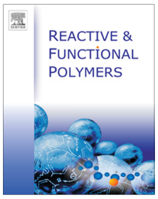
Reactive & Functional Polymers 86 (2015) 52–59

Contents lists available at ScienceDirect

Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react



Alternate and random (co)polymers composed of anthracene and chloromethylstyrene units through controlled radical ring-opening polymerization: Synthesis, post-functionalization, and optical properties

Kazuhiro Nakabayashi [a], Ayumi Tsuda [a], Hiroshi Otani [a], Hideharu Mori [b,*]

[a] Department of Polymer Science and Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16, Jonan, Yonezawa 992-8510, Japan
[b] Department of Organic Device Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16, Jonan, Yonezawa 992-8510, Japan

ARTICLE INFO

Article history:
Received 11 July 2014
Received in revised form 16 November 2014
Accepted 18 November 2014
Available online 24 November 2014

Keywords:
RAFT polymerization
Ring-opening polymerization
Alternate polymer
Anthracene-containing polymer

ABSTRACT

A cyclic monomer containing the chloromethyl unit 10-methylene-9,10-dihydroanthryl-9-spiro(4′-chloromethylphenyl)cyclopropane (MDCMS) was polymerized using a controlled radical ring-opening polymerization via a reversible addition-fragmentation chain transfer (RAFT) process to afford a nonconjugated alternate polymer composed of anthracene and chloromethylstyrene (CMS) units. Well-defined random copolymers were obtained through the ring-opening RAFT copolymerization. Various functional groups were incorporated into the alternate polymer. The alternate polymer containing imidazole rings exhibited fluorescence quenching as a result of charge transfer. Fluorescence resonance energy transfer (FRET) was observed in the alternate polymers containing naphthalene and thiophene rings. The random copolymers obtained by copolymerization followed by post-functionalizations exhibited characteristic optoelectronic properties that differed from those of the alternate polymers.

1. Introduction

Anthracene-containing polymers, which possess strong fluorescence and phosphorescence properties, have been extensively explored for a wide range of applications, such as fluorescent labels, photon harvesters, and optoelectronic applications [1–8]. In particular, considerable attention has been focused on conjugated polymers that contain anthracene units in the main chain because the characteristic properties of these polymers can be easily modified by adjusting the degree of conjugation and by incorporating functional groups into the polymers [1–8]. The design and synthesis of nonconjugated polymers that contain anthracene units in the main chain linked at the 9,10-positions with flexible alkyl chains are another central aspect to developments in these fields [9–12]. Recently, considerable effort has been devoted to controlling the polymer structure, such as the molecular weight, polydispersity, composition, and sequence, because the characteristic optoelectronic properties can be drastically enhanced by controlling these parameters [13,14]. However, controlling these parameters is still difficult for anthracene-based polymers, and therefore, a new approach that can readily control the polymer structure in anthracene-based nonconjugated polymers is required.

We previously reported the synthesis of well-defined nonconjugated polymers that contain anthracene units in the main chain from 10-methylene-9,10-dihydroanthryl-9-spirophenyl-cyclopropane (MDS)-based cyclic monomers through radical ring-opening polymerization via a reversible addition-fragmentation chain transfer (RAFT) process [15–19]. The driving force of this process is the release of ring strain in the cyclopropane ring, which results in the formation of a stable aromatic ring. In all cases, the desired nonconjugated polymers containing anthracene units in the main chain with narrow polydispersities were successfully synthesized. Furthermore, the incorporation of optoelectronic functional groups during the post-functionalization was successfully performed in the presence of a palladium catalyst using poly(MDS-X)s (X = Cl or Br), which were derived from halostyrene derivatives. Interestingly, the post-functionalized polymers exhibited fluorescence resonance energy transfer (FRET) between anthracene and the incorporated optoelectronic units (triphenylamine, *n*-phenylcarbazole, and *n*-phenylphenothiazine) [17]. For poly(MDS4P) and poly(MDS2P) composed of anthracene and 4- and 2-vinylpyridine units, fluorescence switching triggered by the pH conditions was observed [19]. Our previous work revealed that well-defined nonconjugated anthracene-containing polymers can possess unique optical characteristics derived from the interactions between the anthracene and the functional units.

---

* Corresponding author. Tel.: +81 238 26 3765; fax: +81 238 26 3749.
E-mail address: h.mori@yz.yamagata-u.ac.jp (H. Mori).

http://dx.doi.org/10.1016/j.reactfunctpolym.2014.11.004
1381-5148/

In the present study, we focused on the use of chloromethylstyrene (CMS) units as the key toward a facile post-functionalization step because reactions that exploit the electrophilicity of the CMS units, such as nucleophilic substitution reactions, click reactions, and Grignard reactions, are quite effective for incorporating various functional groups [20–27]. We investigated the synthesis of alternate polymers composed of anthracene and CMS units using the novel cyclic monomer 10-methylene-9,10-dihydroanthryl-9-spiro(4′-chloromethylphenyl)cyclopropane (MDCMS, Scheme S1, Supporting Information). The controlled synthesis of an anthracene-CMS alternate polymer was successfully achieved through a radical ring-opening polymerization via a RAFT process using a suitable chain transfer agent (CTA), as shown in Scheme 1. The copolymerization of MDS and CMS was also performed, which afforded the desired random copolymers composed of anthracene-styrene and CMS units with narrow polydispersities (Scheme 1B). Three functional groups (imidazole, naphthalene, and thiophene) were successfully incorporated into these polymers via imidazolization, the Williamson ether reaction, and the alkyne-azido click reaction, respectively (Scheme 2). The light absorption and fluorescence properties of these polymers were also investigated in detail.

2. Experimental section

2.1. Materials

2,2′-Azobisisobutyronitrile (AIBN, Kanto Chemical, 97%) was recrystallized with methanol. Benzyl dithiobenzoate (CTA1) [28,29], benzyl 1-pyrrolecarbodithioate (CTA2) [30,31], MDS [15], and 2-ethynylthiophene [32] were synthesized according to the literature. CMS was purified by column chromatography (hexane). The other reagents and solvents were used as received unless otherwise noted.

2.2. Synthesis of ACMC

A toluene solution (100 mL) containing 10-diazo-10H-antracen-9-one (2.2 g, 0.01 mol) and *p*-chloromethylstyrene (11.6 mL, 0.10 mol) was refluxed for 15 h under a nitrogen atmosphere (Scheme S1). Then, the reaction solution was concentrated and poured into hexane (700 mL). The precipitates were collected by filtration and purified using column chromatography (hexane:ethyl acetate = 3:1) to afford a yellow solid (0.91 g, 41%). ^{1}H NMR ($CDCl_3$, δ, ppm): 8.5–8.3 (dd, 2H, Ar), 7.7 (t, 1H, Ar), 7.5 (t, 1H, Ar), 7.3–7.0 (m, 7H, Ar), 6.5 (d, 1H, Ar), 4.6 (s, 2H, $-CH_2Cl$), 3.1 (t, 1H, CH), 2.6 (m, 2H, CH_2).

2.3. Synthesis of MDCMS

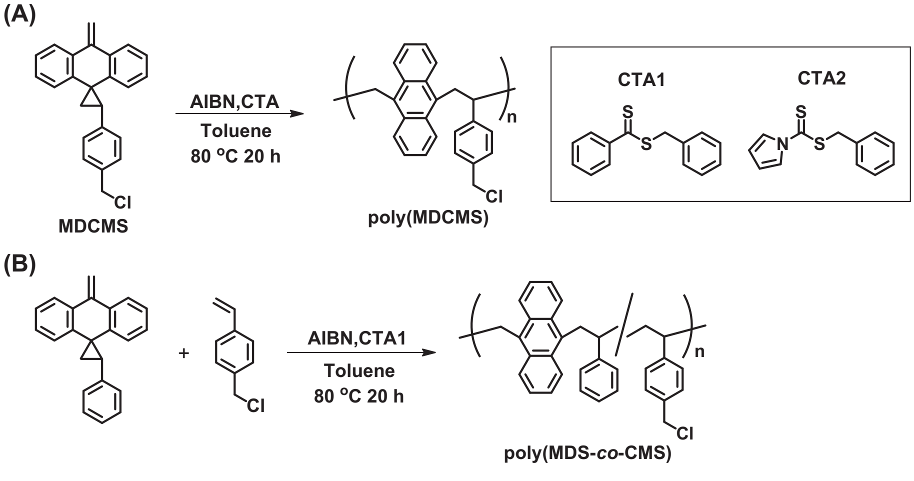
A solution of *n*-butyl lithium (2.09 mL, 2.6 M in hexane) was added dropwise at 0 °C to a dry THF solution (20 mL) containing methyltriphenylphosphonium bromide (2.16 g, 6 mmol), and then the reaction mixture was stirred at room temperature for 30 min. Then, a dry THF solution (20 mL) containing ACMC (1.5 g, 5 mmol) was added dropwise, and the reaction mixture was stirred at room temperature for 2 h. The reaction mixture was then poured into diethyl ether and filtered to remove the precipitates. The concentrated filtrate was then poured into hexane to remove the precipitates again, and then the filtrate was purified using column chromatography (hexane:ethyl acetate = 3:1) to afford a yellow powder (0.49 g, 33%). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.7–6.7 (m, 12H, Ar), 5.5 (d, 2H, CH_2=), 4.4 (s, 2H, $-CH_2Cl$), 2.4–2.3 (m, 3H, $-CH_2$ CH–Ar). Note that the cyclic monomer was highly reactive and that the neat product could not be handled at room temperature. Therefore, the purified products were immediately diluted with dry toluene (conc. = 0.04 g/mL) after purification, and the evaporation of the eluent was performed under mild conditions to avoid unfavorable polymerization. In general, the stock solution containing the monomer and dry toluene was prepared in a silanized glass tube capped with a two-way glass stopper under a nitrogen atmosphere, and it was stored in the dark at approximately 0 °C.

2.4. General polymerization procedure

The typical polymerization procedure is as follows (Run 6 in Table 1): a dry toluene solution containing MDCMS (1.4 mL, 0.175 mmol), AIBN (1.0 mg, 0.007 mmol), and CTA2 (3.0 mg, 0.014 mmol) was placed in a silanized glass ampule equipped with a magnetic stirring bar, and then the solution was degassed using three freeze-evacuate-thaw cycles. After the ampule was flame-sealed under vacuum, the reaction was conducted at 80 °C for 20 h with stirring. Then, the reaction was stopped by rapid cooling with liquid nitrogen. After filtration, the filtrate was poured into diethyl ether to afford a yellow powder (9 mg, 16%). ^{1}H NMR ($CDCl_3$, δ, ppm): 8.2–6.2 (m, 12H, Ar), 4.4 (bs, 2H, $-CH_2Cl$), 4.2–3.4 (m, 5H, $-CH_2CH-$). ^{13}C NMR ($CDCl_3$, δ, ppm): 145.1, 135.9, 132.0, 130.0, 128.5, 128.1, 125.0, 49.2, 46.1, 33.7. $M_n = 3800$ ($M_w/M_n = 1.17$).

2.5. General copolymerization procedure

The typical copolymerization procedure is as follows (Run 2 in Table 2): a dry toluene solution containing MDS (3.0 mL,



Scheme 1. Synthesis of (A) poly(MDCMS) and (B) poly(MDS-*co*-CMS).