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Synthesis and Optoelectronic Properties of Alternating Copolymers Containing Anthracene Unit in The Main Chain by Radical Ring-Opening Polymerization

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ABSTRACT: Novel alternating copolymers composed of anthracene moiety and halostyrene unit were synthesized by ring-opening polymerization of cyclic monomers, 10-methylene-9,10-dihydroanthryl-9-spiro-*p*-chlorophenylcyclopropane and its bromo derivative. Reversible addition−fragmentation chain transfer and conventional free radical polymerizations were employed for the purpose. In both cases, the ring-opening polymerization proceeded predominantly to afford alternating copolymer containing anthracene unit in the main chain. Incorporations of optoelectronic groups, involving diphenylamine, carbazole, and phenothiazine, on the halostyrene moieties of the alternating copolymers were conducted by palladium-catalyzed reactions. Novel nonconjugated copolymers having perfect alternating structures were obtained, in which the alternate arrangement of two distinct electronic functionalities is formed owing to the ring-opening polymerization system. Resulting anthracene-based alternating copolymers having two distinct electronic functionalities exhibited characteristic fluorescence resonance energy transfer, as confirmed by UV−vis and fluorescence spectra.

Introduction

The design and synthesis of novel polymers having two distinct electronic functionalities, such as donor and acceptor chromophores, are attracting significant attention, because of interesting photophysical and optoelectronic properties, and possible applications for organic light emitting devices, photovoltaics, and organic field-effect transistors.[1−7] For these optoelectronic applications, it is important to control various factors, such as electron donating and accepting properties involving highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) energy levels, polymer architectures (dendrimers and block and alternating copolymers) with the location and stacking of the chromophores, and interfaces of two distinct functionalities. In particular, the manipulations of energy, electron, and charge transfers between two distinct electronic components play crucial roles to achieve excellent photophysical and optoelectronic properties.

Anthracene-containing polymers have attracted significant research interest, due to their attractive features as fluorescent labels, photon harvesters, and electro- and photoluminescent materials. In addition to anthracene-based conjugated polymers, increasing attention has been recently paid to nonconjugated polymers with anthracene units in the main chain, such as poly(trimethyleneanthrylene)s,[8,9] poly(octamethyleneanthrylene)s,[10] and poly(9,10-oxymethyleneanthrylene)s.[11] 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.[11] Various polyamides,[12,13] polyesters,[14,15] polyethers,[14] and polyurethanes[13] containing anthracene units in the main chain have been synthesized by several groups. Much attention has been also paid to anthracene-based polymers and molecules having an additional optoelectronic component, such as triphenylamine,[16−19] carbazole,[20−22] and phenothiazine,[23,24] because the combination of two distinct electronic functionalities in a single system provides a great variety of photophysical and optoelectronic properties. In order to manipulate characteristic energy, electron, and charge transfers between the two distinct electronic functionalities, various architectures have been employed, such as conjugated and nonconjugated polymers having anthracene moiety in the side chain[18,22] and main chain,[19,21] Langmuir−Blodgett films,[20] and small molecules.[17,23,24]

In a previous communication,[25] 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. 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,[26] which cannot be achieved by conventional radical polymerization of vinyl monomers. Recently, several attempts have been made to extend the controlled radical polymerization to ring-opening polymerization of cyclic monomers, such as cyclic ketene acetals[27−30] and cyclic acrylates,[31] which afford well-defined polyesters and poly(α-ketoester)s, respectively. Another important advantage of the radical ring-opening polymerization is the feasibility to obtain perfect alternating structure, which is originated from the structure of cyclic monomers having two different potential monomer units. In our previous system,[25,32] 10-methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane (MDS)[33,34] was employed as a cyclic monomer, and the resulting polymer actually had a perfect alternating structure composed of the anthracene moiety and styrene unit, owing to the ring-opening polymerization system (Scheme 1). There are two possible mechanisms for the homopolymerization

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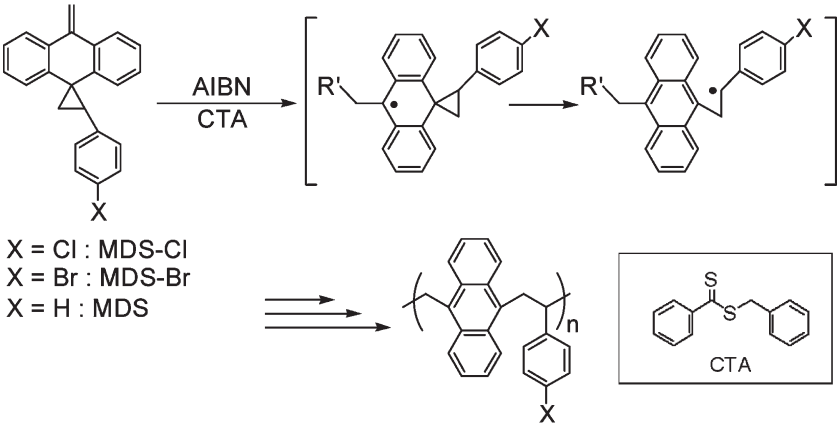
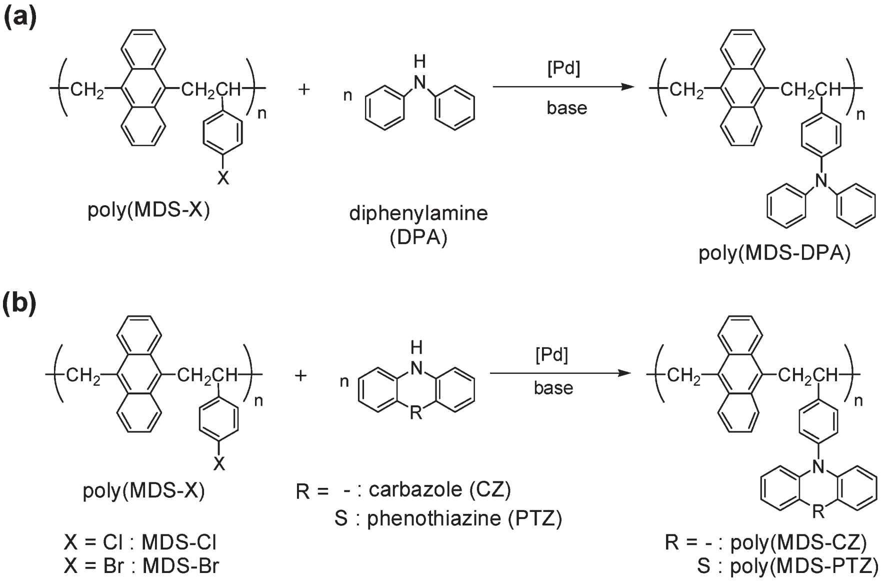
Scheme 1. Ring-Opening Polymerization of 10-Methylene-9,10-dihydroanthryl-9-spirohalophenylcyclopropane, Where AIBN = 2,2′-Azobis-(isobutyronitrile) and CTA = Benzyl Dithiobenzoate



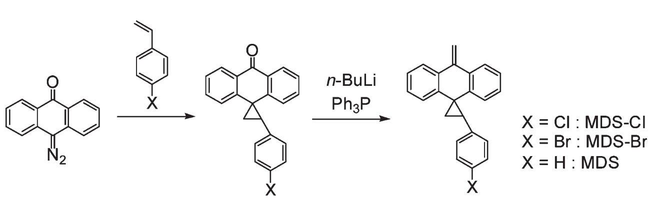
Scheme 2. Postmodifications of Alternating Copolymers Comprised of Anthracene Moiety and Halostyrene Unit



of MDS; conventional 1,2-vinyl addition to afford vinyl polymer having the cyclopropane ring in the side chain and ring-opening reaction to furnish directly the anthracene moiety in the main chain. In this system, ring-opening of the cyclic monomer was found to proceed predominantly during radical polymerization in the presence of a suitable chain transfer agent (CTA).[25,32] In addition to the strain release of the cyclopropane ring and aromatization, the formation of a stable benzyl radical may be another driving force to open the ring and to attain the anthracene-containing polymers having low polydispersity via RAFT polymerization.

In this study, we focused on the controlled synthesis of the alternating polymers composed of the anthracene unit with an additional optoelectronic group, such as triphenylamine, phenothiazine, and carbazole derivatives. Polymers with carbazole pendant groups are of considerable scientific and industrial interest due to their attractive features, such as hole-transporting, high charge-carrier, and electroluminescent properties.[35] Phenothiazine is a heterocyclic compound with electron-rich sulfur and nitrogen heteroatoms. Compared with carbazole derivatives, phenothiazine ring acts as a stronger electron donor by virtue of the extra sulfur heteroatom.[36,37] Triphenyl amine is a well-known electron donor due to electron rich nitrogen atom and a famous hole transporting materials that have been widely employed as a constitutional unit for organic light-emitting diodes and organic photovoltaic functional materials.[18,19,38] As cyclic monomers, here we employed 10-methylene-9,10-dihydroanthryl-9-spiro-*p*-chlorophenylcyclopropane (MDS−Cl) and its bromo derivative (MDS−Br), which are vinylcyclopropane derivatives having halophenyl groups. Similar to the nonsubstituted cyclic monomer (MDS),[33,34] both MDS−Cl and MDS−Br undergo 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, as shown in Scheme 1. The radical ring-opening polymerization of the cyclic monomers, MDS−Cl and MDS−Br, afforded to novel alternating copolymers composed of the anthracene moiety and halostyrene unit. 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.[39−45] Incorporations of optoelectronic groups on the halogen moiety of the halostyrene unit were conducted by palladium-catalyzed postmodifications (Scheme 2). Resulting polymers are composed of the anthracene moiety in the main chain and additional optoelectronic moiety, triphenylamine, *N*-phenylcarbazole, and *N*-phenylphenothiazine, in the side chain. These copolymers can be regarded as nonconjugated copolymers

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



having perfect alternating structures, in which the alternate arrangement of two distinct electronic functionalities is formed owing to the ring-opening polymerization system.

Experimental Section

Materials. 2,2′-Azobis(isobutyronitrile) (AIBN, Kanto Chemical, 97%) was purified by recrystallization from methanol. The synthesis of benzyl dithiobenzoate (BDB) was conducted according to procedures reported previously.[46,47] BDB was purified by vacuum distillation using a glass tube oven (Shibata GTO-250RS) to give a red oil.

10-Diazoanthrone was prepared by the reaction of anthrone with tosylazide according to a method reported previously.[48] *p*-Chlorostyrene (Kanto Chemical, 98%), *p*-bromostyrene (ACROS, 96%), methyltriphenylphosphonium bromide (ACROS, 98%), *n*-BuLi (Kanto Chemical, 2.6 M hexane solution), toluene (dehydrated, Kanto Chemical, 99.5%) carbazole (Kanto Chemical, 97%), phenothiazine (Kanto Chemical, >98.0%), diphenyl amine (Tokyo Kasei Kogyo, >99.0%), sodium *tert*-butoxide (NaO-*t*-Bu, Tokyo Kasei Kogyo, >98.0%), tri-*tert*-butylphosphine (P(*t*-Bu), Wako Chemicals, 96%), and bis(dibenzylidene acetone)palladium ($Pd_2(dba)_3$, ACROS) were used as received. Other materials were used without further purification.

Monomer Synthesis. The cyclic monomer 10-methylene-9,10-dihydroanthryl-9-spiro-*p*-chlorophenylcyclopropane (MDS−Cl) was prepared by Wittig reaction of anthrone-9-spiro-*p*-chlorophenylcyclopropane (Scheme 3), according to a method reported previously.[25,33] The cyclopropane compound was prepared by the reaction of 10-diazoanthrone with vinyl monomer, *p*-chlorostyrene, according to the procedure reported in the literature[49] with slight modifications.

A solution of 10-diazoanthrone (4.40 g, 0.0194 mol) and 25.4 mL of *p*-chlorostyrene (27.7 g, 0.200 mol) in toluene (200 mL) was refluxed for 24 h. After the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure to give a yellow viscous product. The crude product was dissolved in a small amount of THF, then it was precipitated into methanol, and the precipitate, which corresponds to polymerized product, was removed by filtration. After the filtrate was evaporated under reduced pressure, the product was finally purified by recrystallization from ethanol/CH_2Cl_2 (v/v = 5/1) to give a yellow solid (2.44 g, 55%); mp = 152 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.57 (m, 2H, CH_2CH−Ar), 3.08 (t, 1H, CH_2CH−Ar), 6.47−7.66 (m, 10H, Ar), 8.30−8.45 (dd, 2H, *C*H−C−C═O in Ar).

The cyclic monomer was prepared by Wittig reaction of anthrone-9-spirophenylcyclopropane derivative according to a method reported previously with some modifications.[33] Methyltriphenylphosphonium bromide (4.35 g, 12.1 mmol) and dry THF (40 mL) were placed in a 200 mL three-necked flask. The hexane solution of *n*-BuLi (2.6M, 4.19 mL, 10.8 mmol) was added dropwise to the mixture at 0 °C by external ice-bath cooling, and then the resulting mixture was stirred at room temperature for 30 min. Then, anthrone-9-spiro-*p*-chlorophenylcyclopropane (3.00 g, 9.1 mmol) in dry THF (40 mL) was added gradually to the reaction mixture, and it was continued at room temperature for 1.5 h. After the reaction, the mixture was dropped into a large excess of diethyl ether. The precipitate, which corresponds to phosphonium oxide, was filtered off and the filtrate was evaporated under reduced pressure to give a crude product. The crude monomer was purified by reprecipitation into hexane, and by column chromatography on silica with hexane/ethyl acetate (v/v = 5/1) as the eluent to afford a pale yellow solid (1.10 g, 28%). ^{1}H NMR ($CDCl_3$): δ (ppm) 2.28−2.37 (m, 3H, CH_2CH−Ar), 5.64 (d, 2H, CH_2═C), 6.79−7.69 (m, 12H, Ar). Note that the monomer, MDS−Cl, was highly reactive and the neat product could not be handled at room temperature. In order to avoid unfavorable polymerization reaction, the purified product was diluted with toluene immediately after the column purification and the evaporation of the eluent was conducted under mild conditions. Typically, a stock solution (0.335M) containing the cyclic monomer (MDS−Cl) and toluene was prepared in a silanized glass tube capped with a two-way glass stopper under nitrogen, and stored in the dark around 0 °C.

Similarly, 10-methylene-9,10-dihydroanthryl-9-spiro-*p*-bromophenylcyclopropane (MDS−Br) was prepared by Wittig reaction of anthrone-9-spiro-*p*-bromophenylcyclopropane, which was prepared by the reaction of 10-diazoanthrone with *p*-bromostyrene. Anthrone-9-spiro-*p*-bromophenylcyclopropane was obtained as a yellow solid (yield = 30%); mp = 145 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.55 (m, 2H, CH_2CH−Ar), 3.04 (t, 1H, CH_2CH−Ar), 6.42−7.70 (m, 10H, Ar), 8.38−8.43 (dd, 2H, *C*H−C−C═O in Ar). MDS−Br was obtained as a yellow solid (yield = 27%). ^{1}H NMR ($CDCl_3$): δ (ppm) 2.29−2.36 (m, 3H, CH_2CH−Ar), 5.64 (d, 2H, CH_2═C), 6.79−7.69 (m, 12H, Ar).

The ^{1}H NMR spectra of the cyclopropane compounds and the cyclic monomers, MDS−Cl and MDS−Br, are shown in Figures S1 and S2, respectively (see Supporting Information).

General Polymerization Procedure. For a typical polymerization, the toluene solution of MDS−Cl (0.335 mol/L, 1.82 mL, 0.61 mmol), BDB (3.0 mg, 0.012 mmol), and AIBN (1.0 mg, 0.006 mmol) were placed in a silanized glass ampule equipped with a magnetic stirring bar. Then, the orange color solution, which may be originated from yellow color of the monomer (MDS−Cl) mixed with red-color of BDB used as CTA, was degassed by three freeze−evacuate−thaw cycles. The ampule was flame-sealed off under vacuum, and it was stirred at 80 °C for desired time. The characteristic orange color solution was changed gradually into a heterogeneous system, in which yellow precipitate was formed during the polymerization. The reaction was stopped by rapid cooling with liquid nitrogen. After the reaction mixture was cooled to room temperature, the precipitate, which correspond to unfavorable side product obtained by dimerization, was filtered off and the filtrate 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 give an orange-tinged yellow solid. The polymer yield determined gravimetrically from the diethyl ether-insoluble polymer sample was 42%. For the determination of the monomer conversion, the ^{1}H NMR spectrum of the polymerization mixture was measured in $CDCl_3$. The monomer conversion determined by a comparison of the integration of the monomer CH_2═C resonance (2H) at around 5.6 ppm to the intensity of the methylene and methine peaks (CH_2CHCH_2) of the polymer at 3.3−4.2 ppm was 72%.

The resulting polymer was soluble in chloroform, THF, and DMF, while insoluble in acetonitrile, diethyl ether, hexane, methanol, and water. ^{1}H NMR ($CDCl_3$): δ (ppm) 3.3−4.2 (broad, 5H, CH_2−CH−CH_2), 6.5−8.5 (broad, 12H, Ar).

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

$$M_{\mathrm{n}}(\mathrm{theor}) = \frac{[\mathrm{monomer}]_0}{[\mathrm{CTA}]_0} \times M_{\mathrm{monomer}} \times \mathrm{yield} + M_{\mathrm{CTA}} \quad (1)$$

where M_{CTA} and M_{Monomer} are molecular weights of chain transfer agent and monomer, and $[\mathrm{monomer}]_0$ and $[\mathrm{CTA}]_0$ are the initial concentrations of monomer and chain transfer agent, respectively.

Table 1. Radical Polymerization of 10-Methylene-9,10-dihydroanthryl-9-spiro-halophenylcyclopropane with 2,2′-Azobis(isobutyronitrile) (AIBN) in Toluene in the Presence and Absence of Chain Transfer Agent (CTA) [a]

run	monomer[b]	[M]/[CTA] /[I]	yield[c] (%)	M_n[d] (theory)	M_n[e] (SEC)	M_w/M_n[e] (SEC)
1	MDS−Cl	100/0/1	45		14 600	1.52
2		100/2/1	42	7100	7500	1.25
3		100/5/1	33	2400	4900	1.39
4	MDS−Br	100/0/1	38		10 900	1.92
5		100/2/1	32	6200	6500	1.85

[a] Conditions: solvent = toluene, temperature = 80 °C, time = 20 h, [M] = 0.335 mol/L, and chain transfer agent (CTA) = benzyl dithiobenzoate (BDB). [b] MDS−Cl = 10-methylene-9,10-dihydroanthryl-9-spiro-*p*-chlorophenylcyclopropane, and MDS−Br = 10-methylene-9,10-dihydroanthryl-9-spiro-*p*-bromophenylcyclopropane. [c] Diethyl ether insoluble part. [d] The theoretical molecular weight ($M_{n,\,theory}$) = (MW of M) × $[M]_0/[CTA]_0$ × yield + (MW of CTA). [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.

Postmodifications. A typical reaction procedure is as follows. Poly(MDS−Br) (0.0573 g, M_n = 12400, M_w/M_n = 2.00, 0.154 unit-mmol), diphenylamine (DPA, 0.761 g, 4.5 mmol), sodium *tert*-butoxide (NaO-*t*-Bu, 0.216 g, 2.25 mmol), and $Pd_2(dba)_3$ (0.034 g, 0.038 mmol) were placed in a 100 mL flask under nitrogen atmosphere. Then, 1,4-dioxane (25 mL) and tri-*tert*-butylphosphine ($P(t\text{-}Bu)_3$, 1.63 M 1,4-dioxane solution, 0.138 mL, 0.23 mmol) were added to the solution at room temperature. The reaction mixture was stirred at 100 °C for 24 h. After cooling to room temperature, the mixture was quenched by the addition of aqueous ammonia (100 mL), and the product was extracted three times with $CHCl_3$. The product was purified by two times reprecipitation into acetonitrile, and two times into diethyl ether. The resulting product was finally dried under vacuum at room temperature to give poly(MDS−DPA) as a brownish gray solid (0.0555 g, 80%). Similarly, the palladium-catalyzed reactions of carbazole (CZ) and phenothiazine (PTZ) into the bromostyrene unit in poly(MDS−Br) afforded poly(MDS−CZ) and poly(MDS−PTZ) as a brownish gray solid and navy blue solid, respectively. These resulting polymers were soluble in chloroform, THF, and DMF, while insoluble in acetonitrile, diethyl ether, methanol, and water.

The same palladium-catalyzed reaction was also employed for the preparation of model compounds, *N*-phenylcarbazole and *N*-phenylphenothiazine, which were prepared by the reaction of bromobenzene with carbazole and phenothiazine, respectively.

Instrumentation. ^1H and ^{13}C NMR spectra were recorded with a JEOL JNM-ECX400. Elemental analysis was carried out on a Perkin-Elmer 2400 II CHNS/O analyzer. Number-average molecular weight (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-guardcolumn 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.

The UV−vis spectra were recorded using a JASCO V-630BIO UV−vis spectrophotometer. Fluorescence spectra were obtained from a JASCO FP-6100 spectrofluorophotometer. Thermogravimetric analysis (TGA) was performed on a SEIKO SSC/5200 at a heating rate of 10 °C/min under N_2.

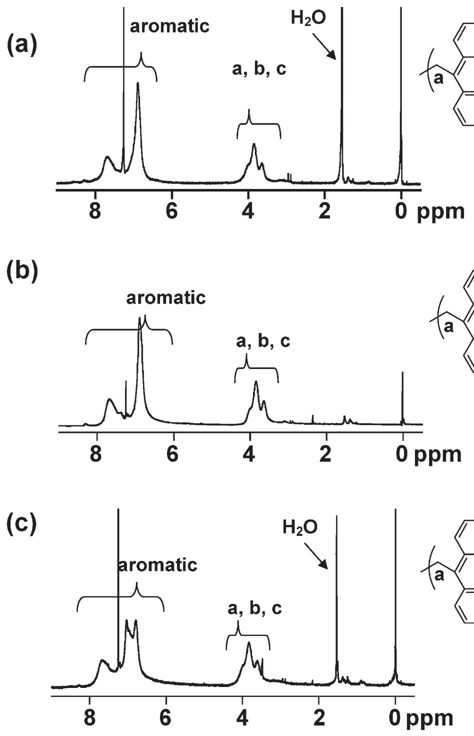


Figure 1. ^1H NMR spectra ($CDCl_3$) of polymers obtained by (a) free radical polymerization of 10-methylene-9,10-dihydroanthryl-9-spiro-*p*-chlorophenylcyclopropane (MDS−Cl), (b) reversible addition−fragmentation chain transfer (RAFT) polymerization of MDS−Cl, and (c) RAFT polymerization of 10-methylene-9,10-dihydroanthryl-9-spiro-*p*-bromophenylcyclopropane (MDS−Br).

Results and Discussion

Polymerization of Cyclic Monomers. Free radical polymerization of the cyclic monomers, MDS−Cl and MDS−Br, was carried out with AIBN as an initiator in toluene at 80 °C for 20 h, and the results are summarized in Table 1. When the polymerization of MDS−Cl was conducted at $[M]_0/[AIBN]_0$ = 100/1, the polymer yield was 45%, and the resulting polymer had M_n = 14600 and M_w/M_n = 1.52 according to SEC in THF using polystyrene calibration. Figure 1a shows the ^1H NMR spectrum of the polymer obtained by the free radical polymerization of MDS−Cl. The comparison of the ^1H NMR spectra of MDS−Cl (see Figure S1b, Supporting Information) and poly(MDS−Cl) reveals that the signals of the cyclopropane ring observed at 2.2−2.4 ppm disappear after the polymerization. The characteristic peaks at 3.3−4.2 ppm are clearly visible, which are attributed to the methylene and methine protons of the backbone formed by ring-opening polymerization of MDS−Cl. In addition to these peaks, broad peaks around 6.0−8.5 ppm are observed, which correspond to the aromatic protons of the anthracene unit. Similar ^1H NMR spectrum was observed in the polymer prepared by the free radical polymerization of the nonsubstituted cyclic monomer, MDS.[25] The ^{13}C NMR spectrum of poly(MDS−Cl) obtained by the free radical polymerization is presented in Figure 2a. In addition to the peaks attributed to the aromatic carbons at 123−145 ppm, two characteristic peaks are clearly observed at 49.0 and 33.7 ppm, which are attributable to two different aliphatic carbons in the polymer backbone formed by the ring-opening process of MDS−Cl. More importantly, the signals of the cyclopropane ring at 39.0 and 12.6 ppm, which were observed

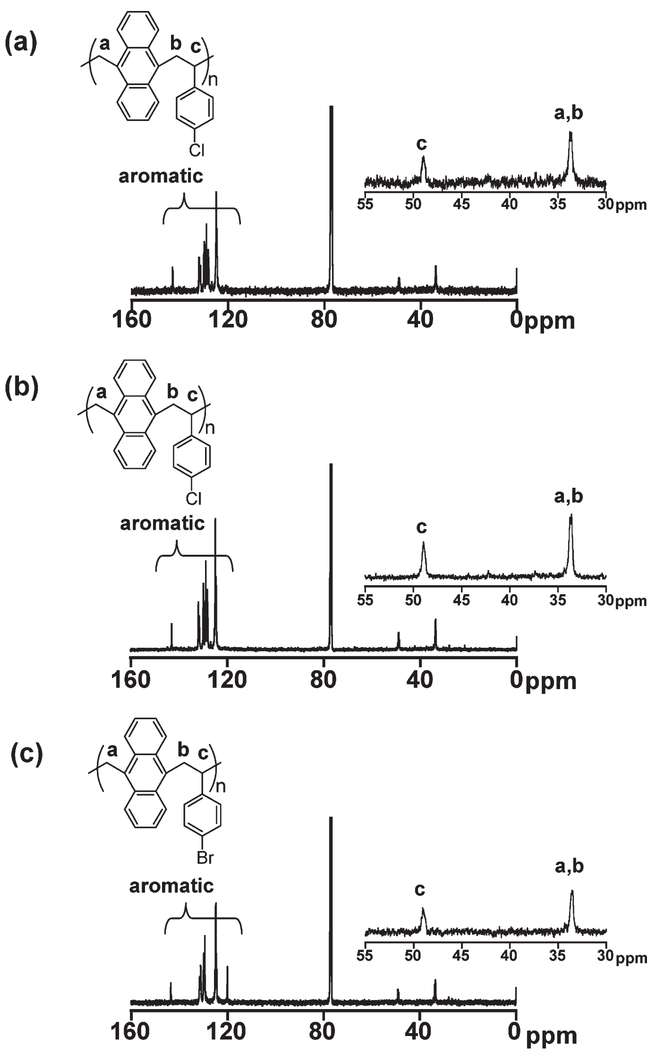


Figure 2. ^{13}C NMR spectra ($CDCl_3$) of polymers obtained by (a) free radical polymerization of 10-methylene-9,10-dihydroanthryl-9-spiro-*p*-chlorophenylcyclopropane (MDS−Cl), (b) reversible addition−fragmentation chain transfer (RAFT) polymerization of MDS−Cl, and (c) RAFT polymerization of 10-methylene-9,10-dihydroanthryl-9-spiro-*p*-bromophenylcyclopropane (MDS−Br).

in the spectrum of the cyclic monomer (MDS−Cl, see Figure S3, Supporting Information), are invisible in the resulting polymer. These results suggest that the ring-opening of MDS−Cl proceeds predominantly during radical polymerization, which should be due to the strain release of the cyclopropane ring, aromatization, and the formation of a stable benzyl radical. The resulting poly(MDS−Cl) can be regarded as an alternating copolymer composed of the anthracene and chlorostyrene units in the main chain.

The free radical polymerization of MDS−Br under the same conditions afforded a polymer having a lower molecular weight and broader molecular weight distribution, with a slight decrease in the polymer yield (Table 1). The polymers obtained from both MDS−Cl and MDS−Br were soluble in chloroform, THF, DMF, while insoluble in diethyl ether, acetonitrile, and water. Relatively low polymer yields in both cases may be due to unfavorable side reactions. In a previous communication,[25] we reported that unfavorable side reactions, such as dimerization, may take place during the free radical homopolymerization of the nonsubstituted cyclic monomer, MDS, which led to the decrease in the polymer yield. In the cases of the free radical polymerizations of MDS−Cl and MDS−Br, the same side reactions may occur, regardless of the substituent group on the benzene ring.

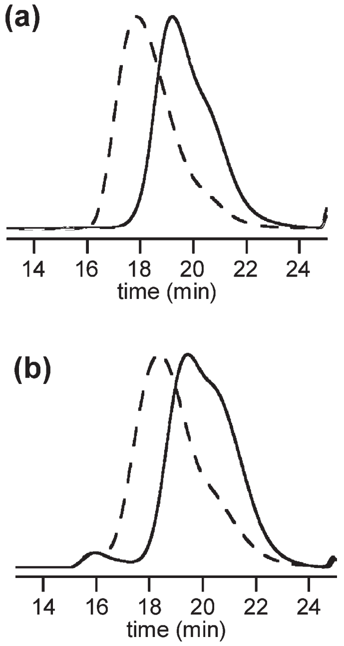


Figure 3. Size-exclusion chromatography (SEC) traces of (a) poly(MDS−Cl)s and (b) poly(MDS−Br)s prepared by free radical polymerization (dotted line) and RAFT polymerization at [monomer]/[chain transfer agent]/[initiator] = 100/2/1 (solid line). See Table 1 for detailed polymerization conditions.

RAFT polymerization of the cyclic monomers were conducted using benzyl dithiobenzoate (BDB), which proved efficient as a chain transfer agent (CTA) for obtaining the polymer with relatively low polydispersity by radical polymerization of MDS.[25] The results are summarized in Table 1. When the polymerization of MDS−Cl was carried out using BDB with AIBN at $[M]_0/[CTA]_0/[AIBN]_0 = 100/2/1$ in toluene at 80 °C for 20 h, the soluble polymer was obtained as an orange-tinged yellow solid. Note that the orange-tinged yellow color may be originated from red-color of the fragments of CTA mixed with pale yellow color of the anthracene-based polymer, even if RAFT polymers using BDB mediator generally appear reddish after precipitation. The polymer yield was 42%, which is comparable to that in the case of free radical polymerization. The number-average molecular weight, measured by a SEC, was $M_n = 7500$, which is comparable to the theoretical value ($M_{n,theory} = 7100$) calculated from the monomer/CTA molar ratio and the polymer yield. The molecular weight distribution was relatively narrow ($M_w/M_n = 1.25$), even if a shoulder peak at lower molecular weight region could be detected in SEC trace of poly(MDS−Cl) prepared by RAFT polymerization (Figure 3a). In contrast, poly(MDS−Cl) prepared by free radical polymerization showed a broad tailing at lower molecular weight region. Figure 1b shows the ^{1}H NMR spectrum of the polymer obtained by RAFT polymerization of MDS−Cl at $[M]_0/[CTA]_0/[AIBN]_0 = 100/2/1$. The characteristic peaks corresponding to the methylene and methine protons of the backbone and the aromatic protons of the anthracene unit are clearly visible at 3.3−4.2 and 6.5−8.5 ppm, respectively. The ^{13}C NMR spectrum of the resulting polymer (Figure 2b) shows resonances attributed to aromatic carbons at 123−145 ppm and two different aliphatic carbons in the polymer backbone at 48.9 and 33.6 ppm. These ^{1}H and ^{13}C NMR analyses suggest that the ring-opening reaction of MDS−Cl predominantly takes place during the polymerization of

Table 2. Palladium-Catalyzed Modification of Poly(MDS−Cl) and Poly(MDS−Br) with Optoelectronic Compound Having Secondary Amino Group [a]

run	polymer[b]	reactant	N content (%)[c]	conversion (%)[d]	yield (%)[e]
1	poly(MDS−Cl)	diphenyl amine	0.63	15	52
2	poly(MDS−Br)	diphenyl amine	2.86	90 (>99[f])	80
3	poly(MDS−Cl)	carbazole	0.27	6.3	36
4	poly(MDS−Br)	carbazole	2.62	83 (88[f])	58
5	poly(MDS−Cl)	phenothiazine	1.50	41	74
6	poly(MDS−Br)	phenothiazine	2.94	> 99 (>99[f])	54

[a] Reaction was conducted in the presence of NaO-*t*-Bu (15 equiv for the *p*-halostyrene unit), $Pd_2(dba)_3$ (25 mol % for the *p*-halostyrene unit), and ligand ($P(t\text{-}Bu)_3$, P/Pd ratio = 3/1) in 1,4-dioxane at 100 °C for 24 h. [b] Poly(MDS−Cl) = poly(10-methylene-9,10-dihydroanthryl-9-spiro-*p*-chlorophenylcyclopropane) and Poly(MDS−Br) = poly(10-methylene-9,10-dihydroanthryl-9-spiro-*p*-bromophenylcyclopropane). [c] Determined by elemental analysis. [d] Conversion of the postmodification (degree of the substitution) was calculated from the N content. [e] Acetonitrile-insoluble part. The yield of the product was calculated on the basis of the amount of the poly(MDS−Cl) or poly(MDS−Br) in the feed and the conversion determined by elemental analysis. [f] Measured by ^1H NMR.

MDS−Cl, regardless of the presence and absence of CTA. These results also suggest that RAFT polymerization of MDS−Cl under suitable conditions proceeded smoothly to afford well-defined alternating copolymer composed of the anthracene and chlorostyrene units in the main chain.

The polymerization of MDS−Cl was also conducted under various conditions. As shown in Table 1, the polymerization at higher CTA-to-initiator ratio ($[CTA]_0/[AIBN]_0 = 5/1$) gave a polymer having a lower molecular weight with a slight decrease in the polymer yield. We also investigated the influences of the solvent (toluene, DMF, chlorobenzene, 1,4-dioxane), monomer concentration (0.168 - 0.335 M), the CTA-to-initiator ratio in different solvents, and stabilizer (triethylenediamine) in terms of the monomer conversion, yield, molecular weights, and the polydispersity of the resulting poly(MDS−Cl)s (see Tables S1−3, Figures S4−6 in Supporting Information). In many cases, a small shoulder peak at high molecular weight region and/or a shoulder peak at low molecular weight region were detected in the SEC traces. The peak at high molecular weight region is most probably attributed to species arising from bimolecular termination reactions of the growing polymer chains. Another possible explanation is the formation of high molecular weight polymer with different structure or mixed structure, in which some units may have fast polymerization rate, forming the higher molecular weight polymers. From these preliminary experimental results, we concluded that the polymerization of MDS−Cl at $[M]_0/[CTA]_0/[AIBN]_0 = 100/2/1$ in toluene ($[M] = 0.335$ mol/L) at 80 °C was the most efficient to obtaining poly(MDS−Cl) having low polydispersity.

RAFT polymerization of MDS−Br was also conducted with BDB under the suitable conditions. As shown in Table 1, the resulting polymer had an $M_n = 6500$, which is comparable to the theoretical value ($M_{n,theory} = 6200$), and $M_w/M_n = 1.85$. The comparison of the conventional radical polymerization and RAFT polymerization of MDS−Br reveals that the addition of CTA leads to the decreases in the molecular weight and polymer yield, which is consistent with the general tendency. As shown in Figure 3b, a small peak at high molecular weight region and a shoulder peak at low molecular weight region can be seen in the SEC trace. Nevertheless, the characteristic resonances at 3.5−4.5 (methylene and methine protons) and 6.5−8.5 ppm (phenyl and anthryl) are clearly observed in the ^1H NMR spectrum of the poly(MDS−Br), as can be seen in Figure 1. In the ^{13}C NMR spectrum of the resulting polymer (Figure 2c), in addition to the resonances attributed to aromatic carbons at 123−145 ppm, two characteristic resonances are clearly observed at 49.1 and 33.6 ppm, which are attributable to two different aliphatic carbons in the polymer backbone. There is no significant difference in the ^{13}C NMR signals between the polymers obtained by RAFT polymerizations of MDS−Cl and MDS−Br. This indicates that the most of the cyclopropane ring in these cyclic monomers are opened and the polymerization predominantly proceeds via the radical ring-opening process, independent of the substituent group on the benzene ring.

Postmodifications. Incorporations of photoactive chromophores on the halogen moieties of the alternating copolymers were conducted by postmodifications. Palladium-catalyzed reactions of the halostyrene unit with photoactive compounds having an N−H bond were conducted using bis(dibenzylidene acetone)palladium ($Pd_2(dba)_3$) as a catalyst, sodium *tert*-butoxide (NaO-*t*-Bu) as a base, and tri-*tert*-butylphosphine ($P(t\text{-}Bu)_3$) as a ligand according to procedures reported previously.[50,51] These reactions can be regarded as Pd-catalyzed amination of the aryl halides with an arylamine (Scheme 2a) and heteroarenes containing N−H bond (Scheme 2b). Table 2 summarizes the results of the palladium-catalyzed reactions of poly(MDS−Cl) and poly(MDS−Br) using diphenylamine (DPA), carbazole (CZ), and phenothiazine (PTZ) under several conditions. The conversion of the postmodification was calculated from elemental analysis (nitrogen content) and ^1H NMR. The yield of the product was calculated on the basis of the amount of the *p*-halostyrene unit in the feed and the conversion.

When the reaction was conducted at $[\text{diphenylamine}]_0/[\text{MDS−Br unit}]_0/[\text{NaO-}t\text{-Bu}]_0/[Pd_2(dba)_3]_0/[P(t\text{-Bu})_3]_0 = 300/10/150/2.5/15$ in dioxane at 100 °C for 24 h, the introduction of the diphenylamine (DPA) on the bromostyrene unit proceeded smoothly with a relatively high conversion to afford alternating copolymer composed of the anthracene unit in the main chain and triphenyl amine unit in the side chain (Scheme 2a). The ^1H NMR spectrum of the product, poly(MDS−DPA), is shown in Figure 4a. All characteristic proton signals from the methylene and methine main chain (3.5−4.5 ppm) and phenyl and anthryl groups (6.5−8.5 ppm) can be identified. The comparison of the ^1H NMR spectra of the poly(MDS−DPA) and poly(MDS−Br) used as a starting polymer reveals the increase in the peak intensity of the aromatic signals after the postmodification. The conversion calculated by comparison of the signals at 3.5−4.5 ppm corresponding to the methine and methylene protons in the main chain to the signal at 6.5−8.5 ppm corresponding to aromatic protons is > 99%, which is in fair agreement with the value determined by the elemental analysis. Palladium-catalyzed reactions of other optoelectronic compounds, carbazole (CZ) and phenothiazine (PTZ), into the bromostyrene unit proceeded with high conversion. The structures of the resulting polymers, poly(MDS−CZ) and poly(MDS−PTZ), were also confirmed by ^1H NMR measurements (Figure 4). In contrast, the conversions of the postmodifications were relatively low in the cases of the modifications on the chlorostyrene unit of poly(MDS−Cl). These results indicate that the Pd-catalyzed reaction is effective to introduce additional optoelectronic component into the bromostyrene unit of the anthracene-based polymer to produce novel alternating copolymers having two distinct electronic functionalities with high conversions (degrees of the substitution) and recoveries.

Optical and Thermal Properties. For the investigation of characteristic optoelectronic properties, we employed three polymers having different substituent groups, poly(MDS−DPA), poly(MDS−CZ), and poly(MDS−PTZ), which were modified with diphenylamine (DPA), carbazole (CZ), and phenothiazine (PTZ), respectively. Three modified polymers and original poly(MDS−Br) having similar molecular weights were employed for the evaluation (Table 3). Figure 5a depicts the absorbance spectra of the poly(MDS−Br) and modified polymers in $CHCl_3$. All anthracene-containing polymers 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 intensities of the first band in the modified polymers are apparently higher than those of original poly(MDS−Br). The modified polymers also exhibit first absorption band around 260 nm and second absorption at 330−430 nm, indicating sufficient incorporation of the anthracene group in the modified polymers. In addition to the peaks attributed to anthracene units, an additional peak is visible at 306 nm for poly(MDS−DPA), 294 nm for poly(MDS−CZ), and 320 nm for poly(MDS−PTZ), respectively. These additional absorptions were also employed for the excitation.

The fluorescence spectra of the anthracene-containing polymers excited at 384 nm, corresponding to the absorption wavelength of the anthracene unit, are shown in Figure 5b. The emission of the poly(MDS−Br) 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 550 nm. In fact, the absorbance and fluorescence of poly(MDS−Br) were comparable to those of the poly(MDS) and poly(MDS−Cl) (Figure S7, see Supporting Information), indicating sufficient incorporation of the anthracene group in the polymers obtained from MDS−Cl and MDS−Br. These fluorescent peaks of poly(MDS−Br) are almost the same as those of poly(MDS−CZ) with slight difference in

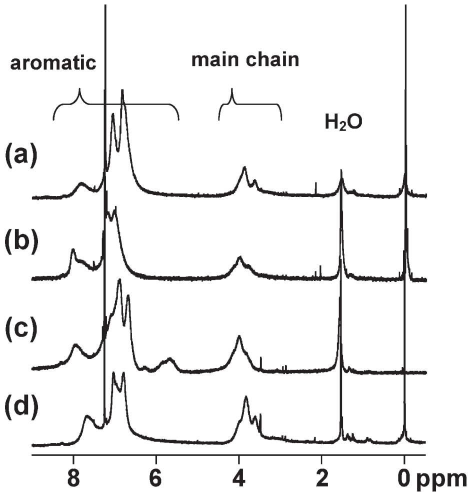


Figure 4. ^1H NMR spectra ($CDCl_3$) of the products, (a) poly(MDS−DPA), (b) poly(MDS−CZ), (c) poly(MDS−PTZ), obtained by the postmodifications with diphenylamine (DPA), carbazole (CZ), phenothiazine (PTZ), respectively, and (d) poly(MDS−Br) used as a starting material.

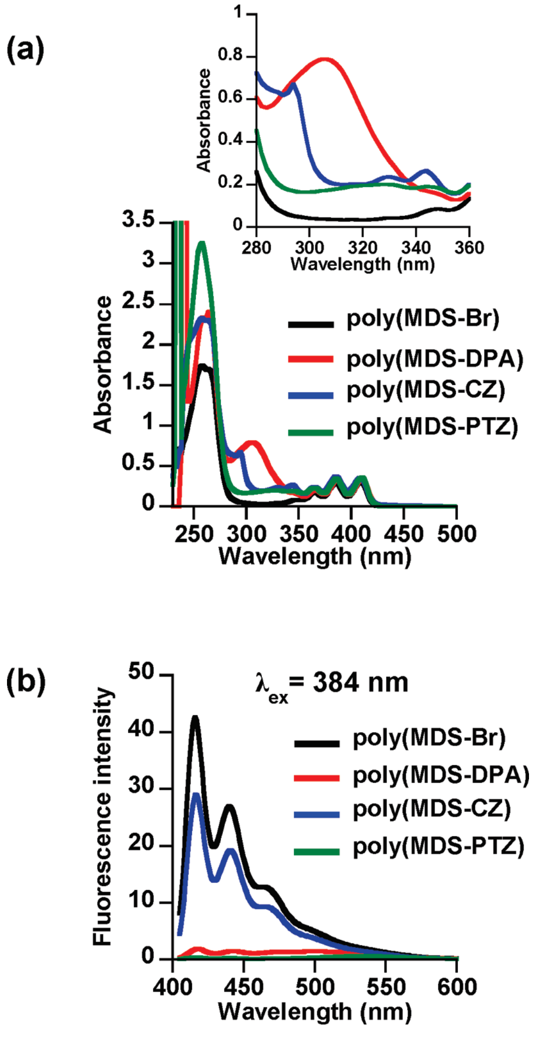


Figure 5. (a) Absorption spectra (concentration = 3.4×10^{-5} anthracene unit mol/L) and (b) fluorescence spectra in $CHCl_3$ (concentration = 1.7×10^{-6} anthracene unit mol/L, λ_{ex} = 384 nm) of poly(MDS−Br) (black line) and the anthracene-containing polymers modified with diphenylamine (poly(MDS−DPA), red line), carbazole (poly(MDS−CZ), blue line), phenothiazine (poly(MDS−PTZ), green line), respectively. See Table 3 for detailed sample information.

Table 3. Summary of Alternating Polymers [a]

run	polymer[b]	M_n[c] (M_w/M_n)[c]	T_{d10}[d] (°C)	solubility[e]				
				DMF	THF	$CHCl_3$	acetonitrile	Et_2O
1	poly(MDS−DPA)	8100 (1.50)	368	+	+	+	−	−
2	poly(MDS−CZ)	7000 (1.76)	354	+	+	+	−	−
3	poly(MDS−PTZ)	7900 (1.52)	382	+	+	+	−	−
4	poly(MDS−Br)	12400 (2.00)	335	+	+	+	−	−

[a] Prepared by radical polymerization of 10-methylene-9,10-dihydroanthryl-9-spiro-*p*-bromophenylcyclopropane (MDS−Br) and postmodifications. [b] The anthracene-containing polymers, poly(MDS−DPA), poly(MDS−CZ), and poly(MDS−PTZ), modified with diphenylamine, carbazole, and phenothiazine, respectively. [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 TGA; heating rate: 10 °C/min, N_2 atmosphere. [e] "+" = soluble at room temperature; "−" = insoluble at room temperature.

the peak intensities (Figure 5b). In contrast, poly(MDS−DPA) and poly(MDS−PTZ) show extremely low peak intensities, which are apparently different from those of the original poly(MDS−Br). We also conducted absorbance and fluorescence measurements in different solvents (DMF and THF), suggesting no significant influence of the solvent on the optoelectronic properties of poly(MDS−Br), as shown in Figure S8 (see Supporting Information). On the basis of these absorbance and fluorescence spectra, it is reasonable to consider that the interaction of the anthracene unit and phenylcarbazole unit in poly(MDS−CZ) is different from those of the anthracene/triphenylamine units in poly(MDS−DPA) and the anthracene/phenylphenothiazine units in poly(MDS−PTZ).

Figure 6a shows the fluorescence spectra of poly(MDS−DPA) obtained by irradiation of the $CHCl_3$ solution at 306 nm, corresponding to the absorption wavelength of the triphenylamine unit in the poly(MDS−DPA). As comparisons, fluorescent peaks of poly(MDS−Br) used as a staring material and triphenylamine were measured independently under the same conditions. A model compound, triphenylamine, shows a broad peak from 400 to 600 nm with a maximum at 530 nm in the fluorescent spectrum. In contrast, poly(MDS−DPA) exhibits peaks at around 420, 445, and 470 nm, which are attributed to the anthracene unit. In the case of poly(MDS−Br), the intensities of the peaks attributed to the anthracene unit decrease apparently, which is due to the absence of triphenylamine unit.

These behaviors could be explained by fluorescence resonance energy transfer (FRET). In general, FRET is referred to as an energy transfer between FRET donor and acceptor, and the efficiency of FRET is very sensitive to the distance between fluorescent donor and acceptor. In our system, the anthracene unit and optoelectronic unit formed by postmodification are close enough to interact, because of the nonconjugated main chain with a predominantly alternating structure. In order to achieve successful FRET efficiency, both donor and acceptor do not significantly overlap with each other, and the emission spectrum of FRET donors overlaps sufficiently with the absorption spectrum of FRET acceptor. As shown in Figure 5a, the maximum absorptions of the anthracene unit at 330−430 nm do not significantly overlap with those at 290−330 nm, which are attributed to the optoelectronic group formed after the postmodification. In the case of poly(MDS−DPA), the increases in the intensities of the anthracene-based peaks, compared with those of the original poly(MDS−Br), are apparently observed with the decrease in the intensity of the triphenylamine-based peak by the excitation at 306 nm. It means that successful FRET occurs from the triphenylamine unit to the anthracene unit. In the case of the excitation at 384 nm, corresponding to the absorption wavelength of the anthracene unit, the energy transfer may take place from the anthracene unit to the triphenylamine unit without emission, resulting in the drastic decrease in the anthracene-based fluorescent peaks. Similar behavior was reported in a series of silylene-spaced divinylarene copolymers having alternating donor−acceptor chromophores that exhibit efficient intrachain energy or electron transfer.[52,53] Luh et al. demonstrated efficient photoinduced electron transfer from amino styrene moiety to anthracene chromophore in the nonconjugated copolymers having a silylene moiety as an insulating spacer.[52]

The fluorescence spectra of poly(MDS−CZ), poly(MDS−Br), and phenylcarbazole were observed by irradiation of the $CHCl_3$ solution at 294 nm, corresponding to the absorption wavelength of the phenylcarbazole unit in the poly(MDS−CZ). As can be seen in Figure 6b, a broad peak at 340−400 nm is seen in the fluorescent spectrum of a model compound, phenylcarbazole, whereas the peak is invisible in the spectrum of poly(MDS−CZ). The poly(MDS−CZ) exhibits strong peaks at 400−570 nm, corresponding to the anthracene unit, which are apparently higher than those of poly(MDS−Br). These results suggest that FRET occurs effectively from the phenylcarbazole unit to the anthracene unit. Similar energy transfer between phenylcarbazole donor and anthracene-based acceptor was observed in Langmuir−Blodgett (LB) films, in which the donor and acceptor could be separately precisely by inert spaces.[20] In contrast, the strong peaks attributed to the anthracene unit are detected in the fluorescent spectrum exited at 384 nm (Figure 5b), indicating negligible energy transfer from the anthracene unit to the phenylcarbazole unit.

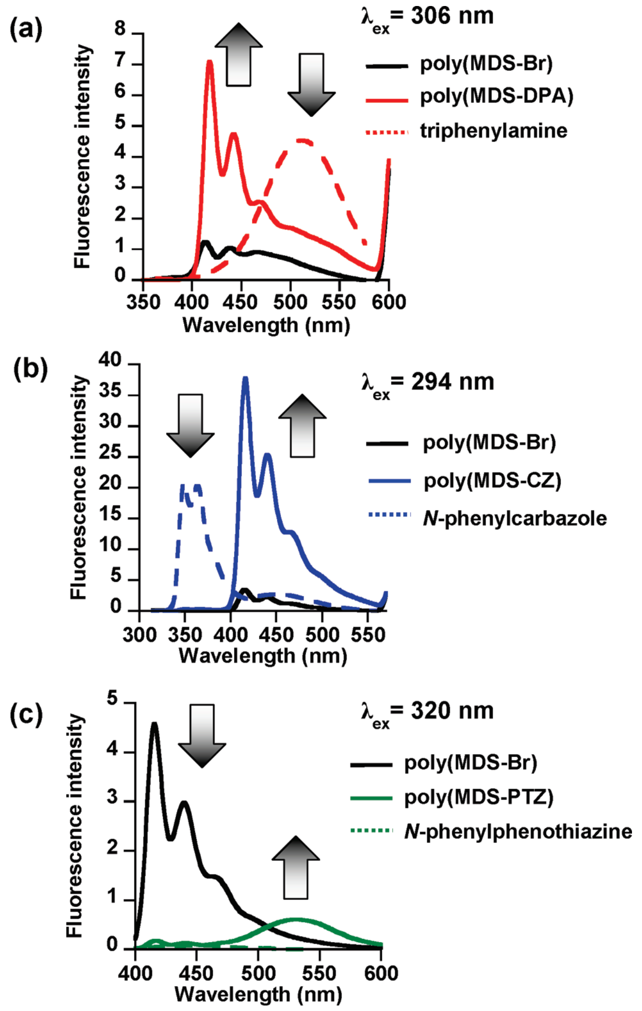


Figure 6. Fluorescence spectra of the modified polymers, model compounds, original poly(MDS−Br) in $CHCl_3$. (a) poly(MDS−DPA) (concentration = 1.5×10^{-6} triphenylamine unit mol/L, λ_{ex} = 306 nm), (b) poly(MDS−CZ) (concentration = 1.4×10^{-6} *N*-phenylcarbazole unit mol/L, λ_{ex} = 294 nm), and (c) poly(MDS−PTZ) (concentration = 1.7×10^{-6} *N*-phenylphenothiazine unit mol/L, λ_{ex} = 320 nm). The concentrations of the anthracene unit of the modified polymers were adjusted to the same to that of poly(MDS−Br) (concentration = 1.7×10^{-6} anthracene unit mol/L). See Table 3 for detailed sample information.

When poly(MDS−PTZ) was excited at 320 nm, corresponding to the absorption wavelength of the phenylphenothiazine unit in the poly(MDS−PTZ), the emission in the range of 450 and 600 nm with a maximum at 530 nm is seen (Figure 6c). The emission maxima at around 420, 445, and 470 nm are hard to detect in poly(MDS−PTZ), suggesting that peak intensities ascribed to the anthracene unit decreases drastically after the

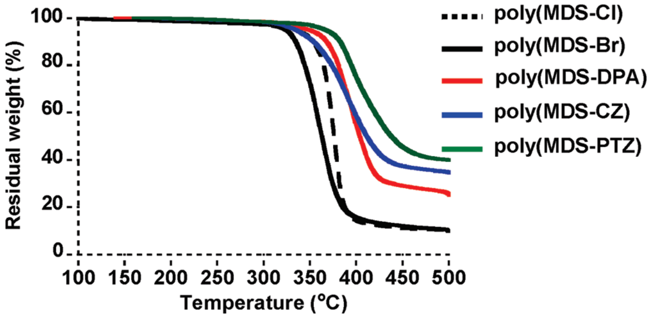


Figure 7. Thermogravimetric analysis (TGA) thermograms of poly(MDS−Br) (black solid line), poly(MDS−Cl) (black dotted line) and the anthracene-containing polymers modified with diphenylamine (poly(MDS−DPA), red line), carbazole (poly(MDS−CZ), blue line), phenothiazine (poly(MDS−PTZ), green line), respectively.

introduction of the phenothiazine moiety on poly(MDS−Br). From these results, it is reasonable to consider that only energy transfer occurs from the anthracene unit to the phenylphenothiazine unit without emission. By the excitation at 384 nm, the energy transfer may take place from the anthracene unit to the triphenylamine unit without emission, resulting in the drastic decrease in the anthracene-based fluorescent peaks (Figure 5b).

To obtain the information on the energy transfer behaviors, we conducted control experiments using model mixtures of poly(MDS) with the optoelectronic molecules, triphenylamine, *N*-phenylcarbazole, and *N*-phenylphenothiazine, respectively. Fluorescent spectra of the model mixtures were compared with those of the modified polymers, poly(MDS−DPA), poly(MDS−CZ), and poly(MDS−PTZ) (Figures S9 and S10, see Supporting Information). As expected, the fluorescent spectra of the model mixtures exited at 384 nm, corresponding to the absorption wavelength of the anthracene unit, were almost the same to those of poly(MDS), which were apparently different from those of poly(MDS−DPA) and poly(MDS−PTZ). When the measurements were conducted upon the excitation at 306, 294, 320 nm, corresponding to the absorption wavelengths of the triphenylamine, *N*-phenylcarbazole, and *N*-phenylphenothiazine, the fluorescent spectra of the model mixtures were consistent with those of the corresponding optoelectronic molecules. These results indicate that the energy transfer is hard to occur in the model mixtures, which may be due to the fact that the anthracene unit in poly(MDS) is far apart from the optoelectronic molecule in the dilute solution. In other words, the energy transfers take place only in the modified polymers, in which the anthracene unit is close enough to the optoelectronic unit in the nonconjugated main chain with a predominantly alternating structure.

The thermal properties of the modified polymers were evaluated by thermogravimetric analysis (TGA) measurements. As shown in Figure 7, the poly(MDS−DPA) was stable up to 330 °C, and then the thermal degradation started. The temperature for the 10% weight loss of poly(MDS−DPA) under a nitrogen atmosphere was 368 °C (Table 3), which is slightly higher than that of poly(MDS−Br) (T_d^{10} = 335 °C). The other modified polymers showed similar thermal stabilities with decomposition occurring above 300 °C. The 10% weight loss temperatures of poly(MDS−CZ) and poly(MDS−PTZ) under a nitrogen atmosphere were 354 and 382 °C, respectively. These TGA results indicated that the modified polymers exhibited high thermal stabilities, regardless of the nature of the substituent groups.

Conclusion

This study reports the synthesis of novel nonconjugated copolymers containing the anthracene moiety in the main chain and an additional optoelectronic unit, involving triphenylamine, *N*-phenylcarbazole, and *N*-phenylphenothiazine, in the side chain. Ring-opening radical polymerization of the cyclic monomers and subsequent palladium-catalyzed modification of the *p*-bromostyrene unit were applied for the purpose. The vinylcyclopropane derivatives with the halophenyl groups were found to predominantly undergo a ring-opening polymerization, regardless of the conventional radical polymerization or RAFT polymerization. Nearly monodispersed polymer with anthracene moieties incorporated into the main chain was prepared by the polymerization of MDS−Cl in the presence of benzyl dithiobenzoate (BDB) under suitable polymerization conditions. The palladium-catalyzed reaction was found to be effective to introduce additional optoelectronic component into the bromostyrene unit of the anthracene-based polymer to produce novel alternating copolymers having two distinct electronic functionalities. The UV absorption and fluorescent spectra of the modified polymers indicated that the characteristic fluorescence resonance energy transfer took place, depending on the combination of two distinct electronic functionalities.

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Supporting Information Available: Figures showing ^{1}H and ^{13}C NMR spectra of the cyclic monomers, SEC traces of poly(MDS−Cl)s obtained by RAFT polymerization under various conditions, and absorption and fluorescent spectra of the polymers and model compounds observed under various conditions and tables summarizing the results of RAFT polymerization under various conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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