wt of graft polymer (g)	Total conversion (g)	Conversion (%)	$R_p \times 10^5$ (M sec^{-1})
5	0.05	0.08	0.13	2.9	3.30
6	0.06	0.10	0.16	3.2	4.40
7	0.07	0.12	0.19	3.2	5.14

*Irradiation time, 60 min; initiator, 100 mg; temperature, 300°.

more and more initiator moiety to light. Further, as the swelling increases, the polymeric initiator becomes a semitransparent gel which facilitates to some extent the penetration of light into the initiator. Thus, for the photopolymerization of MMA in bulk with 100 mg of the polymer-bound initiator, a linear increase in the conversion could be noticed during the first 20 min and then there is a sudden increase in the conversion.

The increased efficiency of the polymer-bound initiator over the soluble initiator for the photopolymerization of MMA under identical conditions can also be explained by considering the termination efficiency of the thiocarbonyl thiyl radical. In the case of the soluble initiator, the radicals generated have enough freedom to move in the solution, particularly for lower monomer conversions. Hence the thiocarbonyl thiyl radicals can easily terminate the growing polymer chain, resulting in the formation of considerable amounts of oligomers, particularly at higher initiator concentrations. In the case of the polymer-bound initiator, the thiocarbonyl thiyl radicals are immobilized on the initiator backbone and hence their termination efficiency may be less. However, for higher monomer conversions, termination of the homopolymer chains by the polymer-bound thiocarbonyl thiyl radicals becomes predominant resulting in a higher graft yield.

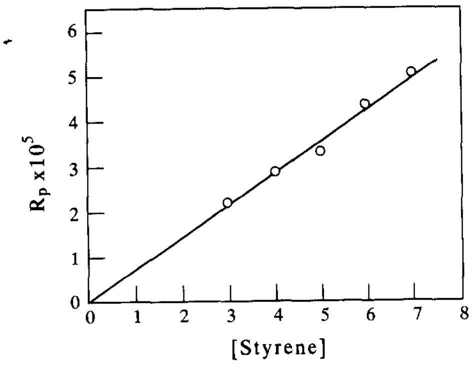


Fig. 3. Relation between the rate of polymerization (R_p) and monomer concentration for the photopolymerization of styrene using the polymer-bound initiator (3).

During the initial stages of polymerization, the benzoyl and the homopolymer radicals have enough freedom to separate from the xanthate radicals which are immobilized on the polymer backbone. However, as the monomer conversion becomes high, the diffusion of the radicals is restricted by the PMMA chains. Thus, the termination of the PMMA chains by the polymer-bound xanthate radicals becomes more efficient, so accounting for the increased formation of graft rather than homopolymers with increasing monomer conversion.

The effect of MMA concentration on the photopolymerization rate was examined using a fixed amount of the polymer-bound initiator. The rate of polymerization after irradiation for 30 min at 30° was calculated on the basis of the total conversion of the monomer (see Table 2). The relationship between R_p and MMA concentration is presented in Fig. 2, which indicates a sudden increase in the rate of polymerization for higher concentration of MMA (>4 M). However, no such deviation was observed for the soluble photoinitiator under identical experimental conditions. Photopolymerization of a 5 M solution of MMA in benzene and pure MMA are compared in Fig. 1, which reveals that the initial rate of conversion is higher for 5 M solution than for pure MMA. This effect could be due to the fact that the polymer-bound initiator swells to a greater extent in a benzene solution of MMA than in pure MMA, so enhancing the photodecomposition of the polymer-bound initiator and increasing the efficiency of polymerization.

The photopolymerization of styrene, initiated by the polymer-bound initiator is much slower than the polymerization of MMA under identical conditions (Table 3). This difference could be partly due to the fact that the short lived triplets of the photoinitiator, if formed, will be quenched by the styrene molecule before the dissociation of the C(=O)—S bond to form radicals. The effect of styrene concentration on the rate of polymerization with the polymer-bound initiator is shown in Table 4. It is evident that R_p increases with increase in styrene concentration and a plot of R_p against monomer concentration gives a linear relationship (Fig. 3).

Acknowledgements—The authors thank the Council of Scientific and Industrial Research, Government of India and the Regional Research Laboratory (CSIR), Trivandrum for financial support of this work. This is Document No. RRLT-PRU-24 from the Photochemistry Research Unit of the Regional Research Laboratory, Trivandrum.

REFERENCES

1. S. P. Pappas. In *UV Curing: Science and Technology*, Vol. 2. Technology Marketing Corp., Norwalk, Connecticut (1984).
2. S. P. Pappas. In *Comprehensive Polymer Science; The Synthesis, Characterization, Reactions and Applications of Polymers*, Vol. 4, Chap. 20. Pergamon Press, Oxford (1989).
3. L. F. Thompson, C. G. Willson and M. J. Bowden. *Introduction of Microlithography; ACS Symposium Series 219*. American Chemical Society, Washington D.C. (1983).
4. J. F. Rabek. In *Mechanisms of Photophysical and Photochemical Reactions in Polymer: Theory and Practical Applications*. Wiley, New York (1987).
5. J. G. Kloosterboer. *Adv. Polym. Sci.* **84,** 1 (1988).
6. H. J. Hageman. In *Photopolymerization and Photoimaging Science and Technology* (edited by N. S. Allen). Elsevier Applied Sciences, London (1989).
7. A. Ajayaghosh, S. Das and M. V. George. *J. Polym. Sci. A. Polym. Chem.* (1992).
8. D. Weir, A. Ajayaghosh, M. Muneer and M. V. George. *J. Photochem. Photobiol. A: Chem.* **52,** 425 (1990).
9. C. Carlini, F. Ciardelli, D. Donati and F. Gurzoni. *Polymer* **24,** 599 (1983).
10. L. Flamigni, F. Barigelletti and P. Bortolus. *Eur. Polym. J.* **20,** 171 (1984).
11. G. LiBassi, G. Broggi and L. Cardona. In *Proceedings of Radcure Europe*. Munich pp. 15 (1987).
12. J. P. Fouassier, D. J. Lougnot, G. LiBassi and C. Nicora. *Polym. Commun.* **30,** 245 (1989).
13. F. Catalina, C. Peinado, R. Sastre and J. L. Mateo. *J. Photochem. Photobiol. A: Chem.* **47,** 365 (1989).
14. S. N. Gupta, L. Thijs and D. C. Neckers. *J. Polym. Sci., Polym. Chem. Edn* **19,** 855 (1981).
15. A. Akelah and D. C. Sherrington. *Polym. Rev.* **24,** 1369 (1983).
16. *Vogel's Textbook of Practical Organic Chemistry* (4th Edn) pp. 269, Longman, England (1984).
17. I. S. Shupe. *J. Assoc. Official Agr. Chem.* **25,** 495 (1942).
18. A. Jayakrishnan, M. C. Sunny and B. Chithamabara Thanoo. *Polymer* **31,** 1339 (1990).