

Graft Photocopolymerization of Styrene with 9-Anthrylmethyl-Substituted Poly(methyl methacrylate)

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ABSTRACT: An investigation was undertaken to achieve the graft copolymerization of styrene (St) in the presence of the 9-anthrylmethyl methacrylate/methyl methacrylate copolymer designed as a macromolecular photoinitiator. UV and ¹H NMR spectral analyses suggested that about 64% of the anthryl chromophore is rapidly consumed by the intramolecular cycloaddition of this chromophore. However, no additional cycloaddition occurred owing to the greatly lowered conformational mobility of polymer side chains. As a result, the homolytic CH₂O–C(=O) bond cleavage in the anthrylmethyloxycarbonyl moiety was induced to form a macroradical which initiates the polymerization of St. While the St homopolymer was produced along with the graft copolymer in our system, these two polymers were readily separated by the use of a Soxhlet extractor. [DOI 10.1295/polymj.37.754]

KEY WORDS Photopolymerization / Graft Polymerization / Radical Polymerization / Cycloaddition /

Macromolecular photoinitiator (MPI) is a subject of growing interest owing to its substantially low mobility and volatility,¹ as well as to its ability to initiate graft copolymerization giving novel functional polymers.^{2–4} While many MPIs require the presence of coinitiator such as amines or photosensitizers in order to express their functions, there are only limited investigations regarding graft copolymerization in the absence of such a coinitiator. It was found in our previous studies that on irradiation 9-anthrylmethyloxy-substituted bichromophoric molecules undergo heterolytic and homolytic bond cleavages competitively to give ions and radicals, respectively.^{5,6} In addition, these bichromophoric molecules were shown to initiate cationic and radical photopolymerizations and, hence, act as novel hybrid-type photoinitiators though their initiation abilities are low.

On the other hand, 9-anthrylmethyloxycarbonyl and related chromophores have been utilized as probes for elucidating photophysical and photochemical behavior of a given chromophore introduced into methyl methacrylate-derived homo- and copolymers.^{7–10} A literature survey reveals that there is no systematic study on the ability of copolymer to initiate radical or ionic polymerization, namely, the ability in MPI. It is likely that the 9-anthrylmethyl methacrylate (AMMA)/methyl methacrylate (MMA)-derived copolymer shows a photochemical behavior similar to that of 9-anthrylmethyl acetate.⁶ If so, this copolymer would function as one of the coinitiator-free MPIs. Taking into account the well-known fact that the

anthracene chromophore has a strong tendency to undergo a photocycloaddition reaction (photocross-linking reaction),^{11,12} we designed AMMA/MMA-derived copolymer so as to keep the distance between anthracene pendants relatively long and investigated the ability of this copolymer to initiate the graft copolymerization of St.

EXPERIMENTAL

Materials

According to the previously described procedure,¹³ AMMA was prepared by the reaction of anthracene-9-methanol with methacryloyl chloride in the presence of triethylamine in chloroform. The crude product was purified by column chromatography over silica gel (70–230 mesh) using chloroform and hexane as the eluent, followed by recrystallization from ethanol. As model compounds of the AMMA/MMA copolymer, 9-anthrylmethyl isopropanoate (AI) and bis(9-anthrylmethyl) glutarate (BAG) were prepared according to the same procedure as above.

9-Anthrylmethyl methacrylate (AMMA): Yield 61%; mp 84.5–86.0 °C. IR (KBr): ν 2925, 1707, 1622, 1453, 1155, 1148 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 1.92 (s, 3H), 5.51 (s, 1H), 6.06 (s, 1H), 6.23 (s, 2H), 7.50 (dd, J = 8.0, 8.2 Hz, 2H), 7.58 (dd, J = 8.0, 8.9 Hz, 2H), 8.04 (d, J = 8.2 Hz, 2H), 8.38 (d, J = 8.9 Hz, 2H), 8.53 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 18.3, 59.1, 124.0 (2C), 125.1 (2C), 126.0, 126.4, 126.6 (2C), 129.07 (2C), 129.12 (2C), 131.1 (2C), 131.4,

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Table I. Radical copolymerization of AMMA with MMA in toluene

| Initiator ^{a)} | $\frac{[\text{AMMA}]}{[\text{MMA}]}$ | Temp. (°C) | Time (h) | Copolymer | | | |
|-------------------------|--------------------------------------|---------------|-------------|--------------------------------------|--------------|----------------------|-----------|
| | | | | $\frac{[\text{AMMA}]}{[\text{MMA}]}$ | Yield (%) | $M_n \times 10^{-4}$ | M_w/M_n |
| AIBN | 5/95 | 60 | 6 | 5/95 | 77 | 2.3 | 1.7 |
| ACN | 20/80 | 80 | 6 | 20/80 | 40 | 3.6 | 4.0 |
| ACN | 20/80 | 80 | 12 | 20/80 | 94 | 3.0 | 2.7 |

^a[Initiator] = 50 mmol dm⁻³, [AMMA] + [MMA] = 2.0 mol dm⁻³.

136.2, 167.6. Analysis: calculated for C₁₉H₁₆O₂: C, 82.47%; H, 5.84%; found: C, 82.47%; H, 5.97%.

9-Anthrylmethyl isopropanoate (AI): Yield 11%; mp 95.0–96.0 °C. IR (KBr): ν 1728, 1150 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 1.54 (d, J = 6.8 Hz, 6H), 2.57 (q, J = 6.8 Hz, 1H), 6.13 (s, 2H), 7.49 (dd, J = 6.8, 8.2 Hz, 2H), 7.57 (dd, J = 6.8, 8.9 Hz, 2H), 8.03 (d, J = 8.2 Hz, 2H), 8.33 (d, J = 8.9 Hz, 2H), 8.51 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 19.0(2C), 34.1, 58.8, 124.0(2C), 125.1(2C), 126.50, 126.54(2C), 129.0(2C), 129.1(2C), 131.1, 131.4(2C), 177.4. Analysis: calculated for C₁₉H₁₈O₂: C, 81.99%; H, 6.52%; found: C, 82.32%; H, 6.62%.

Bis(9-anthrylmethyl) glutarate (BAG): Yield 59%; mp 160.0–161.0 °C. IR (KBr): ν 1724, 1134 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 1.95 (dd, J = 7.4, 7.4 Hz, 2H), 2.35 (dd, J = 7.4, 7.4 Hz, 4H), 6.11 (s, 4H), 7.45 (dd, J = 8.0, 7.7 Hz, 4H), 7.51 (dd, J = 7.7, 8.6 Hz, 4H), 8.00 (d, J = 8.0 Hz, 4H), 8.28 (d, J = 8.6 Hz, 4H), 8.48 (s, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 20.1, 33.2(4C), 58.8(2C), 123.9(4C), 125.1(4C), 126.1(2C), 126.6(4C), 129.1(4C), 129.2(2C), 131.0(4C), 131.3(2C), 173.1(2C). Analysis: calculated for C₃₅-H₂₈O₄: C, 82.01%; H, 5.51%; found: C, 81.87%; H, 5.58%.

Commercially available MMA and St were distilled under reduced pressure before use. 2,2'-Azobisisobutyronitrile (AIBN) and 1,1'-azobis(cyclohexane-1-carbonitrile) (ACN) were recrystallized from methanol. Toluene was purified by the conventional method.

Polymerization Procedures

Thermal copolymerization of AMMA with MMA was carried out in a degassed and sealed glass tube. The polymerization mixture was poured into *n*-hexane and the resulting precipitate was dried *in vacuo* at 40 °C. Photopolymerization of St in the presence of the AMMA/MMA copolymer (MPI_{Ant}) was carried out in a degassed and sealed glass tube with light of wavelengths longer than 340 nm from a 500 W high-pressure mercury lamp (Corning 0–52 and Toshiba IRA-25S glass filters). The irradiation light intensity was 170 mW cm⁻². The polymerization mixture was poured into aqueous methanol and the resulting precipitate was dried *in vacuo* at 40 °C.

Photoirradiation of MPI_{Ant}, AI, and BAG

A toluene solution of MPI_{Ant}, AI, or BAG was irradiated with light of wavelengths longer than 340 nm from a 450 W high-pressure mercury lamp (Corning 0–52 and Toshiba IRA-25S glass filters). The irradiation light intensity was 3.0 mW cm⁻² in this case.

Measurements

The molecular weight distribution of the polymer was measured with a Tosoh 8000 series gel permeation chromatography (GPC) system equipped with a TSKgel MutiporeH_{XL}-M \times 2 at 40 °C. A calibration curve from 500 to 1.11×10^6 was obtained by using the standard polystyrene (polySt). ¹H and ¹³C NMR spectra were recorded on a JEOL JNM-A500 spectrometer at 500 and 125 MHz, respectively. Tetramethylsilane was employed as an internal standard. UV spectra were taken with a Hitachi U-3300 spectrophotometer. The irradiation light intensity was determined by the use of an ORC UV-M03 intensity meter equipped with a UV-SN35-M10 photodetector (Tokyo, Japan).

RESULTS AND DISCUSSION

Copolymerization of AMMA with MMA

As described in the Introduction, there remains the possibility that photocycloaddition between anthracene chromophores in the AMMA/MMA copolymer occurs in competition with the graft photocopolymerization of this copolymer with St. It is, thus, preferable to minimize the contribution of the undesirable cycloaddition. For this end, the AMMA/MMA mole ratio was allowed to be less than 1/5. As shown in Table I, the reaction of AMMA with MMA under some conditions gave the corresponding copolymer in high yield, and the ¹H NMR spectrum of this copolymer was depicted in Figure 1. The copolymer composition was estimated from the area ratio of the aryl and methoxy methyl proton signals. As a MPI_{Ant} for the graft copolymerization of St, we employed the AMMA/MMA copolymer ($M_n = 3.0 \times 10^4$) obtained from the reaction mixture heated for 12 h at 80 °C. The average number of 9-anthrylmethyloxycarbonyl group in MPI_{Ant} ($N_{\text{Ant}} = 44$) was calculated from the M_n , the

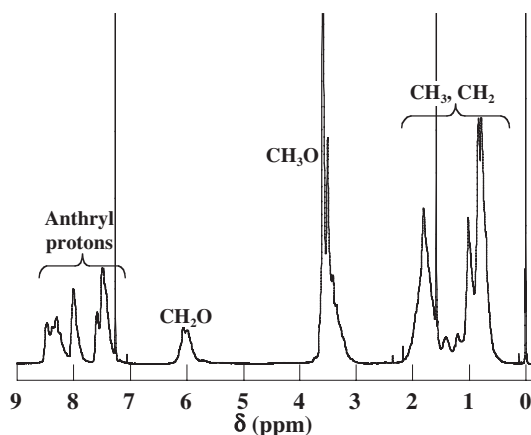


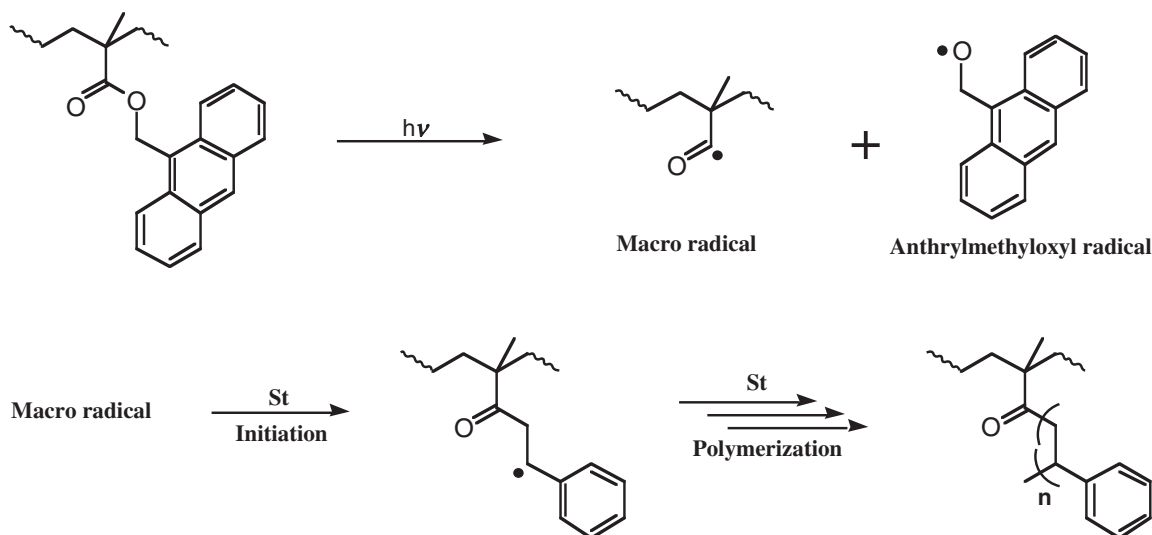
Figure 1. ^1H NMR spectrum of the AMMA/MMA copolymer ($M_n = 3.0 \times 10^4$) in CDCl_3 .

copolymer composition ($[\text{AMMA}]/([\text{AMMA}] + [\text{MMA}]) = 0.20$) of MPI_{Ant} , and the molecular weights of AMMA ($M_a = 276$) and MMA ($M_m = 100$) by using the following equation: $\{30000/[0.20 \times M_a + (1 - 0.20) \times M_m]\} \times 0.20 = N_{\text{Ant}}$. The average number of MMA unit in MPI_{Ant} ($N_M = 176$) was estimated similarly based on the value: $[\text{MMA}]/([\text{AMMA}] + [\text{MMA}]) = 0.80$.

Scheme 1 shows a plausible initiation mechanism in the St photopolymerization where MPI_{Ant} was used as a macroinitiator. It is possible that the anthrylmethyloxycarbonyl moiety undergoes the homolytic $\text{CH}_2\text{O}-\text{C}(=\text{O})$ bond cleavage as well as the heterolytic CH_2-O bond cleavage in its excited singlet state, as demonstrated from such competitive homolytic and heterolytic bond cleavages caused by the irradiation of 9-anthrylmethyl acetate in methanol.⁶ On the other hand, the recent finding that the photolysis of 9-anthrylmethyl 4-methylbenzoate in the nonpolar

solvent, toluene, generates predominantly radical derived products¹⁴ strongly suggests that in St (of polarity being comparable to that of toluene) the $\text{CH}_2\text{O}-\text{C}(=\text{O})$ bond in MPI_{Ant} undergoes its homolysis in the excited singlet state yielding macroradical and anthrylmethyloxyl radical. The former radical enables the initiation of St polymerization *via* addition to the $\text{C}=\text{C}$ double bond in St. It is likely that the addition of the latter radical to this double bond is not so fast owing to its oxy radical nature.¹⁵

In Figure 2(a) are shown UV absorption spectral changes caused by the irradiation ($\lambda > 340 \text{ nm}$) of MPI_{Ant} in toluene at room temperature. This figure also contains UV spectral changes in the model compounds, BAG and AI, irradiated under the same conditions [Figures 2(b) and 2(c)]. Because BAG contains two anthrylmethyloxycarbonyl groups at the near position, these groups have a strong tendency to undergo a photocycloaddition reaction. In contrast, AI has only one anthrylmethyloxycarbonyl group and its concentration is sufficiently low, so that the cycloaddition is very unlikely to occur efficiently. In addition, in these two model compounds the $\text{CH}_2\text{O}-\text{C}(=\text{O})$ bond cleavage proceeds at almost the same rate and also with low efficiencies.⁶ A difference in these reaction efficiencies may be clearly reflected in a difference in the decay rates of UV absorption spectra: namely, less efficient photoreaction exhibits slower UV spectral changes. As seen from Figure 2, on irradiation BAG shows fast UV spectral changes but AI does not, being consistent with our expectation. Thus, the finding that MPI_{Ant} gives rapid UV spectral changes at the early stage of the reaction and then much slower spectral changes are observed after 5 min irradiation confirms that both the photocycloaddition and the less efficient $\text{CH}_2\text{O}-\text{C}(=\text{O})$ bond cleavage in the



Scheme 1.

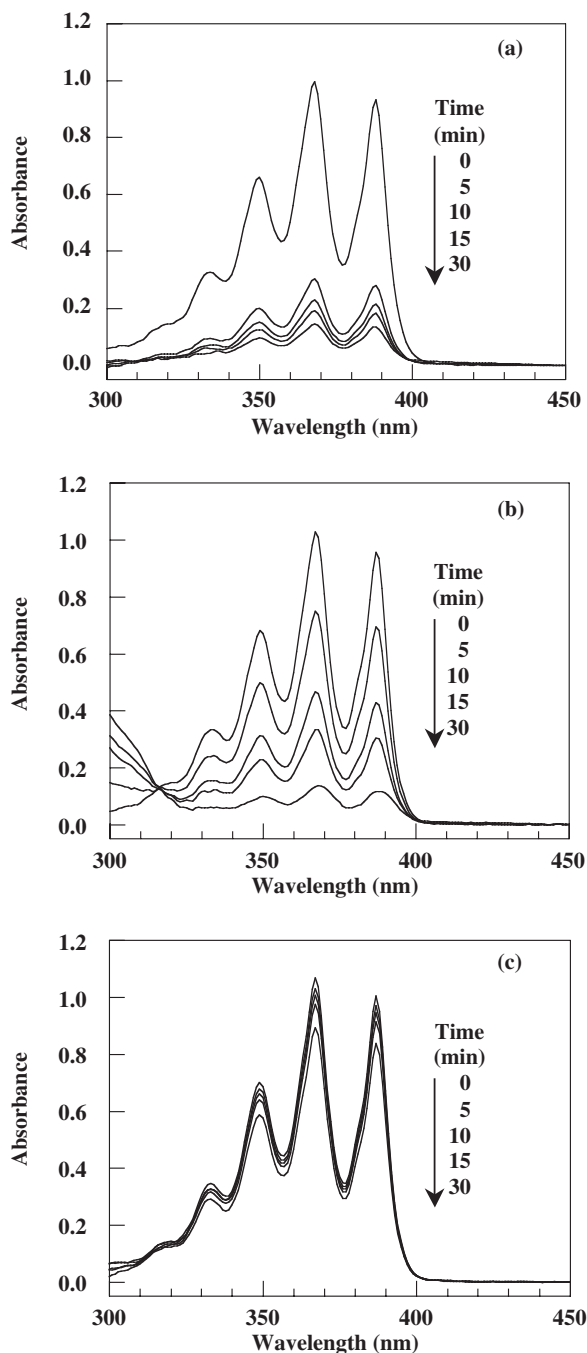


Figure 2. UV absorption spectral changes of MPI_{Ant} (spectra a, 69 g dm⁻³), BAG (spectra b, 5.0 × 10⁻⁵ mol dm⁻³), and AI (spectra c, 1.0 × 10⁻⁴ mol dm⁻³), caused by their irradiations in toluene.

anthrylmethyloxycarbonyl moiety proceed competitively. It is worthwhile to note here that the intramolecular photocycloaddition of the anthracene chromophore is responsible for the decreased conformational mobility of this chromophore in MPI_{Ant}.

Our attention is now directed to ¹H NMR spectral changes caused by the irradiation of MPI_{Ant} in toluene at room temperature. As depicted in Figure 3, on the spectrum recorded after 5 min irradiation the area of the anthryl-substituted methyloxy proton signal

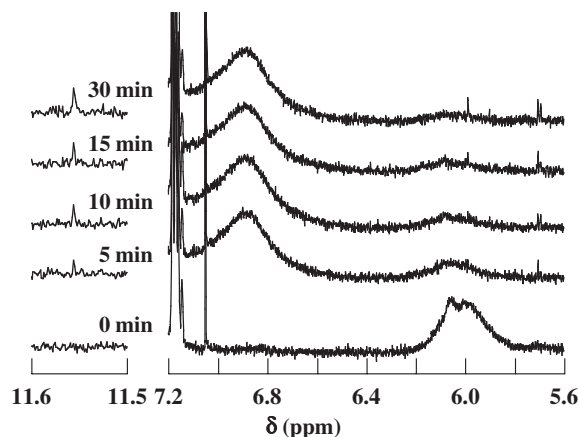


Figure 3. ¹H NMR spectra of MPI_{Ant} in CDCl₃, measured before and after its irradiation. A toluene solution of MPI_{Ant} (69 g dm⁻³) was prepared and irradiated. After its irradiation, toluene was evaporated to dryness and the resulting residue was dissolved in CDCl₃ for ¹H NMR spectral measurements.

Table II. Graft photopolymerization of St with MPI_{Ant}^{a)}

| Time (h) | Yield (g dm ⁻³) | $M_n \times 10^{-4}$ | M_w/M_n |
|----------|-----------------------------|----------------------|-----------|
| 2 | 18 | 2.5 | 11.0 |
| 4 | 21 | 2.2 | 7.0 |
| 8 | 48 | 1.7 | 3.9 |
| 16 | 56 | 2.9 | 8.4 |

^{a)} [MPI_{Ant}] = 13 g dm⁻³, [St] = 2.0 × 10⁻³ mol dm⁻³ = 2.1 × 10² g dm⁻³ in toluene at 60 °C.

(detected at 6.0 ppm) was decreased up to 36% of the initial area, while a signal assignable to cycloaddition product-derived aromatic proton was observed at 6.9 ppm.¹⁶ These observations substantiate our proposal that about 64% of the AMMA unit undergoes the photocycloaddition described above and the remaining AMMA unit does homolytic bond cleavage to eventually give anthracenecarbaldehyde, the characteristic signal of which can be detected at 11.55 ppm.

Photoinitiation Ability

The results obtained by the photopolymerizations of St with MPI_{Ant} as a macroinitiator are summarized in Table II. The polymer yield is clearly increased with irradiation time, indicating that MPI_{Ant} acts as a macromolecular photoinitiator. Since the concentration of this initiator was adjusted so as to minimize the contribution of intermolecular photocycloaddition between the anthracene chromophores, the enhanced concentration of MPI_{Ant} is very likely to result in an increase in polymer yield. In addition, the finding that the presence of TEMPO (0.10 mol dm⁻³) inhibits the photopolymerization almost completely substantiates the participation of radical-initiated polymerization reaction (Scheme 1).

An analysis of the molecular-weight distribution

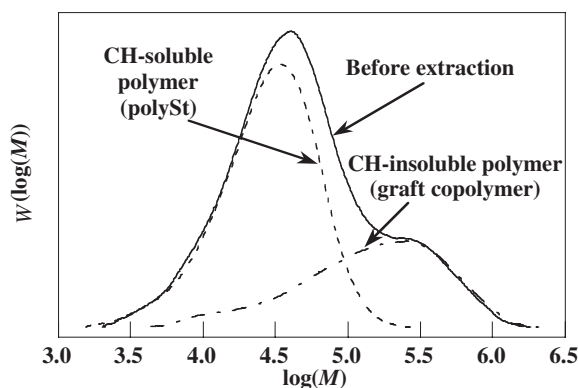


Figure 4. GPC elution curves of polymers obtained by the 16 h irradiation ($\lambda > 340$ nm) at 60°C of St (2.0×10^{-3} mol dm $^{-3}$) in the presence of MPI_{Ant} (13 g dm $^{-3}$) in toluene. Cyclohexane is abbreviated as CH.

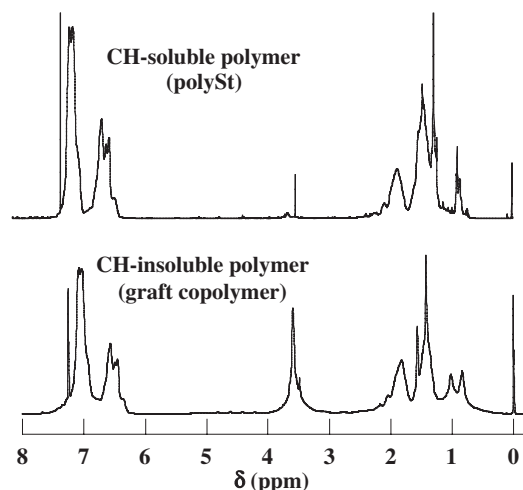


Figure 5. ^1H NMR spectra of CH-soluble and CH-insoluble polymers in CDCl_3 . The polymer mixture was obtained by the 16 h irradiation ($\lambda > 340$ nm) at 60°C of St (2.0×10^{-3} mol dm $^{-3}$) in the presence of MPI_{Ant} (13 g dm $^{-3}$) in toluene.

curve of polymer obtained by 16 h irradiation, depicted in Figure 4, reveals that this curve is bimodal and, hence, is consistent with the presence of the St homopolymer which would be formed *via* hydrogen abstraction of the 9-anthrylmethyloxyl radical from a solvent molecule. In order to separate the St homopolymer from the polymer mixtures containing poly-(AMMA-*co*-MMA)-*graft*-poly(St), the Soxhlet extraction was performed using cyclohexane (CH) which is a good solvent for poly(St) but a poor solvent for poly(MMA). The M_n value of CH-soluble polymer (2.0×10^4) was found to be smaller than that of CH-insoluble polymer (7.0×10^4), as shown in resolved GPC elution curves (Figure 4). The ^1H NMR spectra of these CH-soluble and CH-insoluble polymers are shown in Figure 5. Because in the former spectrum

there are signals assigned to the phenyl (6.4–7.4 ppm) and methylene (0.8–2.1 ppm) protons but no methoxy methyl proton signals, the CH-soluble polymer is attributable to the St homopolymer. On the other hand, the latter CH-insoluble polymer exhibits the phenyl proton signals around 6.4–7.4 ppm (St unit) and the methoxy methyl proton signals around 3.4–3.9 ppm (MMA unit). Additionally, the M_n value for the latter polymer was found to be larger than that for MPI_{Ant}. These findings, therefore, led us to conclude that the CH-insoluble polymer is the graft copolymer, poly(AMMA-*co*-MMA)-*graft*-poly(St).

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