Minimization of Homopolymer Formation and Control of Dispersity in Free Radical Induced Graft Polymerization Using Xanthate Derived Macro-photoinitiators†

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ABSTRACT: Several macro-photoinitiators of different composition and molecular weights were prepared by the copolymerization of a photosensitive monomer, *S*-methacryloyl *O*-ethyl xanthate (MAX), using MMA or styrene as the comonomers. These macro-photoinitiators were used for the controlled grafting of monomers such as MMA and styrene under various experimental conditions using 350 nm irradiation. The graft yields and the molecular weights of the graft copolymers increased with increase in irradiation time. Similarly, the molecular weights of the graft copolymers increased with increase in mole percentage of the xanthate chromophores in the macroinitiators. The polydispersities of the graft copolymers remained below 1.5, which is the theoretical limiting value for free radical induced polymerization reactions, except in the case of graft polymers obtained after prolonged irradiation. Noticeably, the formation of homopolymers could be suppressed, which is a great advantage of the present approach. The control over homopolymerization and polydispersities has been explained on the basis of the distinctly different reactivities of the free radicals generated by the macroinitiator. The macroradicals generated are mainly responsible for initiating the grafting of monomers whereas the less reactive thiocarbonylthiyl radicals are primarily involved in the termination of the graft chains, thereby preventing the homopolymer formation to a large extent. Thus, the use of xanthate-derived macro-photoinitiators is a simple and easy method for the synthesis of narrow dispersed graft copolymers, which are less contaminated with homopolymers.

Introduction

Graft and block copolymerizations are novel approaches to combine the chemical and physical properties of two or more different monomers to a single polymeric chain.[1−7] Free radical induced polymerization is the easiest and widely accepted procedure for this purpose. However, one of the major limitations of the free radical polymerization approach is the formation of the unwanted homopolymer, which generally proceeds in parallel with the block and graft copolymerizations. In addition, free radical methods lack control over molecular weight and polydispersity of the block and graft polymers. Even though these problems can be solved to a great extent by anionic or cationic mechanisms, their use in polymerization processes are severely limited by the stringent requirements on reaction conditions and monomer purity.[8−17] Consequently, the concept of "living" free radical polymerization has been introduced, which attracted considerable interest in block and graft copolymer synthesis due to the possible control of molecular weight, polydispersity, and macromolecular structural characteristics.[18−23]

When compared to other modes of free radical initiated graft and block copolymer synthesis, light-induced initiation has the advantage of being applicable at low temperatures, especially at room temperature. Moreover, because of the selective absorption of certain chromophores, it is possible to produce free radical initiation sites at definite positions in the macromolecules. In such cases, the polymerization processes can also be controlled by varying the intensity and wavelength of the light used. Several reports pertaining to the light-induced block and graft copolymer synthesis are available in recent literature.[24−27] However, as in the case of the conventional free radical polymerization, the major problems of photografting are the formation of homopolymers and the lack of control on molecular weights and polydispersity of the resulting graft copolymers. Therefore, several methods have been proposed for the control of homopolymer formation during photoinduced block and graft copolymer synthesis. One of the efficient methods involves the use of polymers containing halogen atoms in the presence of compounds of certain transition metals such as manganese and rhenium carbonyls as photoinitiators.[28] Homopolymerization has been considerably prevented in these cases since no free radicals are generated in the reaction mixture other than the macroradical. Nevertheless, considerable cross-linking occurs in these cases due to the recombination of the graft chains.

One of the earliest attempts toward controlled graft copolymerization is the photochemical *iniferter* approach of Otsu and co-workers using dithiocarbamates.[29] A *pseudo* "living" free radical mechanism has been suggested for polymerization using photoiniferters, which involves the stepwise incorporation of monomers leading to the growth of the molecular weight with increase in monomer conversion. Several people have exploited the dithiocarbamate photochemistry for the block and graft copolymer synthesis.[30−33] The major limitation of the dithiocarbamate-based photoiniferter method is the formation of block and graft copolymers with broad polydispersity as in the case of conventional free radical polymerization. This observation reveals that the original mechanism proposed for the block and graft copolymerization using dithiocarbamates is complicated

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Table 1. Photografting of Styrene (Bulk) on to MAX-*co*-MMA at Various Time Intervals under 350 nm Irradiation[a]

run	time (min)	graft yield (%)	cross-link yield (%)	M_n	M_w/M_n
1	45	4	0	14 000	1.3
2	90	9	0	17 000	1.3
3	140	15	2	20 000	1.4
4	240	32	6	28 000	1.9

[a] MAX-*co*-MMA = 0.017 g/mL (M_n = 2700, 16 mol % of xanthate).

by some secondary reactions.[31,32] Since dithiocarbamates absorb light in the short wavelength region, the photoinitiation has to be performed around the 280−290 nm region. Under such conditions, the monomer may also absorb light, thereby facilitating the self-initiation of the monomer leading to the formation of considerable amounts of homopolymers. Therefore, better methods for the synthesis of narrow polydispersed graft copolymers with controlled molecular weight and minimized homopolymerization are of great significance. Recently, we have shown that acyl or aroyl xanthates are efficient photoinitiators which are sensitive to ≥350 nm irradiation with significant control over the free radical polymerization pathways.[34] Here, we report the use of xanthate-based macroinitiators which facilitate the photoinduced synthesis of narrow dispersed graft copolymers by significantly suppressing the homopolymer formation.

Results and Discussion

Macroinitiators employed for the present studies have been prepared by the thermal copolymerization of *S*-methacryloyl *O*-ethyl xanthate (MAX) with MMA and styrene (St) using AIBN as the initiator. It has been observed earlier that the compositions of the copolymers and their molecular weights largely depend on the amount of the MAX present in the monomer feed.[35] We have earlier investigated the photo-cross-linking and photoinitiation properties of analogous copolymers containing pendant xanthate groups.[36] In the present study, photografting of MMA and St on MAX-*co*-St and MAX-*co*-MMA, respectively, was performed either using bulk monomer or in benzene solution under 350 nm irradiation as shown in Schemes 1 and 2. After various intervals of irradiation, graft copolymers along with minor quantities of cross-linked polymers were isolated by precipitation from methanol. The soluble graft copolymers were isolated by Soxhlet extraction using THF and subjected to size exclusion chromatography (SEC) which showed a single elusion peak. Attempts to isolate any homopolymer from the polymerization mixture by the differential solubility method in various solvents indicated its suppressed formation. In addition, formation of cross-linked polymers was considerably reduced in all graft reactions. These observations are in agreement with the earlier findings that the thiocarbonyl thiyl radicals are mainly involved in the primary radical termination of almost every graft chain radicals.[33,34]

Tables 1 and 2 summarize the data obtained for the photografting of St onto the macroinitiator MAX-*co*-MMA under various experimental conditions. The initial grafting reactions were performed using MAX-*co*-MMA (M_n = 2700 g/mol) having approximately 16 mol % of the photoinitiator moiety, under 350 nm at various intervals of irradiation. The data in Table 1 reveal that

Table 2. Photografting of Styrene (Bulk) on to MAX-*co*-MMA Having Different Copolymer Compositions and Molecular Weights[a]

run	mol % of xanthate	M_n of the macro-initiator	graft yield (%)	cross-link yield (%)	M_n of the graft polymer	M_w/M_n
1	12	2500	11	0	14 000	1.4
2	14	2500	12	0	18 000	1.4
3	16	2700	15	2	20 000	1.4
4	21	2200	15	5	23 000	1.4

[a] λ_{irr} = 350 nm, time of irradiation = 140 min; MAX-*co*-MMA = 0.017 g/mL.

Table 3. Photografting of MMA onto MAX-*co*-St at Various Time Intervals under 350 nm Irradiation[a]

run	time (min)	graft yield (%)	cross-link yield (%)	M_n	M_w/M_n
1	10	8	0	13 000	1.3
2	30	22	0	16 000	1.3
3	60	41	4	20 000	1.4
4	70	43	5	32 000	1.5

[a] MMA = 5 M in benzene; MAX-*co*-St = 0.017 g/mL (M_n = 3400, 20 mol % of xanthate).

yields and molecular weights of the graft copolymers increased gradually with the time of irradiation. Interestingly, the polydispersities of the graft copolymers obtained under different polymerization conditions remained below 1.5, except in the case of prolonged irradiation, which yields small amounts of cross-linked polymers. The effect of the copolymer composition of the macroinitiator MAX-*co*-MMA on the graft copolymerization of styrene is summarized in Table 2. The molecular weights of the graft copolymers were found increased with increase in mole percentage of the xanthate moieties of the macroinitiator. In all these cases the homopolymer formation could be suppressed to a considerable extent.

The results of the photografting of MMA using MAX-*co*-St as the macroinitiator as a function of irradiation time are shown in Table 3. MAX-*co*-St of molecular weight 3400 g/mol, containing approximately 20 mol % of the pendant xanthate moieties, has been used for the grafting. The percentage yields of the graft polymers are found to increase with irradiation time as noticed in the case of the grafting of St to MAX-*co*-MMA. Along with the progress in grafting, 4−5% of cross-linked polymers is also formed. The increased formation of cross-linked polymer with increasing yield of graft copolymer can be explained on the basis of the decrease in monomer concentration in the polymerization mixture. Under this condition, the coupling of the macroradicals will be facilitated, leading to the increased formation of the cross-linked polymers.

The effects of the copolymer compositions of MAX-*co*-St used for the photografting of MMA are summarized in Table 4. It has been found that the yields of the grafted and cross-linked polymers increased with increase in the mole percentage of the xanthate moieties in the MAX-*co*-St macroinitiator as we have observed in the case of MAX-*co*-MMA. The effect of the amount of the macroinitiator on the photografting of MMA using MAX-*co*-St is summarized in Table 5. The total conversion of the monomer is found to increase with the increase in the concentration of the macroinitiator while the yields and the molecular weights of the graft copolymers decreased due to the increased formation of cross-linked polymers. Under higher macroinitiator

Table 4. Photografting of MMA onto MAX-*co*-St of Various Copolymer Compositions and Molecular Weights[a]

run	mol % of xanthate	M_n of the macro-initiator	graft yield (%)	cross-link yield (%)	M_n of graft polymer	M_w/M_n
1	9	2900	38	0	20 000	1.4
2	11	3300	39	1	24 000	1.3
3	15	2800	42	1	26 000	1.4
4	20	3400	43	5	32 000	1.5

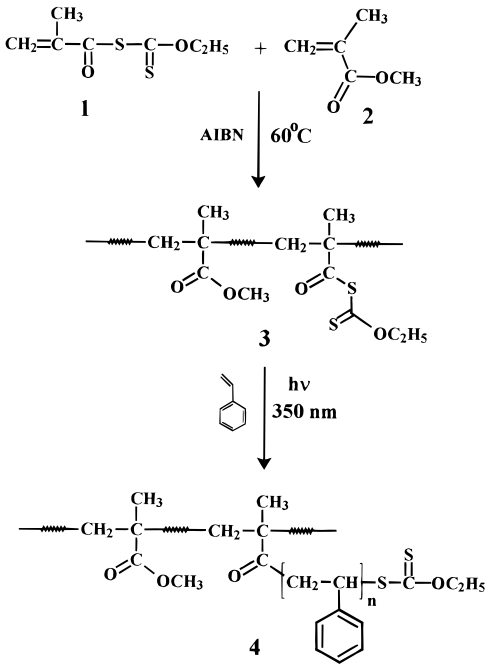
[a] $\lambda_{irr} = 350$ nm, time = 70 min, MMA = 5 M in benzene, MAX-*co*-St = 0.017 g/mL.

Table 5. Effect of Macroinitiator Concentration for the Photografting of MMA onto MAX-*co*-St[a]

run	MAX-*co*-St (mg/L)	total conv (%)	graft yield (%)	cross-link yield (%)	M_n	M_w/M_n
1	10	43	40	3	24 000	1.3
2	50	46	34	12	14 000	1.4
3	80	59	29	30	12 000	1.4
4	100	68	20	48	12 000	1.3

[a] $\lambda_{irr} = 350$ nm, MMA = 5 M in benzene, $M_n = 3500$ (18 mol % of xanthate).

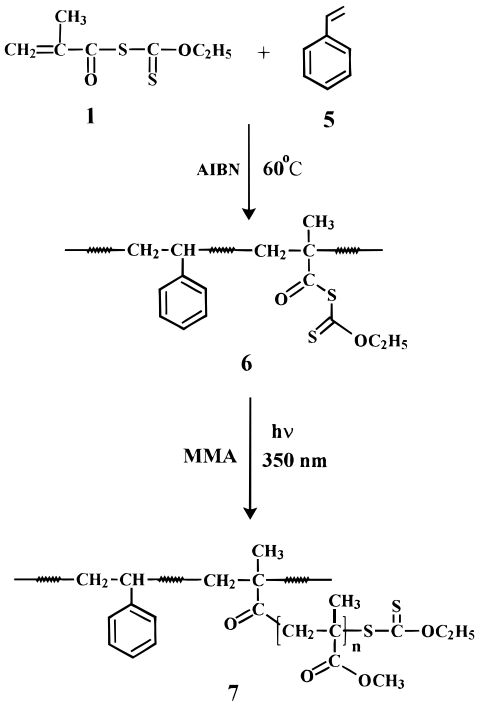
Scheme 1



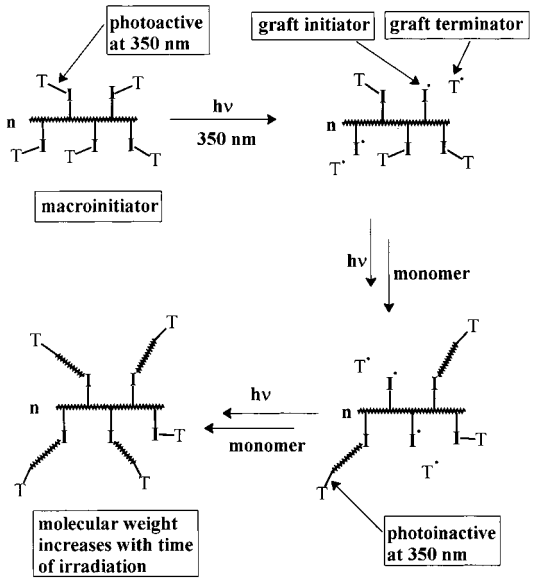
concentrations, photoirradiation will lead to the formation of a large number of immobilized radical centers within the polymerization mixture. High local concentration of the radical centers on the macroinitiator competes for photografting as well as the intermolecular radical−radical coupling, resulting in the formation of the cross-linked copolymer.

The observed increase in molecular weight of the graft copolymers with irradiation time is very significant when compared to the photopolymerization of analogous low molecular weight xanthate photoinitiators, where the molecular weights of the resulting polymers remained unchanged with irradiation time. In the case of a low molecular weight photoinitiator, for example *S*-acetyl *O*-ethyl xanthate, each initiating radical will lead to the formation of new individual polymer chains on continued irradiation which are reversibly terminated by the xanthate radicals. In this case the average molecular weight remains the same irrespective of the

Scheme 2



Scheme 3



irradiation time. On the other hand, in the case of a macroinitiator, where several initiating groups are immobilized on a single polymer chain, it will lead to the collective addition of graft chains leading to a net growth in molecular weight with irradiation time. This can be explained by the mechanistic representation of the grafting processes as depicted in Scheme 3. For example, the macroinitiator MAX-*co*-St of molecular weight 3400 g/mol having approximately 20 mol % of xanthate chromophores is expected to have 4−5 photoinitiating moieties per macroinitiator chain. Photoirradiation of several of such macroinitiators will generate reactive radical centers on the macroinitiator backbone, leaving the less reactive thiocarbonyl thiyl radicals into the solution. This can facilitate the exclusive formation of graft chains on the macroinitiator, which will be terminated by the sulfur-centered radicals, thereby suppressing the initiation of the homopolymerization.

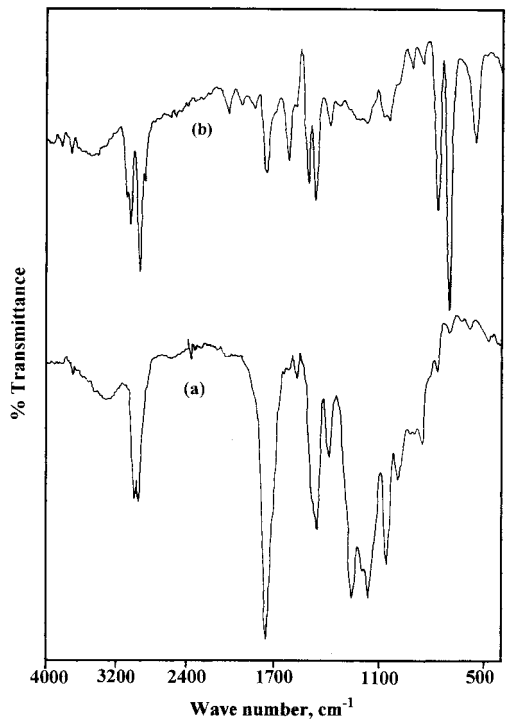


Figure 1. IR spectrum of MAX-*co*-MMA, (a) before grafting and (b) after grafting of styrene.

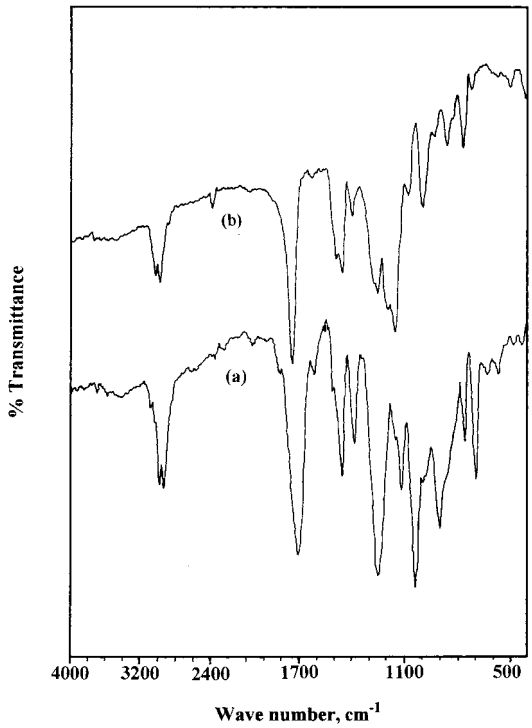


Figure 2. IR spectrum of MAX-*co*-St, (a) before grafting and (b) after grafting of MMA.

With the progress in irradiation time more and more of the graft chains will be incorporated onto the macroinitiator, thereby increasing the number of graft chains per macroinitiator and thus the overall molecular weight.

Evidence for the photoinduced grafting of St and MMA onto MAX-*co*-MMA and MAX-*co*-St, respectively, can be obtained from spectral analysis of the graft polymers. For example, the UV spectra of MAX-*co*-MMA and MAX-*co*-St before graft polymerization showed a broad absorption around 395 nm, which is due to the pendant xanthate chromophore. After graft copolymerization, the absorption at 395 nm disappeared, indicating the cleavage of the (C═O)−S bond of the parent macroinitiator. The IR spectra of MAX-*co*-MMA and MAX-*co*-St before and after the grafting of St and MMA are shown in Figures 1 and 2, respectively. The IR spectrum of MAX-*co*-MMA (Figure 1a) shows absorption peaks at 1739 cm^{-1} due to carbonyl groups and 1251 and 1046 cm^{-1} due to the thiocarbonylthiyl groups. In the IR spectrum of the graft copolymer MAX-*co*-MMA-*g*-St (Figure 1b), the intensities of these absorptions have been considerably reduced, and new absorption peaks at 756 and 696 cm^{-1} characteristic of the aromatic phenyl ring of polystyrene have appeared. The IR spectrum of MAX-*co*-St (Figure 2a) shows considerable decrease in the intensity of absorption at 1252 and 1041 cm^{-1} due to the thiocarbonylthiyl groups and at 756 and 696 cm^{-1} due to the phenyl ring after grafting of MMA. In addition, the relative intensity of the carbonyl absorption at 1740 cm^{-1} has been significantly increased in the grafted polymer when compared to the intensity of the absorption due to the thiocarbonyl thiyl group at 1041 cm^{-1} (Figure 2b).

The ^1H NMR spectra of MAX-*co*-MMA before and after grafting of styrene which are shown in Figure 3 strongly support the efficient grafting of styrene. For example, the intensity of the OCH_3 protons at δ 3.6 ppm of the MMA moiety has been significantly reduced, and

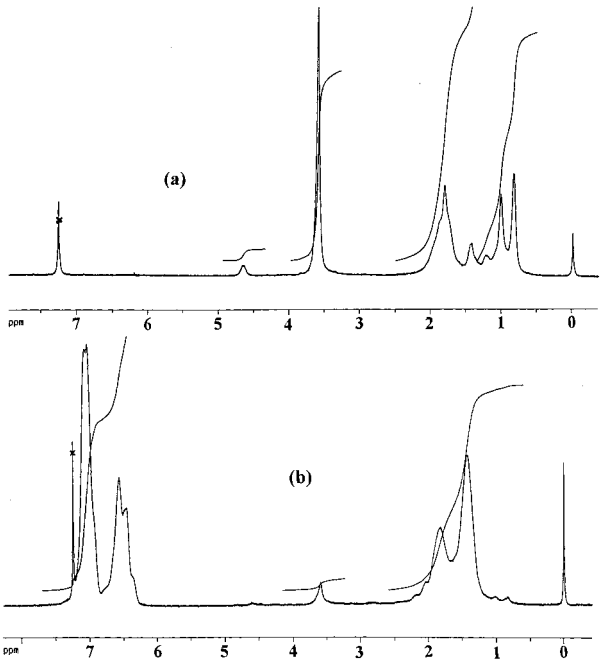


Figure 3. ^1H NMR (300 MHz, $CDCl_3$) spectrum of MAX-*co*-MMA, (a) before grafting and (b) after the grafting of styrene.

at the same time, two new peaks between δ 6 and 7.5 ppm due to the aromatic protons appeared after the grafting (Figure 3b), indicating the presence of the grafted polystyrene chains. The results of the thermogravimetric analysis of MAX-*co*-MMA and MAX-*co*-St and their respective graft copolymers are shown in Figure 4. The traces a and c are for MAX-*co*-MMA and MAX-*co*-St, respectively, before grafting and the traces b and d after grafting. Considerable weight loss was observed at 170 °C before grafting which is due to the decomposition of the pendant xanthate chromophores in addition to the major weight loss above 200 °C due

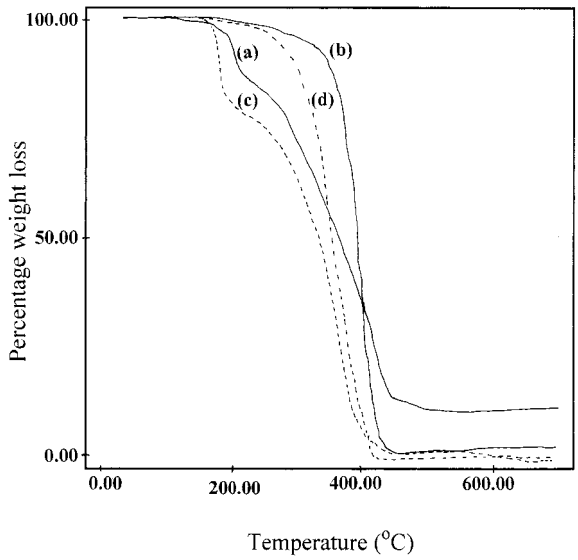


Figure 4. Thermogravimetric analysis of (a) MAX-*co*-MMA, (b) MAX-*co*-MMA-*g*-St, (c) MAX-*co*-St, and (d) MAX-*co*-St-*g*-MMA.

to the decomposition of the macroinitiator backbone. On the other hand, the thermal stability has been considerably improved after the grafting of MMA and styrene, and no substantial weight loss could be seen below 200 °C.

In conclusion, copolymers of MAX with MMA and styrene have been used as macro-photoinitiators for the controlled grafting of monomers such as MMA and St. The advantage of the present approach is that the homopolymer formation, which is an unwanted side reaction of conventional free radical induced grafting processes, has been considerably suppressed, and significant control on molecular weight and polydispersity could be achieved. This could be the result of the differences in the reactivities of the macroradicals and the sulfur-centered radicals toward the monomers employed for the graft polymerization. Thus, we have demonstrated that xanthate derived macro-photoinitiators can be used for the synthesis of narrow dispersed graft copolymers with minimal contamination due to homopolymer formation.

Experimental Section

Infrared (IR) spectra and the electronic spectra were recorded on a Perkin-Elmer model 880 and a Shimadzu 2100 A spectrometer, respectively. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a JEOL EX 90 or a Bruker DPX 300 spectrometer using $CDCl_3$ as solvent and tetramethylsilane as internal standard. Gel permeation chromatography (GPC) was carried out on a Shimadzu LC-6A GPC system equipped with a refractive index detector and three Shim-pack columns, 802, 804, and 80 M which are connected in series. Calibrations were done with standard polystyrene samples. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 mL min^{-1} at 28 °C. Thermal analysis data (TGA) were recorded on a Shimadzu TGA-50H thermal analyzer.

The monomers MMA and styrene were purified by washing twice with 5% aqueous NaOH and then several times with distilled water. These were then dried over anhydrous sodium sulfate and distilled under reduced pressure. AIBN was recrystallized twice from methanol. All solvents used were dried and distilled before use. *S*-Methacryloyl *O*-ethyl xanthate (MAX) was prepared as reported earlier.[35]

Preparation of the Macro-photoinitiator MAX-*co*-MMA. MAX (0.76 g, 4 mmol), MMA (0.6 g, 6 mmol), AIBN (120 mg), and benzene (0.5 mL) were taken in a glass tube and stoppered with a rubber septum. The polymerization mixture was purged with dry nitrogen for 15 min and heated at 60 °C for 24 h. The viscous reaction mixture was poured into excess methanol, and the pale yellow precipitate formed was collected by filtration. After two reprecipitations from methanol, the copolymer MAX-*co*-MMA was dried in a vacuum oven at 40 °C for 12 h. Yield 56%. IR ν_{max} (neat film): 1739, 1251, and 1046 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.68 (broad, s, OCH_2), 3.6 (s, OCH_3), 1.8−0.84 (m, aliphatic). $M_n = 2712$, $M_w/M_n = 2.1$.

Preparation of the Macro-photoinitiator MAX-*co*-St. MAX (0.76 g, 4 mmol), styrene (0.63 g, 6 mmol), AIBN (40 mg), and benzene (2 mL) were taken in a glass tube and stoppered with a rubber septum. After purging with nitrogen for 15 min the reaction mixture was heated at 60 °C for 10 h. The macroinitiator MAX-*co*-St was isolated as described in the case of MAX-*co*-MMA. Yield 36%. IR ν_{max} (neat film): 1740, 1252, 1041, 756, and 696 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.2 (broad, aromatic), 4.6 (broad, s, OCH_2), 2.1−0.8 (broad, m, aliphatic). $M_n = 3379$, $M_w/M_n = 1.9$.

Photografting of MMA Using MAX-*co*-St. MAX-*co*-St (170 mg, 20 mol % of xanthate) and MMA (10 mL, 5 M in benzene) was taken in a Pyrex glass vial and stoppered with a rubber septum. The solution was purged with dry argon for 10 min and irradiated for 70 min using a Rayonet photoreactor (RPR) equipped with eight 350 nm fluorescent lamps. The viscous polymerization mixture obtained was diluted with chloroform (50 mL) and poured into excess methanol. The precipitate obtained was Soxhlet extracted first with acetonitrile and subsequently with THF. The extracts were concentrated under reduced pressure and poured separately into methanol. No isolable products were obtained from the acetonitrile extract, indicating the absence of graft polymers. The graft polymer obtained from the THF extract was collected and dried in a vacuum oven for 24 h. Yield of the graft copolymer was 43%. IR ν_{max} (KBr): 1738 (C=O, strong), 1252 and 1041 (C=S, weak) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.1 (aromatic), 4.6 (OCH_2), 3.6 (OCH_3); $M_n = 32\,000$, $M_w/M_n = 1.5$.

Photografting of St Using MAX-*co*-MMA. MAX-*co*-MMA (170 mg, 21 mol % of xanthate) and styrene (10 mL) was irradiated for 140 min as described in the case of the photografting of MMA. The precipitated polymer was extracted with cyclohexane and THF to isolate the homopolymers and graft polymers, respectively. The cyclohexane fraction did not yield any isolable amount of homopolymer on pouring into methanol. The graft polymer was isolated from the THF fraction after precipitation by methanol. Yield 15%. IR ν_{max} (KBr): 1739 (C=O, weak), 1605 (aromatic), 1251 and 1046 (C=S, weak), 756 and 696 (aromatic, strong) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.1−6.5 (aromatic), 3.6 (OCH_3), 1.8−1.4 (aliphatic); $M_n = 23\,000$, $M_w/M_n = 1.4$.

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