5976 *Macromolecules* **2006,** *39,* 5976−5978

Ring-Opening RAFT Polymerization Based on Aromatization as Driving Force: Synthesis of Well-Defined Polymers Containing Anthracene Units in the Main Chain

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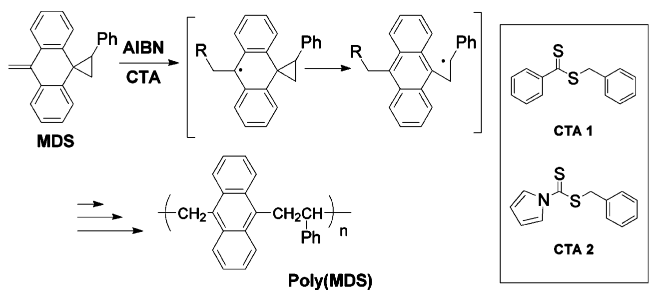
Received June 9, 2006
Revised Manuscript Received July 20, 2006

Anthracene-containing polymers are of considerable scientific and industrial interest due to their attractive features as fluorescent labels, photon harvesters, and electro- and photoluminescent materials. Although much attention has been paid to conjugated polymers, such as poly(anthrylene)s,[1,2] poly(anthrylenevinylene)s,[3−5] poly(anthryleneethynylene)s,[6,7] and their copolymers with extended conjugation, in some cases high crystallinity of the anthracene units prevents the formation of stable flexible film. Another drawback of these systems is that the anthracene rings do not lie in the same plane due to the steric hindrance and rotation in carbon−carbon single bond, resulting in relatively low conjugation along the backbone.

Recently considerable interest has been devoted to nonconjugated polymers with anthracene units in the main chain, in which electrophonic anthracene units are connected by nonconjugated segments. For instance, Müllen et al. reported the synthesis of a series of nonconjugated polymers having anthracene units linked in the 9,10-position with flexible alkyl chains, which include poly(trimethyleneanthrylene)s,[8,9] poly(octamethyleneanthrylene)s,[10] and poly(9,10-oxymethyleneanthrylene)s.[11] They also demonstrated that these nonconjugated polymers could be successfully doped with iodine to afford paramagnetism and enhanced electrical conductivity; i.e., extended conjugation along the main chain is not a prerequisite for achieving enhanced electronic conductivity.[11] Synthesis and characterization of various polyamides,[12,13] polyesters,[14,15] polyethers,[14] and polyurethanes[13] containing anthracene units in the main chain have also been reported by several groups. However, it was difficult to control the molecular weights, polydispersity, composition, and their architectures, since these polymers were synthesized by stepwise polymerization.

This communication reports the synthesis of well-defined polymers containing anthracene units in the main chain by radical ring-opening polymerization via reversible addition−fragmentation chain transfer (RAFT) process. To manipulate unique electronic and photonic functions of these anthracene-containing polymers, it is desirable to control various factors, including chemical structures of the main chain, chain length, location, and stacking of the anthracene units. For the purpose, we employed 10-methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane (MDS) as a vinylcyclopropane derivative, which 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.[16,17] Among various controlled radical polymerizations, we selected 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.[18,19]

Scheme 1. Ring-Opening Polymerization of 10-Methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane (MDS) in the Presence of Chain Transfer Agent (CTA) with 2,2′-Azobis(isobutyronitrile) (AIBN)



Free radical ring-opening polymerization produces polymers with functional groups, such as ethers, esters, amides, and carbonates incorporated into the backbone of polymer chain,[20] which cannot be achieved by conventional radical polymerization of vinyl monomers. Recently, several attempts have been made to extend the controlled radical polymerization of vinyl monomer to ring-opening polymerization process of cyclic monomers. However, cyclic monomers employed for ring-opening controlled radical polymerizations were mainly limited to cyclic ketene acetals[21−24] and cyclic acrylates,[25] which afforded polyesters and poly(α-ketoester)s, respectively.

In this study, the cyclic monomer (MDS) was synthesized by the Wittig reaction of anthrone-9-spirophenylcyclopropane, which was prepared by the reaction of a large excess of styrene with 10-diazoanthrone. The cyclic monomer, MDS, is highly reactive and could not be handled at room temperature without a stabilizer.[16] From our preliminary results (see Supporting Information, Table S1), we selected the cyclic monomer containing 1 wt % triethylenediamine and the silanized glass ampule for further investigations. The cyclic monomer was polymerized using two different chain transfer agents (CTAs), namely benzyl dithiobenzoate (CTA 1)[26,27] and benzyl 1-pyrrolecarbodithioate (CTA 2)[28,29] as shown in Scheme 1, under various conditions. The results are summarized in Table 1. When the polymerization was carried out using CTA 1 with AIBN as an initiator at $[M]_0/[CTA]_0/[AIBN]_0 = 100/2/1$ in toluene at 80 °C for 20 h, the characteristic pale red solution remained during the polymerization. The polymer was obtained as a powder after the precipitation into diethyl ether, and the polymer yield was 80%, which is slightly lower than the monomer conversion (94%) determined by ^{1}H NMR spectroscopy. As can be seen in Figure 1b, the resulting polymer showed symmetrical SEC peak with relatively narrow molecular weight distribution ($M_w/M_n = 1.43$). The number-average molecular weight, measured by a GPC in DMF with 10 mM LiBr, was $M_n = 5900$, which is lower than the theoretical value ($M_n = 12\,000$) calculated from the monomer/CTA molar ratio and the polymer yield. The resulting polymer was soluble in dichloromethane, chloroform, THF, dioxane, and DMF while insoluble in ethyl acetate, diethyl ether, hexane, ethanol, methanol, and water.

The polymerization of the cyclic monomer, MDS, in the presence of CTA 2 under the same conditions afforded a

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10.1021/ma0612879 CCC: $33.50

Table 1. Polymerization of 10-Methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane (MDS) Using 2,2′-Azobis(isobutyronitrile) (AIBN) in Toluene[a]

entry	CTA	$[M]_0/[CTA]_0/[I]_0$[b]	temp (°C)	time (h)	yield[c] (%)	M_n[d] (theory)	M_n[e] (SEC)	M_w/M_n[e] (SEC)
1			80	20	50		9000	1.66
2	CTA 1	100/2/1	80	20	80	12000	5900	1.43
3	CTA 1	100/2/1	60	20	15	2500	3000	1.17
4	CTA 2	100/2/1	80	20	59	9000	5600	1.53
5	CTA 1	100/1/1	80	20	72	21000	6800	1.52
6	CTA 1	100/5/1	80	20	60	3800	2700	1.14
7	CTA 1	500/5/1	80	48	54	16000	4400	1.20

[a] Monomer concentration = 0.17 g/mL. [b] CTA 1 = benzyl dithiobenzoate, CTA 2 = benzyl 1-pyrrolecarbodithioate (see Scheme 1), where M = 10-methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane (MDS), CTA = chain transfer agent, and I = 2,2′-azobis(isobutyronitrile) (AIBN). [c] Diethyl ether-insoluble part. [d] The theoretical molecular weight ($M_{n,theory}$) = (MW of MDS) × $[MDS]_0/[CTA]_0$ × 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 *N*,*N*-dimethylformamide (DMF, 10 mM LiBr).

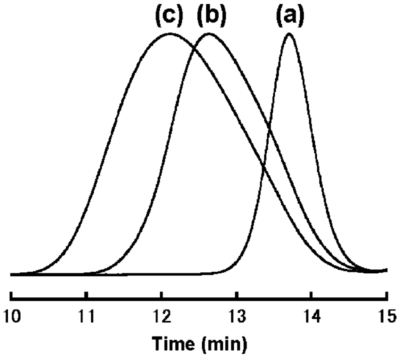

Figure 1. Size-exclusion chromatography (SEC) traces of poly(MDS)s prepared by the polymerizations at $[MDS]_0/[CTA\ 1]_0/[AIBN]_0$ = 100/5/1 (a) and 100/2/1 (b) and without chain transfer agent (CTA) (c), where MDS = 10-methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane, CTA 1 = benzyl dithiobenzoate, and AIBN = 2,2′-azobis(isobutyronitrile).

homopolymer with lower yield (59%), while there was no significant difference in the polydispersity and molecular weights (M_n = 5600 and M_w/M_n = 1.53). In contrast, the polymer with slightly higher molecular weight and broader polydispersity (M_n = 9000 and M_w/M_n = 1.66, entry 1) was obtained by a conventional radical polymerization in the absence of CTA. In this case, the polymer yield (50%) was apparently lower than the conversion (97%) determined by ^{1}H NMR spectroscopy, which may be due to unfavorable side reactions, such as dimerization, resulting in the decrease in the polymer yield. This behavior may also leads to the fact that the conventional polymerization had a lower yield than the polymerization with CTA 1 under the same conditions. Further studies on this point are now in progress and will be communicated separately. The polymerization of MDS with AIBN and CTA 1 at lower temperature, 60 °C, produced the polymer with a narrow molecular weight distribution (M_w/M_n = 1.17, M_n = 3000), while achieving only 15% polymer yield even after 20 h.

The influence of the ratio of CTA to initiator on the polymerization behavior was also investigated. The polymerization of the cyclic monomer was conducted with different $[CTA]_0/[AIBN]_0$ ratios at a constant monomer-to-initiator, $[M]_0/[AIBN]_0$ = 100, in toluene at 80 °C for 20 h. As shown in Table 1, a significant influence on the polydispersity was observed, as the concentration ratio of CTA 1 to initiator increased up to $[CTA]_0/[AIBN]_0$ = 5/1. When the polymerization was conducted at $[M]_0/[CTA]_0/[AIBN]_0$ = 100/5/1, the polymer having a narrow polydispersity (M_w/M_n = 1.14, M_n = 2700, Figure 1a) was obtained with a moderate conversion (62%). In this case, the polymer yield was 60%, which is apparently lower than those observed at $[CTA\ 1]_0/[AIBN]_0$ = 1 and 2 (yield = 72−80%), suggesting that a higher $[CTA]_0/[AIBN]_0$ ratio resulted in lower rates of the polymerization due to a decrease in the number of radicals available for propagation. The polymerization of MDS was also conducted at different $[M]_0$:$[CTA\ 1]_0$ ratios between 20 and 100, keeping the CTA-to-initiator ratio at a constant value of $[CTA\ 1]_0/[AIBN]_0$ = 5/1. Under the conditions, the values of the molecular weight distributions remain low (M_w/M_n = 1.14−1.20).

Table 1 shows that in all cases the experimental molecular weights are lower than calculated ones, which is due to the difference in hydrodynamic volume between poly(MDS) and the linear polystyrene standards used for GPC calibration. This presumption was confirmed by measuring representative samples using GPC with a right-angle laser light scattering detector (GPC-RALLS), which was used for the determination of the absolute molecular weights. The polymers obtained at the $[MDS]_0/[CTA\ 1]_0/[AIBN]_0$ ratios of 100/2/1 and 100/1/1 had $M_{w,GPC-RALLS}$ = 11 000 and M_w/M_n = 1.34 ($M_{n,GPC-RALLS}$ = 8200, as determined by GPC-RALLS), compared to $M_{n,GPC(THF)}$ = 5400 (M_w/M_n = 1.40), $M_{n,GPC(DMF)}$ = 5900 (M_w/M_n = 1.43), and $M_{w,GPC-RALLS}$ = 14 000 and M_w/M_n = 1.48 ($M_{n,GPC-RALLS}$ = 9500), compared to $M_{n,GPC(THF)}$ = 6400 (M_w/M_n = 1.48), $M_{n,GPC(DMF)}$ = 6800 (M_w/M_n = 1.52), respectively.

The structures of the resulting polymers were confirmed by FT-IR, ^{1}H NMR, and ^{13}C NMR measurements. In the ^{13}C NMR spectrum of the resulting polymer, in addition to the resonances attributed to aromatic carbons at 124−145 ppm, two characteristic resonances are clearly observed at 49.3 and 33.5 ppm (see Supporting Information, Figure S1), which are attributable to two different aliphatic carbons in the polymer backbone. The comparison of the ^{13}C NMR spectra of the cyclic monomer, MDS, and poly(MDS) reveals that the signals of the cyclopropane ring observed at 39.7 and 12.3 ppm completely disappear after the polymerization. The characteristic resonances at 3.5−4.5 (methylene and methine protons) and 6.5−8.2 ppm (phenyl and anthryl) were clearly observed in the ^{1}H NMR spectrum of the poly(MDS) (see Supporting Information, Figure S2). The resonances around 2.1−2.4 ppm, which were observed in the spectrum of the cyclic monomer, were invisible, suggesting the absence of the polymer having cyclopropane ring structure. In addition, the signals at 8.3 and 7.4 ppm attributed to the dithioester end group were clearly observed in poly(MDS) prepared by RAFT polymerization (Figure S2b), indicating that the polymer chain end is capped with the fragments of CTA as expected according to the general mechanism of the RAFT process. The molecular weight 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 8.3 ppm corresponding to two protons of the end group is $M_{n,NMR}$ = 2500, which is comparable to the theoretical value ($M_{n,theory}$ = 2500) and the observed value ($M_{n,GPC}$ = 3000).

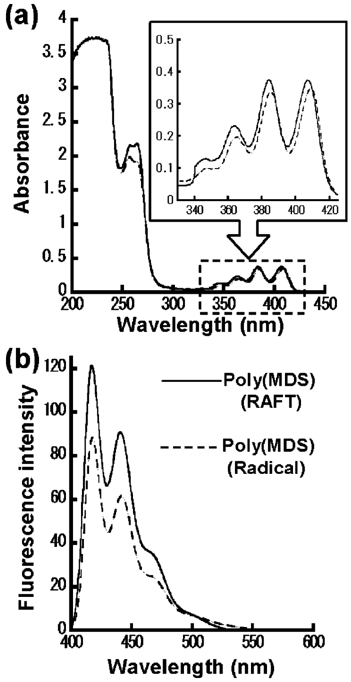

Figure 2. (a) Absorption (3.4×10^{-5} anthracene unit mol L^{-1}) and (b) fluorescent (8.5×10^{-7} anthracene unit mol L^{-1}, $\lambda_{ex} = 384$ nm) spectra of the poly(10-methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane)s, poly(MDS)s, obtained by reversible addition−fragmentation chain transfer (RAFT) polymerization in the presence of chain transfer agent (CTA) (entry 6, Table 1) and conventional radical polymerization (entry 1).

The FT-IR spectrum of the resulting polymer showed a strong absorption at 748 cm^{-1} (see Supporting Information, Figure S3). This can be assigned to the typical C−H out-of-plane bending mode of the four adjacent hydrogen on the anthracene units,[30] indicating the 9,10 linkage of the anthracene moieties in the backbone. The strong peak observed at 910 cm^{-1} in the monomer disappeared completely, suggesting the comsumption of the vinyl group during the polymerization. The C−H stretching vibration at 2900−3100 cm^{-1} and bending vibration at 1450 and 1365 cm^{-1} were also observed. These spectroscopic results clearly indicate that the cyclopropane ring in the cyclic monomer was opened completely, and the polymerization proceeded predominantly via the radical ring-opening process.

Figure 2 shows the absorbance and fluorescence spectra of the poly(MDS)s measured in $CHCl_3$. The 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 adjacent anthracene moieties. The emission of poly(MDS)s exited 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 observed until around 570 nm. There is no significant difference in the peak position between the polymers obtained in the presence and absence of CTA. The poly(MDS)s exhibited a blue fluorescence upon excitation at 365 nm (see Supporting Information, Figure S4). From these absorbance and fluorescence spectra, it is reasonable to consider that the main-chain anthracene groups in poly(MDS) are close enough to produce electronic interaction in solution.

In conclusion, we have demonstarted that RAFT polymerization of the cyclic monomer (MDS) allowes the synthesis of well-defined polymers containing anthracene units in the main chain. To the best of our knowledge, this is the first attempt to synthesize nonconjugated polymers having low polydispersity with anthracene units in the main chain via the chain ring-opening RAFT process.

Acknowledgment. The authors acknowledge Professor Seigou Kawaguchi for help with excess refractive index increment (d*n*/d*c*) measurement.

Supporting Information Available: Experimental procedures and details; preliminary polymerization results using conventional and surface-treated ampules; ^{1}H and ^{13}C NMR and FT-IR spectra of the monomer and polymer; appearance of the polymer illuminated with visible and UV light. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA0612879