A Xanthate-Derived Photoinitiator that Recognizes and Controls the Free Radical Polymerization Pathways of Methyl Methacrylate and Styrene[†]

A. Ajayaghosh* and R. Francis

Contribution from the Photochemistry Research Unit, Regional Research Laboratory, CSIR, Trivandrum 695 019, India

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Abstract: A xanthate derived photoinitiator, *S*-methacryloyl *O*-ethyl xanthate (MAX) bearing an electron-deficient polymerizable double bond has been found to be capable of distinguishing MMA and styrene, thereby dictating their polymerization pathways in distinctly different and controlled fashion. The structure, molecular weight, and the polydispersity of each polymer have been determined by spectral analysis and size-exclusion chromatography (SEC). Photopolymerization of MMA using MAX under 350-nm irradiation led to the formation of narrow dispersed ($M_w/M_n < 1.5$) linear "macroinitiators" with methacryloyl and thiocarbonyl thiyl end functional groups by a controlled free radical mechanism where the molecular weights remained nearly the same, independent of irradiation time. The presence of the thiocarbonyl thiyl group was further confirmed by the block copolymerization of methyl acrylate using the macroinitiator. On the other hand, photopolymerization of styrene with MAX showed considerable increase in molecular weights and polydispersities with irradiation time, as in the case of a *pseudo*-"living" free radical polymerization. Nevertheless, in the present case, the molecular weight increase and the broad polydispersity of polystyrene are explained on the basis of the branching of the polymer chain, which is supported by IR and NMR spectral analysis. This unusual behavior of MAX is attributed to its "tricky" approach toward MMA and styrene, making use of the electron availability around their double bonds. MAX behaves only as a photoinitiator toward the electron-deficient MMA, whereas it plays the dual role of a photoinitiator as well as a co-monomer toward electron-rich styrene due to a weak donor–acceptor interaction, leading to the initial formation of a macro-photoinitiator and the subsequent formation of branched and cross-linked polymers. Interestingly, *S*-benzoyl *O*-ethyl xanthate, an analogous photoinitiator without a polymerizable double bond, did not show any differences in the polymerization of MMA and styrene, thereby emphasizing the role of the methacryloyl moiety of MAX in controlling their polymerization pathways.

Introduction

The quest for the designing of novel macromolecular architectures having new and/or improved properties has led to the synthesis of linear, block, and branched polymers with well-defined terminal functional groups, controlled molecular weights, and narrow molecular weight distributions. Traditionally, control of polymerization processes has been achieved with "living" polymerization techniques such as ionic, group transfer, and transition-metal-catalyzed processes.[1] However, these methods suffer from rigorous synthetic requirements and incompatibility with a variety of functional monomers. Therefore, much interest has recently been focused toward free radical chemistry to achieve control over polymerization process due to their tremendous commercial significance. Even though free radical initiated polymerizations are synthetically less rigorous and are compatible with a wide variety of monomers, they, in general, lack the ability to accurately control molecular weight distribu-

tion and end functional groups. This is mainly due to the uncontrollable propagation and termination processes of the growing polymer radicals. Therefore, the concept of "living" free radical polymerization has been introduced in which the control of living polymerization and the advantages of free radical polymerization are put together in a single operation.[2] In this approach the growing polymer radicals are in dynamic equilibrium with dormant species, which facilitates stepwise incorporation of monomers, thereby achieving accurate control over the molecular weight, polydispersity, and end functional groups.

* To whom correspondence should be addressed. E-mail: ajay@csrrltrd.ren.nic.in.
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Living free radical polymerization has undergone tremendous progress in the past few years, particularly in the area of nitroxide-mediated free radical polymerization.[3] The success of this approach can be related to the ability of stable nitroxide free radicals such as 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) to react at near diffusion controlled rates with the carbon-centered free radical of the growing polymer chain end in a thermally reversible process. Hawker and co-workers have extensively exploited TEMPO-based initiators in achieving molecular weight control by a living free radical mechanism.[4] An alternate strategy for controlling the molecular weight and polydispersity is the atom transfer radical polymerization (ATRP) using various transition-metal complexes.[5] Recently, several modifications have been suggested for many of the existing living free radical polymerization reactions, the latest being a reversible addition fragmentation chain transfer (RAFT) process.[6]

In contrast to thermal initiation processes, the photoinitiated free radical polymerization would have the advantages of performing under low temperature with wavelength specificity. Nevertheless, it is not possible to attain molecular weight and end functional group control by conventional photoinitiated free radical polymerization. One of the earliest attempts to control molecular weight and end functional groups by a photoinitiated free radical chemistry is the *iniferter* method introduced by Otsu and co-workers using dithiocarbamates.[7] In this case, the photoinitiator decomposes homolytically to generate two un-symmetrical free radicals, one of which acts as the initiator while the other behaves as the molecular weight controlling agent. This should be possible if one of the radicals is a stable resonance-stabilized species with strong affinity for reversible primary radical termination. In this way, the overall concentration of the reactive radicals can be controlled, and the termination can be restricted to a primary radical termination process. However, this approach is inefficient in many respects, particularly because, under UV irradiation, considerable amount of the light will be absorbed by the monomer leading to uncontrolled polymerization and side reactions. As a result, the polymers obtained by the *iniferter* approach were found to have polydispersities similar to those from conventional free radical processes. Moreover, several authors have questioned the validity of the proposed "living" radical mechanism of the

Scheme 1
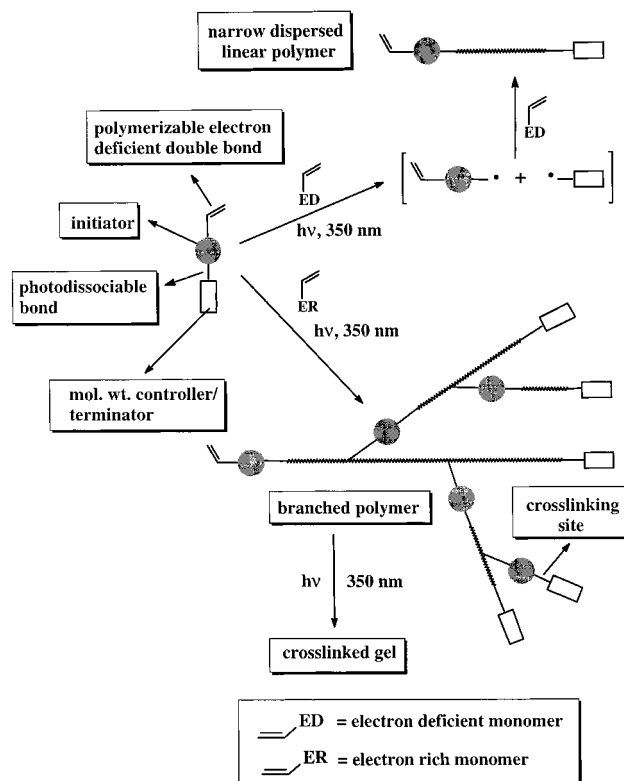
iniferter method due to parallel side reactions, which occur during photolysis of dithiocarbamates.[8]

Recently, the concept of a self-condensing free radical initiator containing a polymerizable moiety has been exploited for the controlled synthesis of hyperbranched and dendrigraft polymers.[9] In these cases, the synthesis of such complex polymers are accomplished in a single step, using tailor-made initiators and/or monomers. Nevertheless, a photoinitiator that can recognize the monomer, making use of its electronic character, to provide different macromolecular structures remains elusive. Even though several photoinitiators bearing polymerizable double bonds have been reported, none of them are being exploited in this direction.[10] In the present study, we describe the use of a "smart" photoinitiator that can differentiate MMA and styrene based on the electron availability over the monomer's polymerizable double bond. The described photoinitiator can thus play the dual role of a photoinitiator as well as a monomer, depending on the choice of the co-monomer employed. We illustrate this with the use of a novel polymerizable photoinitiator *S*-methacryloyl *O*-ethyl xanthate (MAX).

The concept of a smart photoinitiator which is shown in Scheme 1 has originated from our preliminary studies on the controlled photopolymerization of MMA using MAX.[11] Structurally, such a photoinitiator should contain a polymerizable

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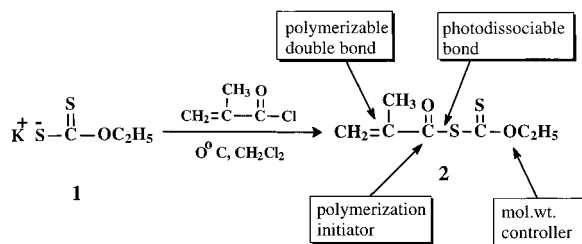(11) Ajayaghosh, A.; Francis, R. *Macromolecules* **1998**, *31*, 1436.

Scheme 2

Table 1. Results of the Photopolymerization^a of MMA in Benzene using MAX as the Photoinitiator under 350-nm irradiation at 32 °C

run	time (min)	conversion (%)	$R_p \times 10^4$ (g s^{-1})	$M_n \times 10^{-4}$	(M_w/M_n)
1	10	5	4.5	2.1	1.4
2	15	8	4.5	2.1	1.3
3	20	11	4.6	2.2	1.4
4	25	13	4.5	2.0	1.3
5	30	15	4.4	1.9	1.2
6	40	16	4.5	1.8	1.3

^{a} [MMA] = 5 M, [MAX] = 5 × 10^{-3} M.

double bond with low reactivity, an initiator moiety, and a molecular weight controlling unit. The initiator moiety and the molecular weight controlling unit should be connected through a photolabile bond which should undergo facile homolytic cleavage, thereby generating a polymerization initiator and a resonance-stabilized inactive radical which can terminate the growing polymer chain. In addition, the initiator should be able to communicate with the monomer employed for the polymerization and should be able to switch over between the role of a simple photoinitiator to a monomer cum initiator, thereby controlling the polymerization pathways leading to the formation of different macromolecular architectures. We have synthesized a novel and simple photoinitiator with these design features and illustrate its use in controlling the free radical polymerization of MMA and styrene in distinctly different pathways.

Results and Discussion

MAX has been prepared by the slow addition of potassium *O*-ethyl xanthate to methacryloyl chloride in dichloromethane and characterized by spectral and elemental analysis (Scheme 2). At any stage of the reaction, excess of the xanthate salt should be avoided to prevent any side reactions of MAX with reactants.[12] MAX has been chosen as the photoinitiator because of its easy synthetic accessibility and its inability to undergo free radical initiated self-polymerization. More importantly, MAX satisfies all of the design features that we have proposed in the general Scheme 1. To test this, we have employed MMA as an electron-deficient monomer and styrene as an electron-rich monomer for the photopolymerization studies.

Photopolymerization of MMA Using MAX. The results of the photopolymerization of MMA (5 M in benzene) using MAX (5 × 10^{-3} M) at different intervals of irradiation are shown in Table 1. The rate of polymerization, molecular weights, and the dispersity of the obtained polymers remained nearly the same, independent of the monomer conversion. Change in irradiation time did not bring any considerable variation either to the molecular weight or to the polydispersity (Figure 1). The polydispersities of all polymers obtained in these cases were between 1.2 and 1.4. Plots of the molecular weights and
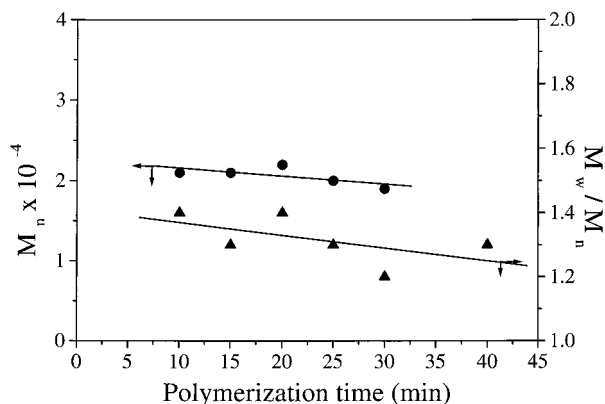
(12) Presence of excess potassium xanthate will facilitate its nucleophilic attack on MAX to form *O*,*O*-diethyl xanthic anhydride and thiomethacrylic anhydride as side products thereby reducing the yield of MAX.

Figure 1. Effect of irradiation time on molecular weight (M_n) and polydispersity (M_w/M_n) for the photopolymerization of MMA (5 M in benzene) using MAX (5 × 10^{-3} M) under 350-nm irradiation.
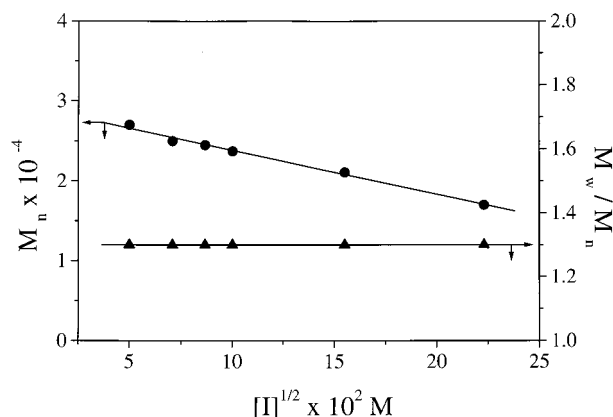

Figure 2. Effect of MAX concentration on molecular weight (M_n) and polydispersity (M_w/M_n) of the PMMA obtained by the photopolymerization of MMA (5 M in benzene) under 350-nm irradiation.
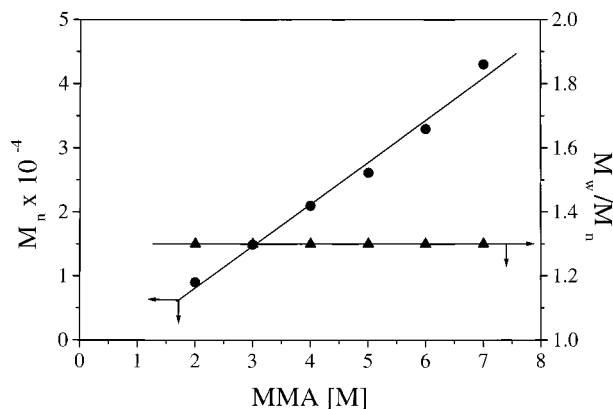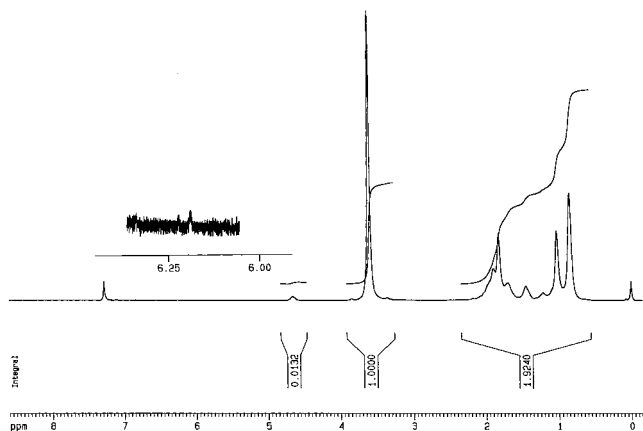

Figure 3. Effect of MMA concentration on molecular weight (M_n) and polydispersity (M_w/M_n) of PMMA obtained by the photopolymerization of MMA using MAX (5 × 10^{-3} M) under 350-nm irradiation.

polydispersities of the polymers obtained under different MAX concentrations are shown in Figure 2. In this case a linear decease in molecular weight is noticed, whereas the polydispersity did not vary considerably. On the other hand, a linear increase in molecular weight was observed for the polymers obtained with an increase in MMA concentrations (Figure 3). In this case also, the polydispersities of the resulting polymers were nearly the same. Surprisingly, the polydispersities of all PMMA obtained under various polymerization conditions were lower than the theoretical limiting value for a conventional free radical polymerization (M_w/M_n < 1.5). The above results reveal that even though the photopolymerization of MMA using MAX

Figure 4. ^{1}H NMR spectrum of PMMA obtained by the photopolymerization of MMA using MAX.

has the characteristic of a simple free radical polymerization, it shows tremendous control over the polymerization processes. From Figures 2 and 3 it is clear that the molecular weights of the polymer can be predefined by the initiator or the monomer concentrations and that the polydispersity can remain narrow as in the case of a living free radical polymerization. This could be possible because the termination step is restricted mainly to primary radical termination by the thiocarbonyl thiyl group, thereby minimizing the disproportionation or polymer radical recombination processes.

FT-IR spectra of the PMMA prepared using MAX showed weak absorption at 1040 cm^{-1}, corresponding to the C=S group in addition to the characteristic absorptions of PMMA. Another characteristic absorption of the thiocarbonyl thiyl group which usually occurs at 1240 cm^{-1} could not be visible in this case probably due to its merging with the strong absorption of the C−O stretching frequency. The ^{1}H NMR spectrum of a representative PMMA is shown in Figure 4. The presence of the thiocarbonyl thiyl end group is clear from the weak resonance signals at δ 4.65 and 1.4 ppm. The extremely weak signals at δ 6.18 and 6.23 ppm could be due to the methacryloyl end group. The end group analysis by the determination of the elemental sulfur content has revealed an average of one thiocarbonyl thiyl group for every polymer chain which supports the efficient bimolecular termination of the propagating polymer radicals by the thiocarbonyl thiyl radicals.

On the basis of the above results the mechanism for the photopolymerization of MMA can be proposed as shown in Scheme 3. By analogy to the earlier reports on the photodissociation of acyl and aroyl xanthates[13] and its extension to photopolymerization processes,[14] it is reasonable to anticipate that homolytic cleavage of MAX generates a methacryloyl radical and a resonance-stabilized thiocarbonyl thiyl radical. In the presence of MMA, the methacryloyl radical would initiate the polymerization, whereas the thiocarbonyl thiyl radical would act as the molecular weight controller by primary radical termination. The inert nature of the thiocarbonyl thiyl radical toward initiation of polymerization and its high affinity for bimolecular termination are well documented in the literature.[15] Alternately, termination may also be possible by chain transfer

Scheme 3
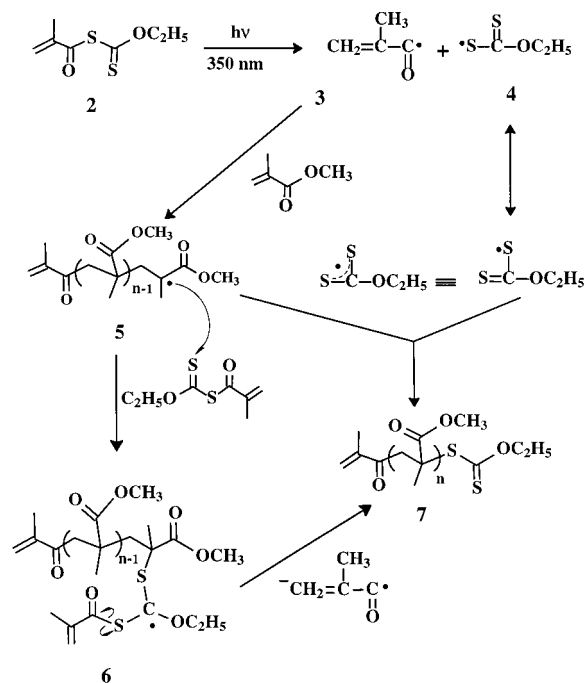
to MAX as shown in Scheme 3. Both mechanisms can lead to polymers end-capped with a thiocarbonyl thiyl group. This can be supported by the earlier observation of Zard and co-workers pertaining to the photochemical addition of *S*-benzoyl *O*-ethyl xanthate with unsaturated compounds.[16]

Thiocarbonyl Thiyl End-Capped PMMA as Macro-Photoinitiator for Block Copolymer Synthesis. Presence of the photoactive thiocarbonyl thiyl end group in PMMA is further confirmed by its use as "macro-photoinitiator" for the photoinduced block copolymerization of methyl acrylate (MA). This is particularly important because block copolymer synthesis without homopolymer formation is often difficult or rather impossible by conventional free radical polymerization strategies.[17] Block copolymer synthesis that occurs exclusively by a free radical mechanism, while being difficult to control in terms of molecular weights, polydispersity, and homopolymer formation, is easy to operate with a wide range of monomers and can tolerate a variety of functional groups. Therefore, any approach to control the molecular weight, dispersity, and homopolymer formation in a free radical induced block copolymerization is a challenging task.[18]

The results of the block copolymerization of MA using the macroinitiator **7** at various time intervals are shown Table 2. In this case, the irradiation should be performed under 300 nm, because the C−S bond of the terminal thiocarbonyl thiyl group is cleavable only at 300 nm or below. MA has been chosen as

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Table 2. Block Copolymerization of MA (5 M in benzene) Using the Macroinitiator **7** (M_n = 16000, 5 mg/mL) under 300-nm irradiation at 32 °C

run	time (min)	yield (%)	M_n	M_w/M_n
1	30	5	39000	2.1
2	60	12	88000	1.9
3	90	25	210000	1.2
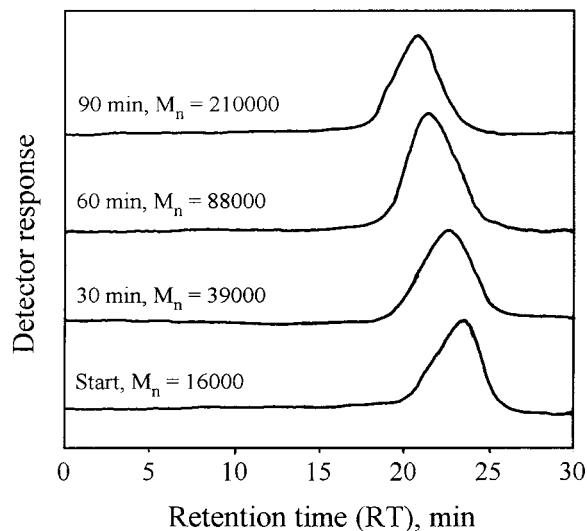
Figure 5. SEC profiles of the block copolymers prepared using the macro-photoinitiator **7** under 300-nm irradiation at different intervals.

the monomer because it does not absorb at 300 nm thereby considerably enhancing the efficiency of the macroinitiator. On top of that, block copolymers of methacrylates and acrylates are interesting due to their morphological and mechanical behavior. Such block copolymers can provide high T_g (methacrylate) and low T_g (acrylate) blocks which can function as thermoplastic elastomers or specialty adhesives with high resistance toward hydrocarbon solvents.[19] The data in Table 2 show considerable increase in molecular weights for block copolymers formed with increase in irradiation time. For example, the molecular weight of PMMA−block−PMA obtained after 30 min of irradiation was 39 000 g/mol which was further increased to 210 000 g/mol after 90 min of irradiation. The SEC elusion patterns of the starting macroinitiator and its block copolymers obtained under different irradiation times are shown in Figure 5. A decrease in the molecular weight distribution was also noticed with time of irradiation.

The observed increase in molecular weights of the block copolymers with the time of irradiation is analogous as in the case of a *pseudo*-living free radical polymerization with macroinitiators containing dithiocarbamate pendent groups. Therefore, a photoiniferter mechanism is proposed for the block polymerization as shown in Scheme 4. Under 300-nm irradiation, the end-capped thiocarbonyl thiyl group undergoes reversible addition fragmentation reactions, thereby inserting the monomer as a function of the irradiation time. The advantage of using the macroinitiator **7** is that the homopolymer formation is significantly controlled due to the inability of the thiocarbonyl thiyl radicals to initiate polymerization under the conditions employed for the block copolymerization.

Photopolymerization of Styrene Using MAX. Results of the photopolymerization of styrene using MAX at 350-nm irradiation under different experimental conditions are shown

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Scheme 4
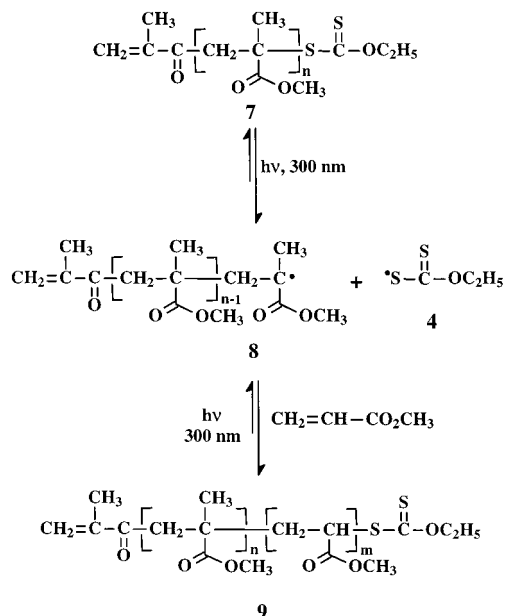
Table 3. Results of the Photopolymerization of Styrene under Various Monomer and Initiator Concentrations Using MAX at 32 °C

styrene [M]	MAX [M]	time (h)	yield (%)	$M_n \times 10^{-4}$	(M_w/M_n)
bulk	5×10^{-2}	0.5	2	1.9	1.4
bulk	5×10^{-2}	1.0	6	2.9	1.7
bulk	5×10^{-2}	1.5	10	3.7	2.3
bulk	5×10^{-2}	2.0	12	5.6	3.4
bulk	1×10^{-1}	4.0	29	gel	
4.5[a]	4.5×10^{-1}	1.0	4	1.3	1.1
4.5[a]	4.5×10^{-1}	4.0	15	1.7	1.2
4.5[a]	4.5×10^{-1}	7.0	29	2.5	1.6

[a] In benzene.
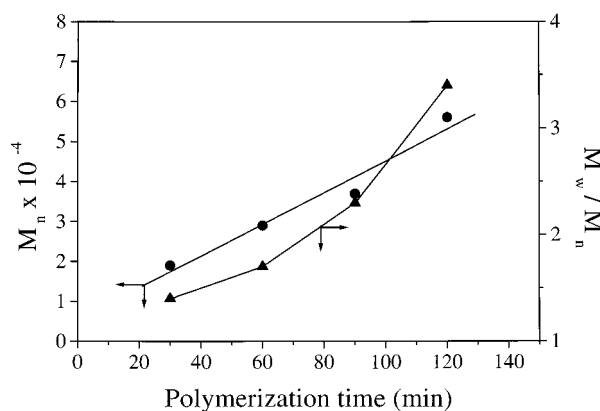
Figure 6. Effect of irradiation time on molecular weight (M_n) and polydispersity (M_w/M_n) for the photopolymerization of styrene (bulk) using MAX (5×10^{-2} M) under 350-nm irradiation.

in Table 3. Surprisingly, in contrast to the photopolymerization of MMA, styrene showed significant increase in molecular weights and polydispersities. The plot of the molecular weights against the time of irradiation showed a linear increase, whereas the corresponding plot of polydispersities showed a drastic increase with irradiation time as shown in Figure 6. It has been found that prolonged irradiation of neat styrene in the presence of MAX resulted in the gelation of the polymerization mixture and insoluble cross-linked materials were formed in every case. However, much better control over the molecular weight and
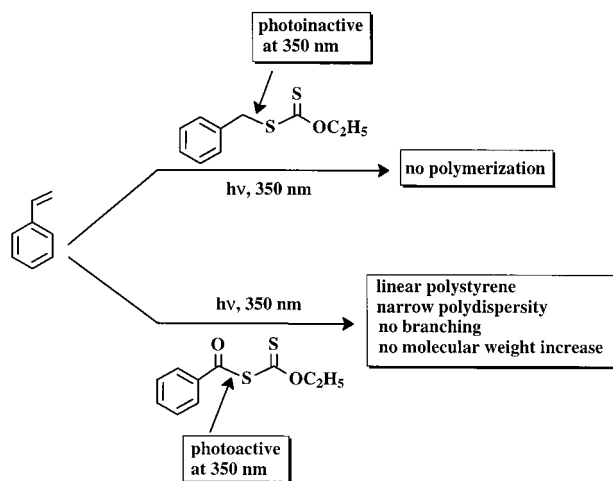
Scheme 5

Table 4. Photopolymerization of Styrene (Bulk) Using *S*-Benzoyl *O*-Ethyl Xanthate[a] under 350 nm at 32 °C

| time (min)	conversion (%)	$R_p \times 10^5$ (g s^{-1})	$M_n \times 10^{-4}$	M_w/M_n
30	2	7.2	1.81	1.4
120	8	9.2	1.76	1.4

[a] 5×10^{-2}.

polydispersities could be obtained when the polymerization of styrene was performed in benzene solution.

Comparison of the polymerization data of MMA and styrene in Tables 1 and 3, respectively, reveal that photopolymerization of styrene has the characteristic of a *pseudo*-living free radical mechanism as in the case of the *iniferter* method. However, in our case, it is hard to believe that the photopolymerization of styrene follows the iniferter mechanism. This is because the *iniferter* method is operational only at 300-nm irradiation. On the other hand, under 350-nm irradiation, as in our case, the end thiocarbonyl thiyl group is not photodissociable, and hence, reversible addition of monomers is not possible. On this ground we have ruled out the *iniferter* mechanism which is again proved by performing two independent irradiations of styrene using *S*-benzyl *O*-ethyl xanthate and *S*-benzoyl *O*-ethyl xanthate as photointiators (Scheme 5). *S*-Benzyl *O*-ethyl xanthate was used as the photoinitiator to prove that the CH$_2$–S bond is not photocleavable at 350 nm and hence could not initiate the polymerization of styrene by the *iniferter* mechanism under this condition which is found to be true. Interestingly, photopolymerization of styrene using *S*-benzoyl *O*-ethyl xanthate or *S*-acetyl *O*-ethyl xanthate gave polystyrenes with relatively lower molecular weights than those of polystyrenes obtained using MAX. In this case, the molecular weights and polydispersities of the resulted polystyrenes did not show any considerable change with the irradiation time as in the case of the MMA polymerization (Table 4). This observation points to the conclusion that the mechanism of the photopolymerization of styrene in the presence of MAX is distinctly different from those in the presence of the other xanthate photoinitiators without polymerizable double bonds. This can be attributed to the unique involvement of the methacryloyl moiety of MAX during the photopolymerization of styrene which is absent in the photopolymerization of MMA.

On the basis of the above assumption, a viable mechanism for the photopolymerization of styrene using MAX can be proposed as shown in Scheme 6. In addition as a photoinitiator, MAX can be considered as a monomer with an electron-deficient polymerizable double bond. In the presence of the electron rich styrene, MAX can act as a weak electron acceptor,

Scheme 6
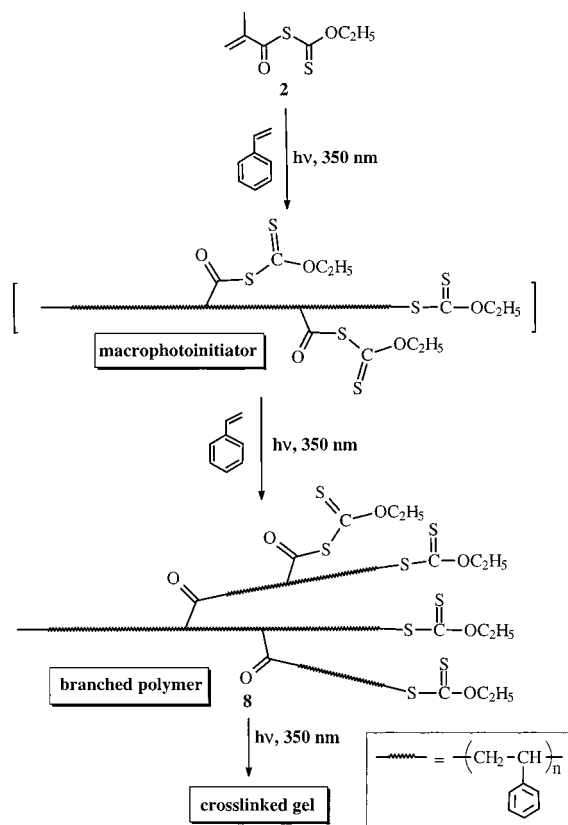
thereby facilitating a close contact between MAX and styrene. Such a weak donor–acceptor interaction may favor the incorporation of a small percentage of MAX on to the polystyrene chain to form an intermediate macroinitiator, which will initiate the branching of the polymer chains. In other words, MAX is forced to behave like a self-condensing photoinitiator by the electron-rich styrene. The number of branch arms can vary with the concentration of MAX, which is responsible for the observed increase in polydispersity. Since MMA is an electron-deficient monomer, such a donor–acceptor interaction is least possible, and hence, there is practically no incorporation of MAX on to PMMA chains thus leading to the formation of linear polymers.

The affinity of MAX toward styrene and its reluctance to copolymerize with MMA can be further clarified from our earlier studies on the thermally induced free radical copolymerization behavior of MAX with MMA and styrene.[20] The copolymer composition analysis in these cases has shown that the copolymers of the MAX–MMA monomer system have a low percentage of MAX, whereas the copolymers of the MAX–St monomer system showed the characteristic of alternate copolymers with a high percentage of incorporation of MAX even under lower concentrations of MAX. This observation again supports our assumption of having a weak donor–acceptor interaction between the electron-rich styrene and the electron-poor MAX. The electrostatic potential surfaces on the energy-minimized conformations of MAX, MMA, and St obtained using the PC SPARTAN AM1 molecular mechanics revealed the presence of electron-deficient double bonds in MAX and MMA, whereas the double bond in styrene is considerably electron-rich (Figure 7).[21] This may support our argument on weak donor–acceptor interaction between MAX and styrene.

(20) Francis, R.; Ajayaghosh, A. *Polymer* **1995**, *36*, 1091.
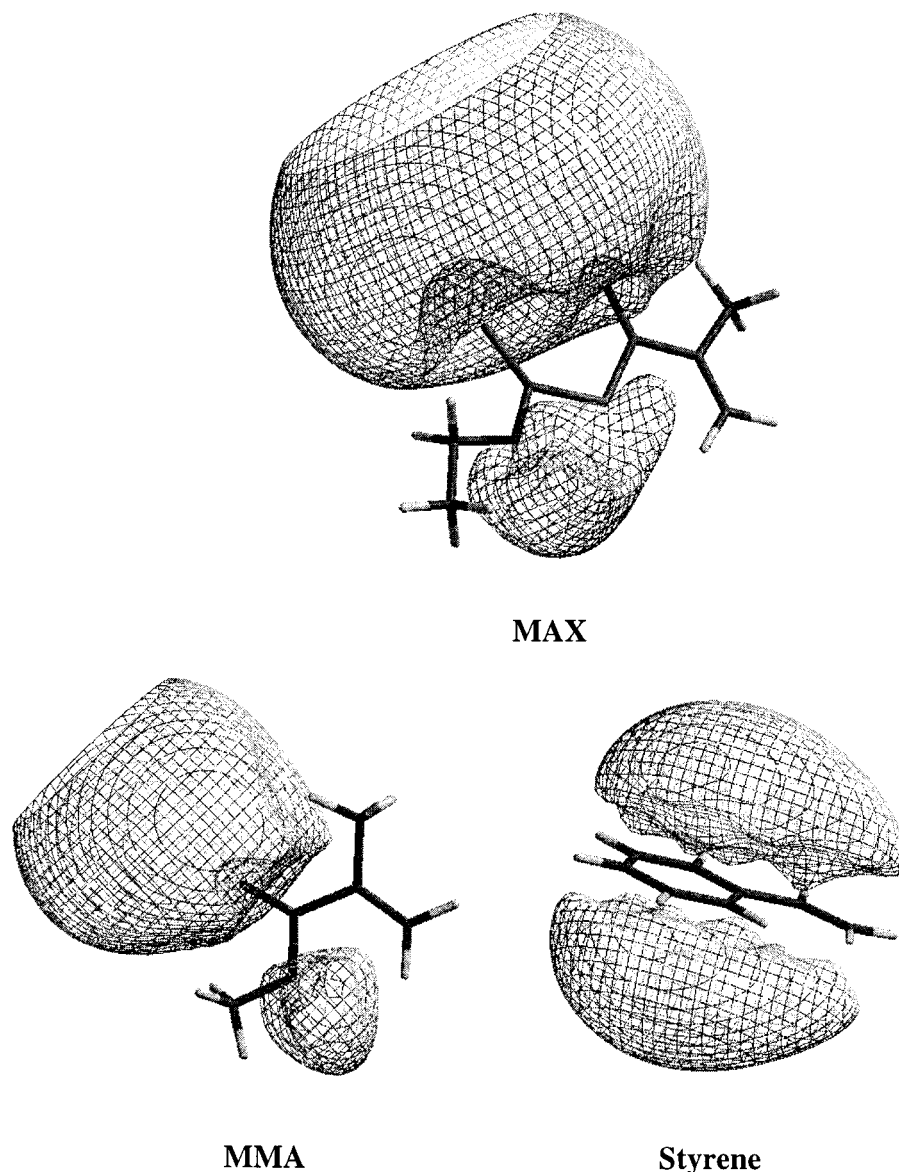(21) PC SPARTAN software from Wave function Inc.; 18401 Von Karman, Suite 370, Irvine, CA 92612.

MAX

MMA **Styrene**

Figure 7. Electron potential surfaces on the energy-minimized conformations of MAX, MMA, and styrene.

Nevertheless, our attempts to obtain experimental evidence for this speculation by UV spectroscopy was not very successful probably due to the extremely weak nature of such an interaction in our system.

Information regarding the branched macromolecular structure of polystyrene prepared with MAX can be obtained from its spectral analysis. In this context, it is interesting to compare the FT-IR and the NMR spectral data of polystyrene with those of the PMMA. For example, for polystyrene of molecular weight nearly identical to that of PMMA, the intensity of absorption at 1040 and 1242 cm^{-1} due to the C$=$S group in the IR spectrum was much stronger, indicating a higher concentration of the thiocarbonyl thiyl end groups in the former due to branching. In addition, an absorption peak at 1700 cm^{-1} was also noticed for polystyrene, indicating the presence of the carbonyl groups of the branch arms. The ^{1}H NMR spectrum of the polystyrene strongly supports the branched structure of the former (Figure 8). The resonance peaks at δ 4.48 and 1.43 in polystyrene are relatively strong when compared to the corresponding peaks in PMMA, indicating a relatively higher concentration of the end-capped thiocarbonyl thiyl groups due to the branched structure of the former. However, the presence of any methacryloyl group in polystyrene is still not very clear from the spectral data.
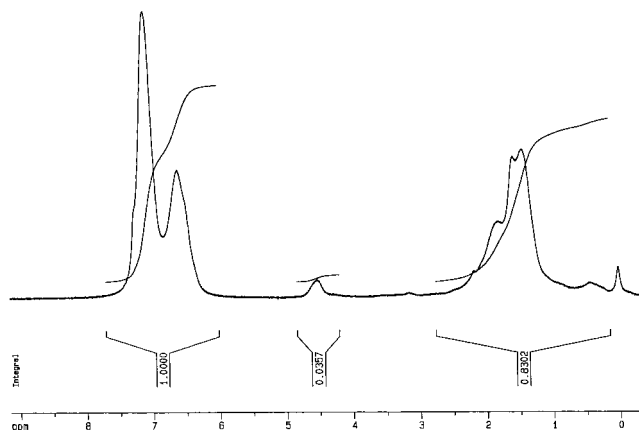
Figure 8. ^{1}H NMR spectrum of polystyrene obtained by the photopolymerization of styrene using MAX.

Conclusions

In the present study a novel concept of a "smart" photoinitiator, MAX, that is capable of dictating the photopolymerization of MMA and styrene in different pathways by sensing the electron availability around their double bonds is described. In

the case of MMA, MAX acts as a photoinitiator, leading to linear polymers with controlled molecular weights and polydispersities. On the other hand, MAX plays the dual role of a photoinitiator and a co-monomer during the photopolymerization of styrene, leading to branched and cross-linked polymers. The observed twist in the photopolymerization of styrene from that of MMA is explained on the basis of a weak donor–acceptor interaction between styrene and MAX. This could be the first report of a smart photoinitiator that can sense the electron availability around the monomer's double bond, thereby facilitating the formation of different macromolecular architectures. We believe that the concept of 'smart' photoinitiators will add a new dimension to the field of free radical mediated controlled synthesis of novel macromolecular materials such as hyperbranched and dendrigraft polymers.

Experimental Section

Infrared (IR) and electronic spectra were recorded on a Perkin-Elmer model 880 and Shimadzu 2100 A spectrophotometers, respectively. Electronic spectra were recorded on a Shimadzu 2100 A spectrophotometer. Mass spectra were recorded on a Hewlett-Packard mass spectrometer model 5791, attached to 5890 series II gas chromatography setup, attached with an OV 101 (25 m long and 0.2 mm i.d.) or with MP-FFAP (25 m long and 0.2 mm i.d.) capillary column, and a FID detector. Nuclear magnetic resonance (NMR) spectra were recorded on a Joel EX 90 or a Brucker DPX 300 spectrometer using CDCl₃ as the solvent and tetramethylsilane as the internal standard. Size-exclusion chromatography (SEC) was performed on a Shimadzu LC-6A system equipped with three serially connected Shimpac columns and a refractive index detector. Calibration was performed with polystyrene standards. THF was used as the mobile phase at a flow rate of 1 mL min^{-1} at 28 °C. Methyl methacrylate (MMA), methyl acrylate (MA), and styrene (St) were purified by distillation under reduced pressure after washing with 5% aqueous NaOH solution. All solvents were dried and distilled before use.

Preparation of *S*-Methacryloyl *O*-Ethyl Xanthate (MAX). To a stirred suspension of potassium *O*-ethyl xanthate (16.0 g, 0.1 mol) in dichloromethane (100 mL), maintained at 0 °C, was gradually added a solution of methacryloyl chloride (10.4 g, 0.1 mol) in dichloromethane (100 mL). The reaction mixture was stirred for an additional period of 1 h and allowed to warm gradually to room temperature. The reaction mixture was washed several times with water, and the organic layer was dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure gave 17.0 g (90%) of MAX as a yellow liquid. IR

ν_{max} (neat) 1720, 1640, 1240, 1050 cm^{-1}; UV λ_{max} (CHCl₃), 280 (ϵ, 10400), 395 (90) nm; ^{1}H NMR (CDCl₃, 90 MHz) δ 5.9−6.5 (2 H, m, CH₂), 4.7 (2 H, q, OCH₂), 2.0 (3 H, s, CH₃), 1.45 (3 H, t, CH₃); ^{13}C NMR (CDCl₃, 22.4 MHz) δ 204, 186, 144, 126, 71, 18, 14. Mass spectrum *m/z* 191 [M$^+$ + 1], 147, 172, 155, 103, 87, 73, 69.

Photopolymerization of MMA Using MAX. A stock solution of MMA in dry benzene (5 M) containing MAX (5 × 10^{-3} M) was prepared, and 10 mL each of this solution was transferred into different Pyrex glass tubes (1.4 cm diameter and 15 cm long). They were stoppered with rubber septa and purged with argon for 15 min followed by irradiation in a Rayonet photochemical reactor (RPR) containing eight 350-nm fluorescent lamps for known periods of time. After irradiation, the contents were poured into excess methanol, and the precipitated polymers were collected by filtration and washed with methanol. Purification of the polymers was achieved by reprecipitation from their chloroform solutions by methanol. After several reprecipitations, the polymers were filtered and dried in a vacuum oven (50 °C) for 24 h. IR ν_{max} (neat) 1721, 1452, 1249, 1148, 1043 and 993 cm^{-1}; ^{1}H NMR (CDCl₃, 300 MHz) δ 6.2 (m, CH₂=C), 4.65 (s (broad), OCH₂), 3.6 (s, OCH₃), 1.8−0.8 (m, aliphatic).

Photoinduced Block Copolymerization of Methyl Acrylate (MA) with Macroinitiator 7. The macroinitiator **7** (50 mg) with a molecular weight of 1.6 × 10^4 g/mol was dissolved in MA (4 M in benzene) (10 mL) and placed in a quartz reaction vial, which was closed with a rubber septum. The polymerization mixture was purged with dry argon for 15 min and irradiated in an RPR with eight 300-nm fluorescent lamps. After 90 min, the reaction mixture was diluted with chloroform, and the contents were precipitated with methanol. The precipitated polymer was purified by redissolving in THF and reprecipitating from hexane. Yield, 25%. M_n = 2.1 × 10^5, M_w/M_n = 1.2.

Photopolymerization of Styrene with MAX. A solution of styrene (4.5 M) and MAX (4.5 × 10^{-1} M) in dry benzene (10 mL) was taken in a Pyrex glass tube and purged with argon for 15 min. The solution was irradiated for 7 h as described in the case of the polymerization of MMA. Yield 29%. IR ν_{max} (neat) 1700, 1600, 1492, 1451, 1242, 1040, 757, 709, and 541 cm^{-1}; ^{1}H NMR (CDCl₃, 300 MHz) δ 7.1−6.3 (m, aromatic), 4.5 (m, OCH₂), 2.1−1.2 (m, aliphatic); M_n = 2.5 × 10^4, M_w/M_n = 1.6.