Ring-Opening Copolymerization of 10-Methylene-9,10-Dihydroanthryl-9-Spirophenylcyclopropane via Free Radical and RAFT Processes

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ABSTRACT: A cyclic monomer, 10-methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane (MDS), and styrene (St) were copolymerized by conventional radical polymerization and reversible addition−fragmentation chain transfer (RAFT) polymerization. In both cases, NMR analyses of the resulting copolymers indicated that the ring-opening polymerization proceeded predominantly to give copolymers containing anthracene units in the main chain. The copolymers having relatively high MDS contents with narrow polydispersity ($M_w/M_n < 1.2$) were obtained by RAFT copolymerization in the presence of suitable chain transfer agents. Free radical copolymerizations of MDS and commercial monomers, such as 4-vinylpyridine (4VP), acrylonitrile, *n*-butyl acrylate, and methyl methacrylate, were studied using 2,2′-azobis(isobutyronitrile) as an initiator. The resulting copolymers absorbed light around 260 nm and 330−430 nm, regardless of the nature of the comonomer. Fluorescent peaks of poly(MDS-*co*-St) were almost the same as those of poly(MDS), whereas poly(MDS-*co*-4VP) showed an extremely broad peak from 420 to 640 nm with a maximum at 530 nm. These copolymers were thermally stable above 300 °C under nitrogen.

Introduction

Anthracene-containing polymers have attracted significant research interest, because of their attractive features as fluorescent labels, photon harvesters, and electro- and photoluminescent materials. In particular, increasing attention has been paid to nonconjugated polymers with anthracene units in the main chain, such as poly(trimethyleneanthrylene)s,[1,2] poly(octamethyleneanthrylene)s,[3] and poly(9,10-oxymethyleneanthrylene)s.[4] A nonconjugated polymer having anthracene units linked in the 9,10-position with flexible alkyl chains was reported to afford paramagnetism by doping with iodine and enhanced electrical conductivity.[4] This indicates that extended conjugation along the main chain is not a prerequisite for achieving enhanced electronic conductivity. Various polyamides,[5,6] polyesters,[7,8] polyethers,[7] and polyurethanes[6] containing anthracene units in the main chain have been synthesized by several groups. To manipulate unique electronic and photonic functions of these anthracene-containing polymers, it is desirable to control various factors, including the chemical structure of the main chain, chain length, and location and stacking of the anthracene units.

In a previous communication,[9] we reported the synthesis of well-defined polymers containing anthracene moieties in the main chain by radical ring-opening polymerization, which belongs to chain-growth polymerization, via reversible addition−fragmentation chain transfer (RAFT) process. We focused on the synthesis of the anthracene-containing polymers with controlled molecular weights and low polydispersity, because they could be regarded as a promising candidate for nanometer-scale device "molecular wires" with well-defined lengths proportional to the molecular weights. As a cyclic monomer, we employed 10-methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane (MDS), which is a vinylcyclopropane derivative and undergoes ring-opening polymerization with the release of the ring strain of the cyclopropane ring and the formation of a stable aromatic ring as the driving force,[10,11] as shown in Scheme 1. Among various controlled radical polymerizations, we have chosen the RAFT process because it is the most versatile with respect to the monomer and the reaction medium, and leads to the development of novel polymeric materials with a variety of functional groups and unique properties.[12−17] Although there are two possible mechanisms for the homopolymerization of MDS, ring-opening of the cyclic monomer was found to proceed predominantly during radical polymerization in the presence of a suitable chain transfer agent (CTA). In addition to the strain release of the cyclopropane ring and aromatization, the formation of a stable benzyl radical, (2) in Scheme 1, may be another driving force to open the ring and to attain the anthracene-containing polymers having low polydispersity via RAFT polymerization. In the initiation step, a radical R$^\bullet$ formed by decomposition of an initiator adds to the double bond of MDS with generation of new radial (1). Then, the ring-opening reaction of the intermediate (1) occurs predominantly with the generation of a benzyl radical (2), which is stabilized by delocalization of the radical over phenyl group. The intermediate radical (1) and benzyl radical (2) are capable of adding CTA to allow RAFT process.

Here, we report the copolymerization of the cyclic monomer, MDS, with conventional monomers via free radical and RAFT polymerizations (Scheme 2). Radical ring-opening polymerization is attractive because functional groups such as ethers, esters, amides, and carbonates can be incorporated into the backbone of polymer chain,[18] which cannot be achieved by conventional radical polymerization of vinyl monomers. How-

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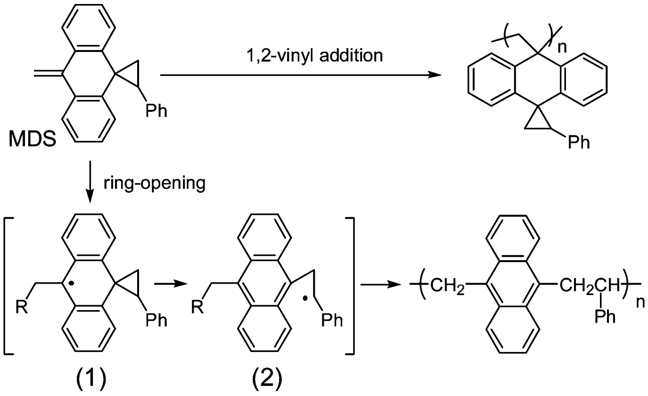
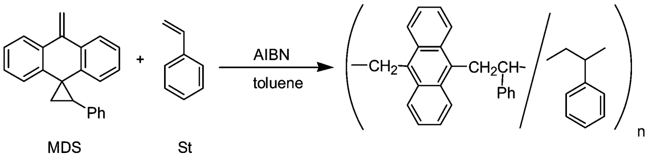
Scheme 1. Two Possible Mechanisms for Homopolymerization of 10-Methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane (MDS), Where R = Fragment of an Initiator



Scheme 2. Ring-Opening Copolymerization of 10-Methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane (MDS) with Styrene (St)



ever, the molecular weights and molecular weight distributions are not well-defined. Recently, several attempts have been made to extend the controlled radical polymerization to ring-opening polymerization of cyclic monomers, such as cyclic ketene acetals[19−22] and cyclic acrylates,[23] which afford polyesters and poly(α-ketoester)s, respectively. Ring-opening copolymerizations of cyclic monomers and commercial vinyl monomers via controlled radical polymerization were also investigated to produce materials with desirable physical properties for practical applications.[23−28] In conventional free radical copolymerization, the chains obtained at the beginning of the polymerization have different compositions than those formed at the last stage of the polymerization, because chains are initiated throughout the polymerization. In contrast, for copolymerization via a controlled fashion, all chains should have a similar composition, as all chains start growing at approximately the same time. This is an attractive feature of a controlled radical polymerization, in addition to various advantages, such as the formation of functional polymers with predetermined molecular weights, narrow polydispersity, and controlled architectures by a facile approach using a wide range of vinyl monomers.

Experimental Section

Materials. Styrene (St, Kanto Chemical, 99.0%) and methyl methacrylate (MMA, Kanto Chemical) were distilled from CaH_2 under reduced pressure. Acrylonitrile (AN, Kanto Chemical, 99.0%) and *n*-butyl acrylate (BA, Kanto Chemical, 99.0%) were dried with $CaCl_2$ and distilled under vacuum. 4-Vinylpyridine (4VP, Kanto Chemical, 95%) and *N*,*N*-dimethylformamide (DMF, Kanto Chemical, 99.5%) were dried with $MgSO_4$ and distilled under vacuum. 2,2′-Azobis(isobutyronitrile) (AIBN, Kanto Chemical, 97%) was purified by recrystallization from methanol. Toluene (Kanto Chemical, 99.5%) was distilled from CaH_2 under vacuum. Other materials were used without further purification.

The syntheses of benzyl dithiobenzoate (CTA 1)[29,30] and benzyl 1-pyrrolecarbodithioate (CTA 2)[31,32] were conducted according to procedures reported previously. CTA 2 was finally purified by column chromatography on silica with *n*-hexane as the eluent to afford the corresponding product as a yellow oil. CTA 1 was purified by vacuum distillation using a glass tube oven (Shibata GTO-250RS) to give a red oil.

The cyclic monomer 10-methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane (MDS) was prepared by the Wittig reaction of anthrone-9-spirophenylcyclopropane (Scheme 3), according to a method reported previously.[9,10] The monomer is highly reactive and cannot be handled at room temperature without a stabilizer. In order to avoid unfavorable polymerization reaction, triethylenediamine was added as a stabilizer immediately after the column purification, and the evaporation of the eluent was conducted gradually at room temperature and stopped before complete removal of the eluent. Typically, a stock solution containing the cyclic monomer (MDS, 1.02 g, 3.46 mmol), triethylenediamine (0.001 g, 1.0 wt % to the monomer, 8.91 × 10^{-3} mmol), and toluene (2.0 mL) was prepared in a silanized glass tube capped with a two-way glass stopper under nitrogen, and stored in the dark around 0 °C.

General Copolymerization Procedure. All polymerizations were carried out with AIBN as an initiator in a silanized glass ampule that was treated with 1,1,1,3,3,3-hexamethyldisilazane before use. For a typical free radical copolymerization, MDS (0.250 g, 0.85 mmol, including 1.0 wt % triethylenediamine), St (0.0884 g, 0.85 mmol), AIBN (2.8 mg, 0.017 mmol), and toluene (1.5 mL) were placed in a silanized glass ampule equipped with a magnetic stirring bar, and then the solution was degassed by three freeze−evacuate−thaw cycles. The ampule was flame-sealed under vacuum, and it was stirred at 80 °C for 24 h. The reaction was stopped by rapid cooling with liquid nitrogen. The reaction mixture was precipitated in a large excess of diethyl ether and isolated by filtration. The resulting product was finally dried under vacuum at room temperature to afford the copolymer as a pale yellow solid (0.178 g, yield = 52%). The resulting copolymer had an M_n (as determined by size-exclusion chromatography, SEC) of 1.4 × 10^4 and a polydispersity index (M_w/M_n) of 1.67. The resulting copolymer was soluble in dichloromethane, chloroform, tetrahydrofuran (THF), dioxane, DMF, and dimethyl sulfoxide (DMSO), and insoluble in diethyl ether, hexane, ethanol, methanol, and water.

A representative example of RAFT copolymerization is as follows: the cyclic monomer (MDS, 0.250 g, 0.85 mmol, including 1.0 wt % triethylenediamine), St (0.0884 g, 0.85 mmol), CTA 1 (8.3 mg, 0.034 mmol), AIBN (2.8 mg, 0.017 mmol), and toluene (1.5 mL) were placed in a silanized glass ampule. After three freeze−evacuate−thaw cycles, the polymerization mixture was stirred at 80 °C for 24 h. The polymer yield was determined gravimetrically from the diethyl ether-insoluble polymer sample (yield = 25%, 0.0865 g), and the resulting copolymer had an M_n (as determined by SEC) of 6.6 × 10^3 and a polydispersity index of 1.10.

The theoretical number-average molecular weight is defined as follows:

$$M_n(\text{theor}) = \frac{([\text{M1}]_0 + [\text{M2}]_0)}{[\text{CTA}]_0} \times M_{\text{Monomer}} \times \text{yield} + M_{\text{CTA}} \qquad (1)$$

where M_{CTA} is the molecular weight of chain transfer agent and $[\text{M1}]_0$, $[\text{M2}]_0$, and $[\text{CTA}]_0$ are the initial concentrations of monomers and chain transfer agent, respectively. M_{Monomer} is the mean molecular weight of a structural unit, which is a function of composition and therefore conversion of each monomer in the copolymerization. In a copolymerization of two monomers, M_{Monomer} is given by eq 2[33]

$$M_{\text{Monomer}} = A_1F_1 + A_2F_2 \qquad (2)$$

where A_1 and A_2 are the molecular weights of M1 and M2, respectively, and F_1 and F_2 are the mole fractions of M1 and M2 in the copolymer, respectively.

Instrumentation. ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded with a JEOL JNM-ECX400. The C−H COSY (C−H correlation spectroscopy) was performed with the JEOL-supplied pulse sequence. Number-average molecular weight

Scheme 3. Synthesis of 10-Methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane

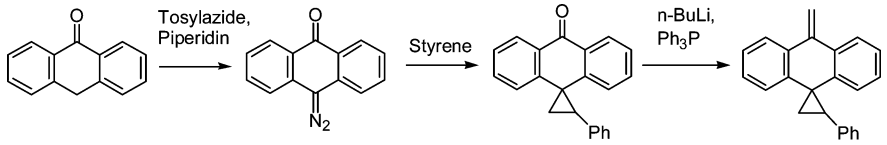


Table 1. Copolymerization of 10-Methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane (MDS) and Styrene (St) with 2,2′-Azobis(isobutyronitrile) (AIBN) in Toluene in the Presence and Absence of Chain Transfer Agent (CTA)[a]

run	CTA[b]	temp (°C)	[MDS]/[St]/[CTA]/[I]	time (h)	yield[c] (%)	M_n[d] (theory)	M_n[e] (SEC)	M_w/M_n[e] (SEC)	composition[f] MDS:St
1		60	50/50/0/1	24	21		8800	1.44	54:46
2		80	50/50/0/1	24	52		14 000	1.67	33:67
3		80	50/50/0/1	48	59		10 000	1.48	36:64
4		80	25/25/0/1	24	27		6300	1.33	53:47
5	CTA 1	60	50/50/2/1	24	13	1700	3800	1.17	65:35
6		80	50/50/2/1	24	25	2500	6600	1.10	42:58
7	CTA 2	60	50/50/2/1	24	13	1700	5400	1.30	67:33
8		80	50/50/2/1	24	29	2700	9000	1.18	34:66

[a] Monomer concentration = 0.17 g/mL, stabilizer = triethylenediamine (1 wt % to the monomer). [b] CTA 1 = benzyl dithiobenzoate, CTA 2 = benzyl 1-pyrrolecarbodithioate. [c] Diethyl ether-insoluble part. [d] The theoretical molecular weight ($M_{n,theory}$) was calculated using eqs 1 and 2. [e] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured by size-exclusion chromatography (SEC) using polystyrene standards in THF. [f] Determined by ^1H NMR spectroscopy.

(M_n) and molecular weight distribution (M_w/M_n) were estimated by size-exclusion chromatography (SEC) using a Tosoh HPLC HLC-8220 system equipped with refractive index and ultraviolet detectors at 40 °C. The column set was as follows: four consecutive columns [Tosoh TSK-GELs (bead size, exclusion limited molecular weight): G4000H$_{XL}$ (5 μm, 4 × 10^5), G3000H$_{XL}$ (5 μm, 6 × 10^4), G2000H$_{XL}$ (5 μm, 1 × 10^4), 30 cm each] and a guard column [TSK−guard column H$_{XL}$−L, 4 cm]. The system was operated at a flow rate of 1.0 mL/min, using THF as an eluent. Polystyrene standards were employed for calibration.

SEC chromatograms of the copolymers prepared with 4VP were obtained in DMF containing 10 mM LiBr at 40 °C at a flow rate of 1.0 mL/min with a Tosoh HPLC HLC-8220 system. The column set was as follows: four consecutive vinyl polymer-based gel columns [TSK−GELs (bead size, exclusion limited molecular weight): α-M (13 μm, > 1 × 10^7), α-4000 (10 μm, 4 × 10^5), α-3000 (7 μm, 9 × 10^4), α-2500 (7 μm, 5 × 10^3), 30 cm each] and a guard column [TSK−guard column α, 4.0 cm].

The UV−vis spectra were recorded with a JASCO V-550-DS spectrophotometer. Fluorescence spectra were obtained from a JASCO FP-6500 spectrofluorophotometer. Thermogravimetric analysis (TGA) was performed on a SEIKO SSC/5200 at a heating rate of 10 °C/min under N_2. For differential scanning calorimetry (DSC) measurements, a SEIKO DSC/6200 apparatus was used (heating rate: 20 °C/min, cooling rate: 5 °C/min). The data collection was carried out on the second heating process, and the glass transition temperature (T_g) was taken to be the midpoint—the temperature corresponding to half of the endothermic shift. The calorimeter was calibrated with an indium standard.

Results and Discussion

Free Radical Copolymerization of MDS and Styrene. The copolymerization of MDS and styrene (St) was carried out with AIBN as the initiator at a constant molar ratio of the two monomers in the feed ($[MDS]_0/[St]_0 = 50/50$) in toluene under various conditions, and the results are summarized in Table 1 (runs 1−4). When the copolymerization was conducted at $[MDS]_0/[St]_0/[AIBN]_0 = 50/50/1$ and 80 °C for 24 h, the copolymer was obtained as a pale yellow powder after the precipitation into diethyl ether, and the polymer yield was 52%. The resulting polymer had an $M_n = 1.4 \times 10^4$ and $M_w/M_n = 1.67$ according to SEC in THF using polystyrene calibration. A longer polymerization time (48 h, run 3) under the same conditions led to a slight increase in the polymer yield, whereas the quantitative yield was hard to attain. A copolymer having a lower molecular weight was obtained at the longer polymerization time, which may be due to unfavorable side reactions that gradually occurred with the polymerization time. In a previous communication,[9] we reported that unfavorable side reactions, such as dimerization, may take place during the free radical homopolymerization of MDS, resulting in a decreased polymer yield. In the cases of the free radical copolymerizations of MDS and styrene, the side reactions are suppressed until a certain period, as they seem to be predominant during the last stage of the polymerization, resulting in the decreased molecular weights. Note that the ^1H NMR spectrum of the reaction mixture obtained just after the free radical copolymerization showed the existence of both monomers even after 24 h at 80 °C (see Supporting Information). A further discussion will be conducted in the next section on the basis of the RAFT copolymerization results. Apparent decreases in the polymer yield and molecular weights were observed for the copolymerizations at lower temperature (60 °C, run 1) and at a higher initiator concentration ($[MDS]_0/[St]_0/[AIBN]_0 = 25/25/1$, run 4), respectively.

The structures of the resulting copolymers were characterized by ^1H and ^{13}C NMR measurements. Figure 1a shows the ^1H NMR spectrum of the copolymer obtained by the free radical copolymerization of MDS and St. The peaks corresponding to both components are clearly observed in the ^1H NMR spectrum measured in $CDCl_3$. The characteristic peaks at 3.5−4.5 ppm are clearly visible, which are attributed to the methylene and methine protons of the backbone formed by ring-opening polymerization of MDS. The presence of the peaks around 1.0−2.4 ppm suggests the incorporation of the St unit in the main chain. In addition to these peaks, broad peaks around 6.0−8.5 ppm are clearly observed, which correspond to the aromatic protons of the anthracene and St units. Broad peaks are also visible around 2.4−3.5 ppm, which were not present for the homopolymers, poly(MDS) and poly(St). As described in the later part, the 2D NMR technique suggested that the broad peaks around 2.4−3.5 ppm are attributed to the methine proton of the St unit. Although the methylene and methine protons of the cyclopropane ring (2.1−2.4 ppm) in the MDS monomer were observed in the same area, the possibility of forming the polymer having a cyclopropane ring structure by vinyl addition can be denied from the result of the ^{13}C NMR measurement mentioned below.

The comonomer composition is an important factor for the copolymerizations, because it can be employed to obtain information about the chemoselectivity of active species consuming the monomer during the polymerization. The comonomer composition was determined using ^1H NMR spectroscopy by a comparison of the peak at 3.5−4.5 ppm attributed to the main chain (3H) of the ring-opened MDS unit and peaks at 1.0−3.5 ppm corresponding to the main chain (3H) of the St unit. For instance, integration of the appropriate peaks gave a composition of 67% St and 33% MDS in the copolymer obtained at $[MDS]_0/[St]_0/[AIBN]_0 = 50/50/1$ and 80 °C for 24 h. This is in agreement with the composition, 65% St and 35%

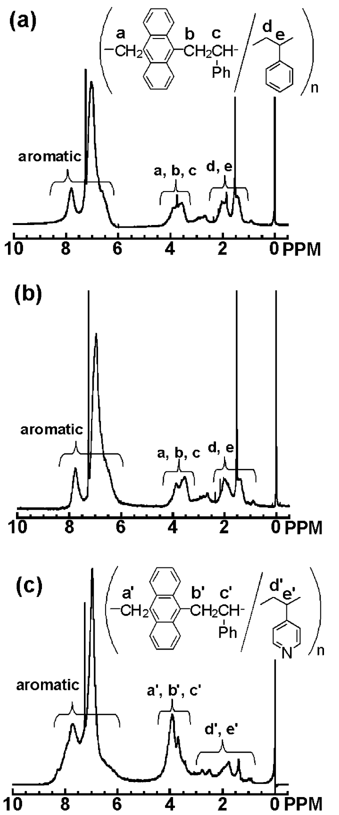


Figure 1. ^{1}H NMR spectra (CDCl$_3$) of poly(10-methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane-*co*-styrene)s; poly(MDS-*co*-St)s obtained by (a) free radical copolymerization (run 2, Table 1) and (b) reversible addition−fragmentation chain transfer (RAFT) copolymerization in the presence of benzyl dithiobenzoate (CTA 1, run 6, Table 1), and (c) poly(MDS-*co*-4-vinylpyridine) obtained by the free radical copolymerization (run 3, Table 2).

MDS, calculated from the conversions of each monomer determined by ^{1}H NMR spectroscopy of the reaction mixture collected just after the copolymerization (see Supporting Information). The MDS content in the copolymer obtained under the conditions is relatively lower than the feed ratio (50 mol %). As shown in Table 1, the lower polymerization temperature and higher initiator concentration led to an increase in the MDS content. In fact, the copolymerization at 60 °C with 50 mol % MDS in the feed resulted in the copolymer with 54 mol % MDS, suggesting that MDS is slightly preferable for adding to a growing polymer carbon radical compared to St at 60 °C.

The ^{13}C NMR spectrum of the copolymer obtained by the free radical copolymerization is presented in Figure 2c. In addition to the peaks attributed to the aromatic carbons at 124−145 ppm, two characteristic peaks are clearly observed at 49.5 and 33.8 ppm, which are attributable to two different aliphatic carbons in the polymer backbone formed by the ring-opening process of MDS. More importantly, the signal of the cyclopropane ring at 12.3 ppm, which was observed only in the spectrum of the cyclic monomer (see Supporting Information), completely disappears in the resulting polymer. This indicates that the cyclopropane ring in MDS is completely opened and the polymerization predominantly proceeds via the radical ring-opening process. The results from the ^{13}C NMR analysis of the random copolymer are analogues to those of the MDS homopolymer. Furthermore, the signals of the St unit are present at 41−47 ppm ($-CH_2CH(C_6H_5)-$) and 40.7 ppm ($-CH_2CH(C_6H_5)-$). Other noticeable peaks are also observed at 45.0, 36.4, and 35.6 ppm, which were characterized by the 2D NMR technique.

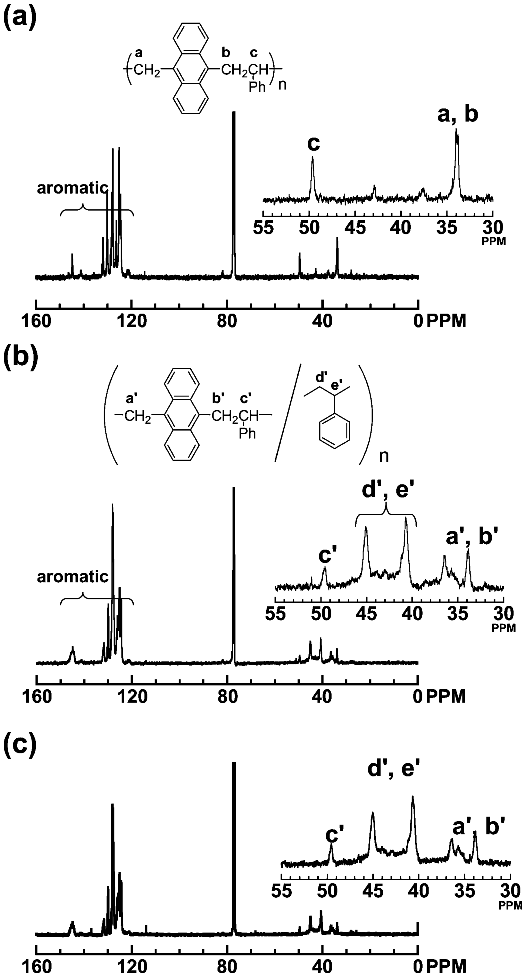


Figure 2. ^{13}C NMR spectra (CDCl$_3$) of (a) poly(10-methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane); poly(MDS) obtained by reversible addition−fragmentation chain transfer (RAFT) polymerization, and poly(MDS-*co*-styrene)s obtained by (b) RAFT and (c) free radical copolymerizations.

The C−H COSY NMR spectrum was recorded in order to obtain further information on the structure of the poly(MDS-*co*-St) produced by free radical copolymerization. As shown in Figure 3a, two separate cross-peaks can be seen by correlation of the protons (a, b, and c) at 3.6−4.2 ppm and a proton (e) at 2.5−3.0 ppm with an aromatic carbon signal around 128 ppm. On the basis of the C−H COSY NMR spectrum, the signals at 3.6−4.2 and 2.5−3.0 ppm could be assigned to the protons attached to the aromatic carbons, which involves the benzene ring in the St unit and the anthracene moiety derived from the MDS unit. Figure 3b clearly shows that the carbon signals around 34, 36, and 49 ppm are related to the proton signals at 3.6−4.2 (a, b, and c) derived from the MDS unit. The proton signal at 2.5−3.0 ppm (e) attached to the aromatic carbon is related to the carbon signals at 45 ppm, which helps with the assignment of the signals at 2.5−3.0 ppm to the methine proton in the St unit. The protons at 2.2 ppm attached to the carbon signal at 40 ppm is assigned to the methylene protons in the St unit, since the proton has no correlation with the aromatic carbon.

RAFT Copolymerization of MDS and Styrene. The copolymerizations of the cyclic monomer, MDS, and St were investigated using AIBN as the initiator in the presence of CTA 1 or CTA 2, and these results are summarized in Table 1. In all cases, the copolymerizations were carried out at a constant comonomer feed ($[MDS]_0$:$[St]_0$ = 50:50), and keeping the chain

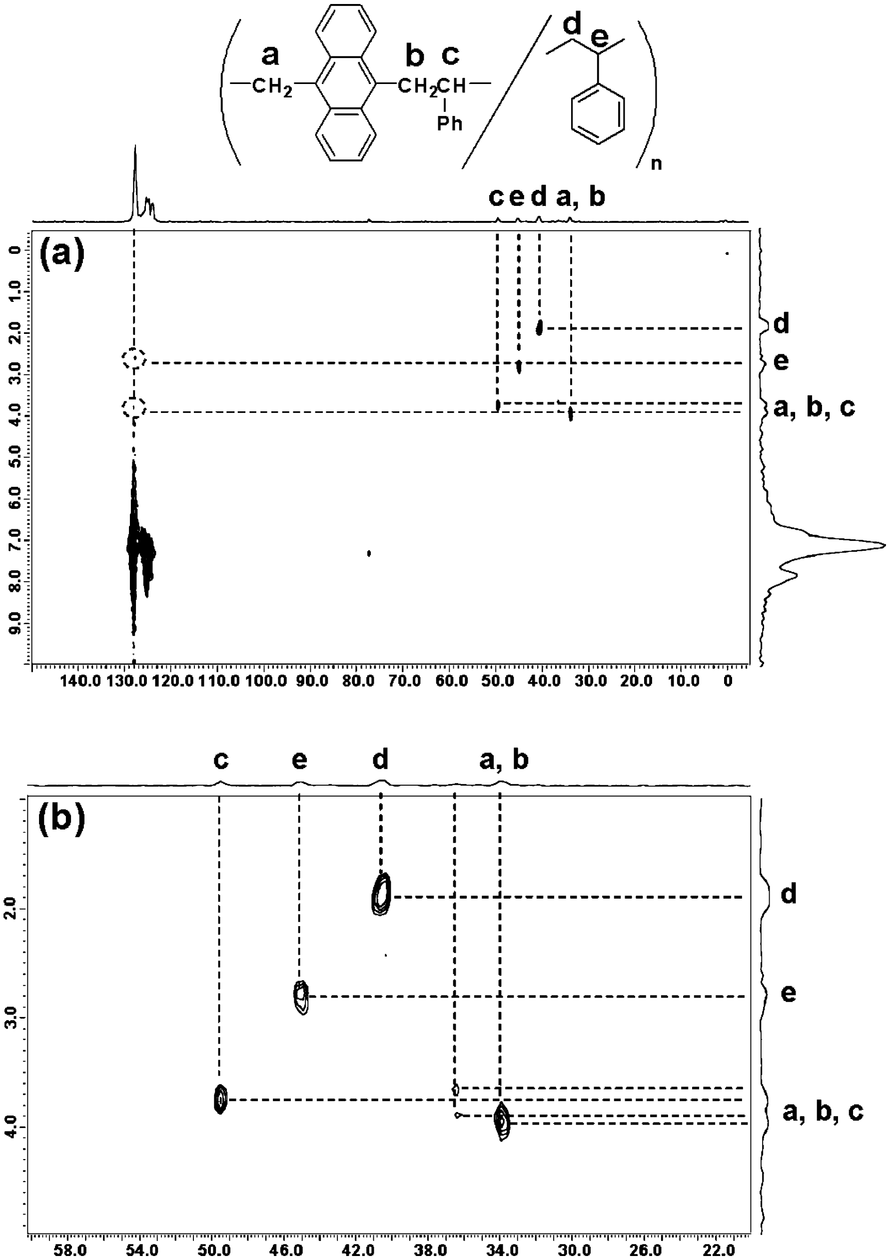


Figure 3. (a) C−H COSY (C−H correlation spectroscopy) NMR spectra ($CDCl_3$) of poly(10-methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane-*co*-styrene); poly(MDS-*co*-St) obtained by free radical copolymerization, and (b) a part of the spectrum: ^{1}H NMR region 1−5 ppm; ^{13}C NMR region 20−60 ppm.

transfer agent-to-initiator ratio at a constant value of $[CTA]_0/[AIBN]_0 = 2/1$. When the copolymerization was carried out using CTA 1 at $[MDS]_0/[St]_0/[CTA\ 1]_0/[AIBN]_0 = 50/50/2/1$ in toluene at 80 °C for 24 h, the characteristic pale red solution remained during the polymerization. The polymer yield was 25%, which is apparently lower than that obtained by the free radical copolymerization under the same conditions. As can be seen in Figure 4, the resulting polymer showed a symmetrical SEC peak with a relatively narrow molecular weight distribution ($M_w/M_n = 1.10$). The number-average molecular weight, measured by a SEC in THF, was $M_n = 6600$, which is apparently higher than the theoretical value ($M_n = 2500$) calculated from eqs 1 and 2. The MDS content in the copolymer is slightly lower than the feed ratio. The copolymerization of the cyclic monomer, MDS, in the presence of CTA 2 under the same conditions afforded a copolymer with a higher molecular weight ($M_n = 9000$, $M_w/M_n = 1.18$, and yield = 29%). In contrast, there were no significant differences in the polydispersity and polymer yield between the copolymerizations with CTA 1 and CTA 2. The tendency is different from that of the homopolymerization of MDS, in which the polymerization with CTA 1 has a higher yield than that with CTA 2.[9] We considered that this might be due to unfavorable side reactions, such as dimerization, resulting in the decreased polymer yield, because the monomer conversion determined by ^{1}H NMR was apparently higher than that of the polymer yield (diethyl ether-insoluble part) in the case of the homopolymerizations without CTA. In contrast, the ^{1}H NMR spectrum of the reaction mixture obtained just after the free radical copolymerization showed the existence of both monomers even after 24 h at 80 °C (see Supporting Information), suggesting that the unfavorable side reactions can be avoided in the cases of the copolymerizations. This behavior may lead to the fact that the nature of CTA has no significant influence on the polymer yield and polydispersity. The copolymerizations with CTA at lower temperature, 60 °C, produced copolymers with relatively narrow molecular weight distribu-

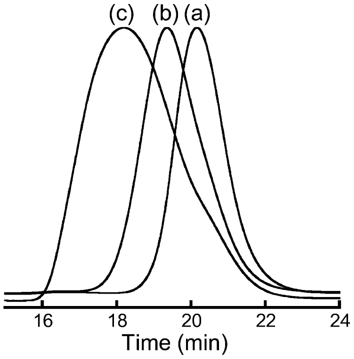


Figure 4. Size-exclusion chromatography (SEC) traces of poly(10-methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane-*co*-styrene)s; poly(MDS-*co*-St)s prepared by the copolymerization at 80 °C for 24 h with (a) benzyl dithiobenzoate (CTA 1), (b) benzyl 1-pyrrolecarbodithioate (CTA 2), and (c) without chain transfer agent (CTA). Key: (a, b) $[\mathrm{MDS}]_0/[\mathrm{St}]_0/[\mathrm{CTA}]_0/[\mathrm{AIBN}]_0 = 50/50/2/1$; (c) $[\mathrm{MDS}]_0/[\mathrm{St}]_0/[\mathrm{AIBN}]_0 = 50/50/1$. See Table 1 for detailed polymerization conditions.

tions ($M_w/M_n = 1.17$ for CTA 1 and $M_w/M_n = 1.30$ for CTA 2), while achieving less than a 15% polymer yield even after 24 h.

The copolymerization at a lower temperature led to an increase in the MDS content of the copolymers, regardless of the nature of the CTA, indicating that the MDS radicals have a much greater tendency to react with an MDS monomer rather than another St monomer, whereas St radicals also prefer to react with the MDS monomer. The same tendency, which is the higher MDS content at a lower polymerization temperature, was observed in the free radical copolymerization of MDS and St. This indicates that MDS has a slightly higher reactivity than St at 60 °C, which may be because the intermediate radical (1, in Scheme 1) formed from MDS is stabilized by two phenyl groups. The growing radical formed during the ring-opening process of MDS is the benzyl radical (2, in Scheme 1), which has the same structure formed during the vinyl polymerization of St. For the copolymerizations at 80 °C, in contrast, St is consumed faster than MDS. The temperature-dependent variation in the comonomer content should be attributed to the relative stabilities of the intermediate MDS radical (1) and the benzyl radical formed in the St unit. Another possibility is that the transformation of the intermediate radical (1) into the benzyl radical (2) through the aromatization and cleavage of the cyclopropane ring during the ring-opening reaction is affected by the polymerization temperature.

In all cases, the experimental molecular weights are higher than the calculated ones, suggesting that the number of polymer chains is less than the CTA used in this study. This is the opposite tendency observed for the homopolymerization of MDS via the RAFT process,[9] in which the experimental molecular weights were slightly lower than the calculated ones, due to the difference in the hydrodynamic volume between the poly(MDS) and the linear polystyrene standards used for the GPC calibration. The relatively low polymer yield and low polydispersities of the copolymers in the presence of CTA might be also attributed to the relatively high chain transfer constants of CAT 1 and CTA 2, respectively. Note that the transfer constant with the dithioester (Z = Ph, $C_{\mathrm{tr}} = 29$) was reported to be apparently higher than that with the aromatic dithiocarbamate (Z = pyrrole, $C_{\mathrm{tr}} = 11$) in a series of benzyl thiocarbonylthio compounds of the general structures, $\mathrm{Z{-}C({=}S)S{-}CH_2Ph}$, for the thermal polymerization of St.[31] The ratio between the observed and calculated M_ns is 2.1−2.5 for the copolymerization with CTA 1, while the ratio is slightly higher (3.0−3.2) for that with CTA 2.

Table 2. Free Radical Copolymerization of 10-Methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane (MDS) and 4-Vinylpyridine (4VP) with 2,2′-Azobis(isobutyronitrile) (AIBN) in DMF[a]

run	temp (°C)	time (h)	yield[b] (%)	M_n[c]	M_w/M_n[c]	composition[d] MDS:4VP
1	60	24	10	4600	1.63	64:36
2	80	24	11	3400	1.61	57:43
3	80	96	22	3900	1.62	48:52
4	100	96	18	3000	1.34	55:45

[a] Monomer concentration = 0.17 g/mL, stabilizer = triethylenediamine (1 wt % to the monomer). [b] Diethyl ether-insoluble part. [c] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured by size-exclusion chromatography (SEC) using polystyrene standards in *N*,*N*-dimethylformamide (DMF, 10 mM LiBr). [d] Determined by ^{1}H NMR spectroscopy.

Since the ring-opening mechanism during the RAFT polymerization of MDS should be the same as that initiated by conventional free radical initiators, it is expected to have no significant difference in the structure of the resulting copolymers. In order to confirm this point, the ^{1}H NMR analysis was used to characterize the products prepared via the RAFT polymerization. As can be seen in Figure 1b, the copolymer obtained by the RAFT copolymerization of MDS and St showed characteristic peaks corresponding to the backbone formed by the ring-opening polymerization of MDS and the main chain of the St unit, in addition to the aromatic protons of the anthracene and St units. As expected, no remarkable difference was detected in the ^{1}H NMR spectra of the copolymers obtained by the RAFT polymerization and conventional free radical polymerization. Parts b and c of Figure 2 compare the ^{13}C NMR spectra of the copolymers obtained by the RAFT and free radical copolymerizations. In both cases, the peaks corresponding to both components are clearly observed, while the peak of the cyclopropane ring at 12.3 ppm is invisible, indicating the occurrence of the predominant ring-opening reaction of the cyclopropane ring in MDS. There is no significant difference in the ^{13}C NMR signals between the copolymers (Figure 2 and Figure S3 in Supporting Information). These ^{1}H and ^{13}C NMR analyses suggest that the ring-opening reaction of MDS predominantly takes place during the copolymerization of MDS and St, regardless of the presence and absence of CTA.

Copolymerization of MDS and Various Comonomers. The free radical copolymerizations of the cyclic monomer, MDS, with various monomers were attempted, aimed at developing novel anthracene-containing copolymers with characteristic properties. We first selected 4-vinylpyridine (4VP) as a comonomer, because the resulting nitrogen-containing polymers can be used in various applications, such as polyelectrolytes, basic polymers for acid−base interaction, and coordination reagents for transition metals. The copolymerizations were carried out at $[\mathrm{MDS}]_0/[\mathrm{4VP}]_0/[\mathrm{AIBN}]_0 = 50/50/1$ in DMF under various conditions. As shown in Table 2, the polymer yields were relatively low in all cases. These values are much lower than those of the comparable copolymerization with St (Table 1). The number-average molecular weights, measured by SEC in DMF with 10 mM LiBr, were $M_n = 3000{-}4600$, and the polydispersity indices (M_w/M_n) were between 1.34 and 1.63. A higher polymerization temperature (100 °C) and longer time (3 days) had no significant influence on the polymer yield, molecular weight, and polydispersity.

Figure 1c shows the ^{1}H NMR spectrum of the copolymer obtained by the free radical copolymerization of MDS and 4VP.

Table 3. Characterization of the Copolymers Prepared by Free Radical Copolymerization of 10-Methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane (MDS)[a]

					solubility[f]				
run	polymer[b]	M_n[c] (M_w/M_n)[c]	MDS[d] content	T_{d10}[e] (°C)	DMF	MeOH	THF	$CHCl_3$	Et_2O
1	poly(MDS)	9000 (1.66)	100	347	+	−	+	+	−
2	poly(MDS-*co*-St)	14000 (1.67)	33	351	+	−	+	+	−
3	poly(MDS-*co*-AN)	4000 (1.24)	85	333	+	−	+	+	−
4	poly(MDS-*co*-BA)	7000 (1.72)	75	341	+	−	+	+	−
5	poly(MDS-*co*-MMA)	8000 (1.37)	55	336	+	−	+	+	−
6	poly(MDS-*co*-4VP)	3400 (1.61)	57	330	+	+	−	+	−

[a] The samples were prepared by free radical copolymerization using AIBN with 50 mol % MDS in the feed. [b] St; styrene, AN; acrylonitrile, BA; *n*-butyl acrylate, MMA; methyl methacrylate, 4VP; 4-vinylpyridine. [c] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured by size-exclusion chromatography (SEC). [d] Determined by ^{1}H NMR spectroscopy. [e] Determined by TGA; heating rate: 10 °C/min, N_2 atmosphere. [f] "+" = soluble at room temperature; "−" = insoluble at room temperature.

The signals at 3.3−4.7 ppm are ascribed to the methine and methylene main chain (3H) formed by the ring-opening of the MDS unit, whereas the peaks observed at 1.0−3.0 ppm correspond to the main chain (3H) of the 4VP unit. As can be seen in Table 2, the comonomer composition determined by the ^{1}H NMR spectroscopy suggests the incorporation of the MDS units into the copolymer, even if the polymer yield was relatively low during the copolymerization of MDS and 4VP. The comonomer composition was also evaluated from the result of the elemental analysis. For example, the atomic composition of the copolymer obtained at $[MDS]_0/[4VP]_0/[AIBN]_0 = 50/50/1$ at 80 °C for 96 h was as follows: N, 2.62; C, 88.15; H, 6.37. On the basis of the nitrogen content, the comonomer composition could be calculated to be 41% 4VP, which is roughly comparable to the value (52% 4VP) observed by the ^{1}H NMR spectral analysis. A lower polymerization temperature resulted in a higher MDS content in the copolymer, which is the same tendency observed for the copolymerization of MDS and St.

The free radical copolymerizations of MDS were conducted with various comonomers, including acrylonitrile (AN), *n*-butyl acrylate (BA), and methyl methacrylate (MMA). The copolymerizations were carried out in toluene at $[MDS]_0/[comonomer]_0/[AIBN]_0 = 50/50/1$ at 80 °C for 24 h to produce poly(MDS-*co*-AN) ($M_n = 4000$, $M_w/M_n = 1.24$, yield = 8%), poly(MDS-*co*-BA) ($M_n = 7000$, $M_w/M_n = 1.72$, yield = 11%), and poly(MDS-*co*-MMA) ($M_n = 8000$, $M_w/M_n = 1.37$, yield = 33%). These results suggest that the copolymerization of MDS with the electron-donor St ($e = -0.8$) shows a higher polymer yield compared to those with the electron-accepting monomers involving AN ($e = 1.23$), BA ($e = 0.85$), MMA ($e = 0.40$), and 4VP ($e = 0.84$).[34] Since MDS might be an electron donating monomer, the charge-transfer complexes might be formed during the copolymerization with the electron acceptors, such as AN and 4VP, leading to the relatively high MDS incorporation into the copolymer. The resulting poly(MDS-*co*-4VP) had a good solubility in chloroform, DMF, and MeOH, while being insoluble in THF and diethyl ether. In contrast, other random copolymers were soluble in chloroform, DMF, and THF, while being insoluble in diethyl ether, hexane, ethanol, methanol, and water (Table 3).

Copolymer Properties. The resulting copolymers were characterized in terms of their optical and thermal properties. Figure 5a depicts the absorbance spectra of the poly(MDS), poly(MDS-*co*-St), and poly(MDS-*co*-4VP) measured in $CHCl_3$. Both the homopolymer and the copolymers exhibit the first absorption band around 260 nm assigned to the anthracene moiety and second absorption at 330−430 nm. The latter band may stem from the adjacent anthracene moieties. The peak intensity of the first band in poly(MDS-*co*-4VP) is apparently higher than those of poly(MDS) and poly(MDS-*co*-St). A similar tendency was also observed in the second adsorption band.

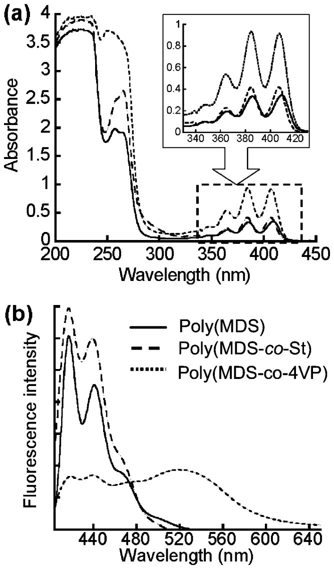


Figure 5. (a) Absorption (3.4×10^{-5} anthracene unit mol L^{-1}) and (b) fluorescent (8.5×10^{-7} anthracene unit mol L^{-1}, $\lambda_{ex} = 384$ nm) spectra of the poly(10-methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane); poly(MDS), poly(MDS-*co*-styrene) and poly(MDS-*co*-4-vinylpyridine).

The fluorescence spectra of the copolymers are shown in Figure 5b. The emission of the poly(MDS-*co*-St) excited at 384 nm is observed at 420 and 445 nm. In addition to these peaks, a shoulder peak is visible at 470 nm and a broad tailing of the peak is detected until around 500 nm. These fluorescent peaks of poly(MDS-*co*-St) are almost the same as those of poly(MDS), but with a slight difference in the peak intensities. In fact, the absorbance and fluorescence of the copolymers, poly(MDS-*co*-AN), poly(MDS-*co*-BA), poly(MDS-*co*-MMA), and poly(MDS-*co*-St) were comparable to those of the poly(MDS) homopolymer (see Supporting Information), indicating sufficient incorporation of the anthracene group in the copolymers. In contrast, poly(MDS-*co*-4VP) shows an extremely broad peak from 420 to 640 nm with a maximum at 530 nm in the fluorescent spectrum. In fact, poly(MDS-*co*-4VP) exhibited a whitish blue fluorescence upon excitation at 365 nm, which was slightly different from the blue fluorescence observed in poly(MDS) and poly(MDS-*co*-St). On the basis of these absorbance and fluorescence spectra, it is reasonable to consider that the anthracene groups in the poly(MDS) main chain are close enough to interact with the pyridine ring in the 4VP units.

The thermal properties of the resulting copolymers were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements. The T_g values

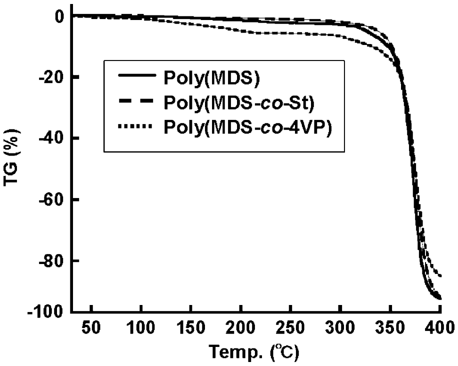


Figure 6. Thermogravimetric analysis (TGA) thermograms of poly(10-methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane): poly(MDS), poly(MDS-*co*-styrene), and poly(MDS-*co*-4-vinylpyridine) under nitrogen atmosphere.

of poly(MDS-*co*-St)s were found to be 207 °C and 175 °C for the copolymers obtained by the free radical polymerization (M_n = 14 000 and M_w/M_n = 1.67, MDS content = 33%) and RAFT polymerization (M_n = 6600 and M_w/M_n = 1.10, MDS content = 42%), respectively. These values were apparently lower than that of the poly(MDS) having similar molecular weights (T_g = 226 °C, M_n = 8400 and M_w/M_n = 1.44), suggesting the feasibility to control the T_g value by the copolymerization. As shown in Figure 6, the poly(MDS-*co*-St) was stable up to 340 °C, and then the thermal degradation started. The temperature for the 10% weight loss of poly(MDS-*co*-St) under a nitrogen atmosphere was 351 °C, which is comparable to that of poly(MDS) (T_d^{10} = 347 °C). The other copolymers prepared in this study showed similar thermal stabilities with decomposition occurring above 300 °C. The 10% weight loss temperatures of other copolymers under a nitrogen atmosphere were 330−350 °C, as shown in Table 3. These TGA results indicated that the resulting copolymers exhibited high thermal stabilities, regardless of the nature of the comonomers.

Conclusion

This study reports the synthesis of copolymers containing anthracene moieties in the main chain by the ring-opening copolymerization of 10-methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane (MDS) as a cyclic monomer with common vinyl monomers. The vinylcyclopropane derivative was found to predominantly undergo a ring-opening copolymerization, regardless of the conventional radical polymerization or the RAFT polymerization, with the release of the ring strain of the cyclopropane ring and the formation of a stable aromatic ring as the driving force. Nearly monodispersed copolymers with anthracene moieties incorporated into the main chain were prepared by the copolymerization of MDS with styrene in the presence of benzyl dithiobenzoate (CTA 1) or benzyl 1-pyrrolecarbodithioate (CTA 2) under suitable polymerization conditions. The UV absorption and fluorescent spectra of the resulting copolymers indicated the preferable formation of the anthracene units in the main chain. An extremely broad peak from 420 to 640 nm with a maximum at 530 nm was observed only in the fluorescent spectrum of poly(MDS-*co*-4VP), which were apparently different from the other copolymers.

Supporting Information Available: Figures showing ^{1}H and ^{13}C NMR spectra of the cyclic monomer, ^{1}H NMR spectrum of a crude reaction mixture collected just after the copolymerization, magnification of ^{13}C NMR spectra of the copolymers, absorption and fluorescent spectra of the copolymers, and the appearance of the copolymers under visible and UV (λ_{ex} = 365 nm) light. This material is available free of charge via the Internet at http://pubs.acs.org.

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