

New azo-chromophore-containing multiblock poly(butadiene)s synthesized by the combination of ring-opening metathesis polymerization and click chemistry

Liang Ding, Liya Zhang, Dan Yang, Wei Huang, Meiran Xie*, Yiqun Zhang

Department of Chemistry, East China Normal University, Shanghai 200062, China

ARTICLE INFO

Article history:

Received 17 November 2009

Received in revised form

16 January 2010

Accepted 1 February 2010

Available online 6 February 2010

Keywords:

Ring-opening metathesis polymerization (ROMP)

Click chemistry

Multiblock copolymers

ABSTRACT

A combination of ring-opening metathesis polymerization (ROMP) and click chemistry approach was utilized for the first time in preparation of multiblock copolymers. The dibromo-functionalized telechelic poly(butadiene) (PBD) was synthesized firstly by ROMP of 1,5-cyclooctadiene in the presence of a symmetrical difunctional chain transfer agent and transformed into diazido-telechelic PBD, which was then reacted with a dialkynyl-containing azobenzene chromophore via click reaction, producing novel multiblock PBDs collected by azobenzene groups and newly formed triazole moieties. The monomer and polymer were characterized by IR, UV-vis, LC/MS, and NMR techniques. The produced multiblock copolymers have molecular weights within 13.3 and 57.8 kDa, and their polydispersity indices ranging from 1.98 to 2.38 by gel permeation chromatography measurement. The multiblock PBDs containing azo chromophores and triazole moieties with or without hydrogen-bonding interreaction with 4,4'-dihydroxybiphenyl molecule exhibited different photoisomerization efficiency from *trans* to *cis* as observation in UV-vis spectroscopy. The morphologies of multiblock PBDs were also investigated by atom force microscopy.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Multiblock copolymers are usually composed of two or more dissimilar repeat blocks or segments arranged in a random or alternating sequence. Meanwhile, the polymer with the same repeating blocks interrupted by small molecule units are also identified as multiblock copolymers in some reports [1–4]. Increasing attention has recently been devoted to multiblock copolymers because of the interest in their widespread application in fields such as adhesives, emulsifiers, barrier materials, impact modifiers, and materials for gene and drug delivery [5,6]. Moreover, lots of studies reveal that multiblock copolymers can often provide more advantageous properties such as good biocompatibility and mechanical properties when compared with diblock or triblock copolymers [7]. It is noteworthy that multiblock copolymers can form unique morphologies, which directly improve these advantageous properties, especially physical properties. Thus, attempting to find easy methods for the synthesis of functional multiblock copolymers is becoming significant interest.

Multiblock copolymers could be prepared by two general strategies. One is to add different types of monomers sequentially

into a living copolymerization system. But this method can only be used to make copolymers with a few blocks, such as tetrablock or pentablock copolymers because each addition of new monomer will inevitably terminate some of living chains due to a trace amount of impurities and each block with a living end cannot be sufficiently reactive to initiate the next added comonomer [8–10]. The other is to make the coupling of several polymer chains with bifunctional end groups. In other words, multiblock copolymers can be synthesized by preparing an α,ω -bifunctional prepolymer and condensing it with another α,ω -bifunctional prepolymer [11–15].

In practice, multiblock copolymers can be prepared by many of the available living polymerization techniques such as atom transfer radical polymerization (ATRP) [16–19], reversible addition-fragmentation chain transfer polymerization [20–26], group transfer polymerization [27,28], anion polymerization [29–31], Wurtz synthesis, [32] and the combination of enzymatic ring-opening polymerization and ATRP [33]. But only a few multiblock copolymers can be obtained from ring-opening metathesis polymerization (ROMP) process. Watkins and Fox [34] reported ABCD-type tetrablock copolymers synthesized by ROMP of norbornenediol bearing various aryl ketones or aldehydes. Nomura and Schrock [35] synthesized sugar-coated ABCD- or ABAB-type tetrablock copolymers by Mo-catalyzed living ROMP techniques. Fujiki and Nomura et al. reported the synthesis of ABAB-type tetrablock copolymers of norbornenes containing acetyl-protected

* Corresponding author. Tel.: +86 21 62233493; fax: +86 21 62232414.

E-mail address: mxie@chem.ecnu.edu.cn (M. Xie).

carbohydrates by the living ROMP with well-defined ruthenium and molybdenum initiators [36], and they also prepared amphiphilic ABCBA-type pentablock copolymers containing acetal-protected sugars from the coupling of an end-functionalized ROMP copolymer by molybdenum-alkylidene initiator with poly(ethylene glycol) [37]. More recently, Hilf and Kilbinger [38] presented a sacrificial approach to generate cleavable ABABA-type pentablock and ABABABA-type heptablock metathesis copolymers through ROMP of 7-membered cyclic acetals and *N*-substituted norbornene dicarboximide derivatives. Although these methods provide robust tools to synthesize different types of multiblock copolymers, all the aforementioned ROMP copolymers were those consisting of several (tetra-, penta-, or hepta-) blocks in the main chain.

ROMP using well-defined ruthenium initiators is a general and easy approach to allow many functional groups to be present in the polymer structure. The method for preparation of end-functionalized ROMP polymers can enable the incorporation of the functional unit to both ends (telechelic) of a polymer chain, and expand the applications of ROMP materials. Generally, there have been three approaches for the synthesis of end-functional polymers [39–46]. The classical technique for preparation of telechelic polymers especially telechelic poly(butadiene)s (PBDs) with 100% 1,4-microstructures is to use a symmetrical difunctional olefinic compound as chain transfer agent (CTA) [39–41]. For example, the ROMP of 1,5-cyclooctadiene (COD) in the presence of an appropriate CTA has provided routes to telechelic PBDs end-capped with amino, hydroxy, methacrylate, and carboxy functional groups [47]. Moreover, ROMP of cyclooctene, norbornene, and cyclopentene in the presence of bis-functionalized CTAs can also result in the high yielding syntheses of bis-functionalized telechelic polymers [48–50].

It is still of interest to seek the other synthetic strategy for multiblock copolymer synthesis under mild conditions. Click chemistry has been extensively used in polymer chemistry due to the high efficiency, near-perfect reliability, the simple reaction conditions, and high yield [51–54]. Most importantly, it is exceptionally tolerant toward most types of functional groups and reaction conditions, which can be conducted in aqueous or organic media with free side reaction in a wide temperature range. Binder and Kluger synthesized the functionalized poly(oxanorbornene) block copolymers via a combination of ROMP and click chemistry [55,56]. Xia and Grubbs reported the preparation of well-defined liquid crystal networks by controlled “click” cross-linking of telechelic polymers produced by ROMP [57]. Recently, Wang and Zhu prepared the multiblock copolymer through multiple coupling procedure using a combination of self-assembly and click chemistry [9]. However, to the best of our knowledge, no multiblock copolymers have been obtained from ROMP and click chemistry process. A combination of these two methods would in principle be suited to provide highly functional polymer blocks, including multiblock copolymers.

Herein, we present the protocol for synthesis of a new type of multiblock copolymers via the efficient combination of ROMP process and click chemistry in two steps (Scheme 1). First, ROMP of COD in the presence of a difunctional CTA was underwent to provide dibromo-telechelic PBD, followed by the transformation of telechelic dibromide into diazido-functionalized telechelic PBD; second, multiple click reactions of diazido-telechelic PBD with a novel dialkynyl-containing azobenzene chromophore was conducted resulting in the formation of multiblock PBD collected by azobenzene groups and newly formed triazole moieties, which can be expected to tune and improve the properties of PBD because these groups have not only the photoresponsive but also the potential to participate in hydrogen bonds when added the

additional molecule. The purpose of this work was to provide highly photoresponsive multiblock PBD for further study on its shape memory properties, or for preparing the light-driven supramolecular multiblock PBD copolymer.

2. Experimental

2.1. Materials

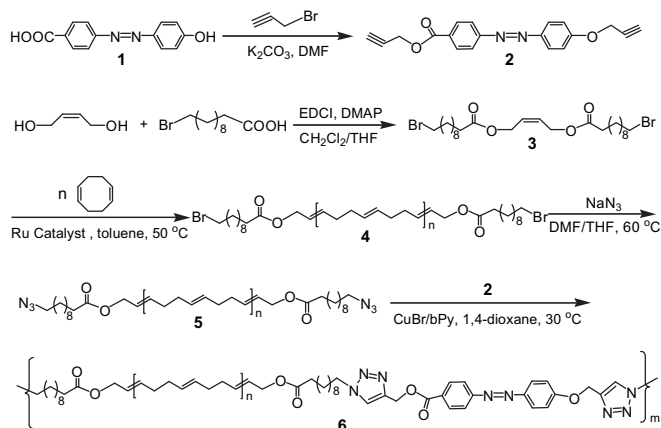
1,5-Cyclooctadiene (COD, 99%), *cis*-1,4-butenediol (99%), α,α' -bipyridyl (bPy, 99%), and benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene] dichloro(tricyclohexylphosphine)ruthenium (second generation Grubbs catalyst) (99.99%) were purchased from Alfa Aesar or Aldrich and used as received without purification. 4-Dimethylaminopyridine (DMAP, 98%), *p*-aminobenzoic acid (99.5%), 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDCI·HCl, >99%), 3-bromo-1-propyne (99%), 11-bromoundecanoic acid (98%), 4,4'-dihydroxybiphenyl (DHBPh, 99%), sodium azide (99.5%), and potassium carbonate (99%) were purchased from Shanghai Chemical Reagents Co, and used as received without purification. Copper(I) bromide (CuBr, Alfa Aesar, 97%) was purified by washing with glacial acetic acid, followed by ethanol and ethyl ether, and then dried under vacuum. Solvents were distilled over drying agents under nitrogen prior to use: methylene chloride (CH₂Cl₂) and 1,4-dioxane from calcium hydride, tetrahydrofuran (THF) and toluene from sodium/benzophenone. *N,N*-Dimethyl formamide (DMF) was freshly distilled and dried by sieves.

2.2. Characterization

FTIR spectra were recorded on a Nicolet Nexus 670 in the region of 4000–400 cm^{−1} using KBr pellets. UV–vis absorption spectra were measured on a UV-1900PC spectrometer. UV irradiation was carried out with 8 W UV lamp with wavelength at 365 nm. Irradiation by visible light was performed using a 23 W Philips day light bulb (>400 nm). ¹H (500 MHz) and ¹³C (125 MHz) NMR spectra were recorded using tetramethylsilane as an internal standard in CDCl₃ or CD₃COCD₃ on a Bruker DPX spectrometer. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (7.8 × 300 mm, 5 μm bead size; 10³, 10⁴, and 10⁵ Å pore size). GPC measurements were carried out at 35 °C using THF as the eluent with a flow rate of 1.0 mL/min. The system was calibrated with polystyrene standards. LC/MS measurements were performed with an agilent technologies 1200 series at 45 °C using H₂O or MeCN as mobile phase, 50 m × 4.6 mm × 3.5 μm diffused column. Atom force microscopy (AFM) observations were performed on SPM AJ-III atomic force microscope at a measure rate of 1.0005 Hz in the tapping mode, and the AFM images were obtained at room temperature in air.

2.3. Synthesis of 4-propargyl (4'-propargyloxyphenylazo) benzoate (**2**)

4-(4-Hydroxyphenylazo) benzoic acid, **1** (4.84 g, 20.0 mmol), potassium carbonate (16.56 g, 120.0 mmol), and 120 mL of DMF were charged into a 250 mL Schlenk flask. The reaction mixture was heated at 80 °C for 6 h under nitrogen allowing for the potassium salt formed. A solution of 3-bromo-1-propyne (4.76 g, 40.0 mmol) in 25 mL of DMF was then added dropwise to the above mixture over a period of 40 min. After 2 days of stirring at 50 °C, the reaction mixture was poured into 2 L water and the crude product was precipitated out, and further purified by recrystallization from ethanol/THF (4/1) to give a dark red crystalline powder **2** (5.76 g,



90.6% yield). ^1H NMR (CD_3COCD_3): δ (ppm) 8.23–8.20 (d, 2H, *o*-ArH-COOCH₂), 8.01–7.98 (m, 4H, *m*-ArH-OCH₂), 7.24–7.21 (d, 2H, *o*-ArH-OCH₂), 5.02–5.01 (d, 2H, ArCOO-CH₂), 4.95–4.94 (d, 2H, ArO-CH₂), 3.16–3.12 (m, 2H, CH \equiv C). ^{13}C NMR (CD_3COCD_3): δ (ppm) 166.19 (CH₂COOAr), 162.56 (ArC-OCH₂), 157.02 (ArC-N=NArC), 148.88 (ArC-N=NArC), 132.50 (CH₂COO-ArC), 132.22 (*o*-ArC-COOCH₂), 126.55 (*m*-ArC-OCH₂), 124.02 (*m*-ArC-COOCH₂), 117.02 (*o*-ArC-OCH₂), 79.84–79.45 (CH \equiv C), 78.24–77.38 (CH \equiv C), 57.44 (ArO-CH₂), 53.90 (ArCOO-CH₂). LC: single peak observed at the retention time of 1.82 min. EI/MS: calcd. for C₁₉H₁₄N₂O₃: 318.3; Found: 318.9.

cis-1,4-Butenediol (1.76 g, 20.0 mmol), 11-bromoundecanoic acid (12.73 g, 48.0 mmol), DMAP (0.60 g, 4.8 mmol), CH₂Cl₂ (65 mL), and THF (15 mL) were charged into a 250 mL round-bottom flask equipped with a magnetic stirrer under nitrogen atmosphere, and the mixture was stirred at 0 °C for 15 min. EDCI (9.21 g, 48 mmol) was then added to the former solution, and stirred for 3 days after the solution warmed to room temperature. The resulting solution was washed three times with deionized water (3×80 mL), and the organic layer was dried over anhydrous Na₂SO₄. Solvent was then evaporated and the crude product was purified by recrystallization from petroleum ether to give a white crystalline powder **3** (8.96 g, 77.1% yield). ¹H NMR (CDCl₃): δ (ppm) 5.75–5.73 (m, 2H, CH=CH), 4.68–4.67 (d, 4H, $2 \times$ CH₂CH=CH), 3.41–3.38 (m, 4H, $2 \times$ CH₂—Br), 2.32–2.91 (m, 4H, $2 \times$ CH₂—COOCH₂CH=CH), 1.88–1.82 (m, 4H, $2 \times$ CH₂—CH₂Br), 1.63–1.58 (m, 4H, $2 \times$ CH₂ CH₂—COOCH₂CH=CH), 1.43–1.28 (m, 12H, $2 \times$ BrCH₂CH₂CH₂CH₂CH₂CH₂CH₂). ¹³C NMR (CD₃COCD₃): δ (ppm) 173.50 (CH₂—COO—CH₂CH=CH), 128.10 (CH=CH), 59.84 (CH₂CH=CH), 34.18–34.07 (CH₂—COOCH₂CH=CH), 32.81–32.63 (CH₂—Br), 29.31–28.85 (BrCH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂), 24.88 (CH₂—CH₂COOCH₂CH=CH). LC: single peak observed at the retention time of 2.14 min. EI/MS: calcd. for C₂₆H₄₆Br·O₄: 582.4; Found: 582.4.

In a nitrogen-filled Schlenk tube, a solution of second generation Grubbs catalyst (5.1 mg, 6.0 μmol) in 3 mL of toluene was added to a solution of monomer COD (3.56 g, 33.0 mmol) and CTA **3** (0.76 g, 1.3 mmol) in 4 mL of toluene, which was degassed with three freeze-vacuum-thaw cycles, to give an initial monomer concentration of 4.7 mol/L. The molar ratio of monomer to CTA was 25:1.

2.6. Synthesis of bis(azidoundecylcarbonyloxy)-functionalized telechelic poly(butadiene) (**5**)

A round-bottom flask was charged with NaN_3 (0.47 g, 7.3 mmol), DMF (15 mL), THF (25 mL) and polymer **4** (2.77 g, 0.73 mmol). The reaction mixture was allowed to stir at 60 °C for 2 days under nitrogen atmosphere. The solution was poured into dilute HCl solution under agitation. The polymer was collected and then dissolved in 8 mL of THF, precipitated twice from an excess of methanol, dried overnight under reduced pressure to give a yellowish viscous polymer **5** with telechelic azide groups (N_3 -PBD- N_3) (2.58 g, 93.2% yield). ^1H NMR (CDCl_3): δ (ppm) 5.79–5.73 (m, $\text{COOCH}_2\text{-CH=CH}$), 5.60–5.37 (m, CH=CH on polymer chain, *cis* and *trans*), 4.62–4.60 (d, $\text{COO-CH}_2\text{CH=CH}$, *cis*), 4.52–4.50 (d, $\text{COO-CH}_2\text{CH=CH}$, *trans*), 3.26–3.23 (m, $\text{CH}_2\text{-N}_3$), 2.31–2.28 (m, $\text{CH}_2\text{-COOCH}_2\text{CH=CH}$), 2.08–2.03 (d, CH=CH-CH_2 on polymer chain), 1.63–1.54 (m, $\text{N}_3\text{CH}_2\text{-CH}_2\text{CO(CH}_2\text{)}_6\text{-CH}_2\text{CH}_2\text{COO}$), 1.36–1.25 (m, $\text{N}_3\text{CH}_2\text{CH}_2\text{-(CH}_2\text{)}_6\text{CH}_2\text{CH}_2\text{COO}$). GPC: $M_n = 4600$, $M_w = 7500$, $M_w/M_n = 1.62$; NMR: $M_n = 3700$.

In a nitrogen-filled Schlenk tube, a mixture of **2** (15.9 mg, 0.05 mmol), **5** (190 mg, 0.05 mmol), CuBr (14.3 mg, 0.105 mmol), bPy (36.1 mg, 0.231 mmol), and 5 mL of 1,4-dioxane were degassed by three freeze–vacuum–thaw cycles, and then heated at 30 °C for 8–96 h. The mixture was poured into water, extracted with CH₂Cl₂, combined the organic layer, and dried over anhydrous Na₂SO₄. The solution was concentrated and dropped into a large amount of methanol, and then the precipitate was dried under vacuum to give the resultant polymer **6** as a red solid. (98.6% yield) ¹H NMR (CDCl₃): δ (ppm) 8.18–8.16 (d, *o*-ArH-COOCH₂), 7.95–7.88 (m, *o*-ArH-N=N-ArH), 7.69, 7.62 (s, triazole), 7.13–7.11 (d, *o*-ArH-OCH₂), 5.78–5.73 (m, COOCH₂-CH=CH), 5.58–5.34 (m, CH=CH on polymer chain, *cis* and *trans*), 5.50 (s, triazole-CH₂COO), 5.31 (s, triazole-CH₂OAr), 4.62–4.60 (d, COO-CH₂CH=CH, *cis*), 4.52–4.49 (d, COO-CH₂CH=CH, *trans*), 4.37–4.33 (m, triazole-CH₂), 2.31–2.27 (m, CH₂-COOCH₂CH=CH), 2.07–2.03 (d, CH=CH-CH₂ on polymer chain), 1.62–1.56 (m, CH₂-CH₂(CH₂)₆-CH₂CH₂COO), 1.31–1.26 (m, CH₂CH₂-(CH₂)₆CH₂CH₂COO). GPC: $M_n = 13\,300$, $M_w = 31,600$, $M_w/M_n = 2.38$ for 8 h; $M_n = 25,600$, $M_w = 52\,500$, $M_w/M_n = 2.05$ for 16 h; $M_n = 34,500$, $M_w = 69,300$, $M_w/M_n = 2.01$ for 32 h; $M_n = 47,700$, $M_w = 94,400$, $M_w/M_n = 1.98$ for 48 h; $M_n = 57,800$, $M_w = 116,700$, $M_w/M_n = 2.03$ for 96 h.

3.1. Synthesis of azobenzene chromophore

Azobenzene chromophore, **1** was synthesized according the literature procedure [58]. **2** was prepared by the condensation of 3-bromo-1-propyne with **1** in the presence of K_2CO_3 in DMF at

80 °C for 6 h and then 50 °C for 48 h under nitrogen atmosphere. The crude product was purified by recrystallization from ethanol/THF to provide pure product with yield of 90.6%. The chemical structure of chromophore **2** was characterized by LC/MS and ^1H NMR spectroscopy. The ^1H NMR spectrum of **2** shown in Fig. 1A indicated the presence of alkynyl groups (protons *a* and *g*) at 3.16, 3.12 ppm and azobenzene structure (phenyl protons *c*, *d*, and *e*) at 8.21, 8.01, and 7.22 ppm. Furthermore, the molecular weight of **2** from MS analysis was in good accordance with the calculated value, and the product also has a high purity estimated from the single

peak of LC chromatogram. All of these points assured that the azobenzene chromophore with dialkynyl has been successfully prepared.

3.2. Synthesis of CTA

CTA **3** was synthesized from the esterification of *cis*-1,4-butenediol with 11-bromoundecanoic acid catalyzed by EDCI/DMAP in CH_2Cl_2 and THF at room temperature (Scheme 1). In order to realize the double substitution of the dihydroxyl groups, excess of 11-bromoundecanoic acid is necessary to have the dihydroxyl consumed completely, and the suitable ratio of diol to acid was 1:2.4. Under this condition, thin layer chromatography analysis showed the expected product was dominant in the reaction mixture. The crude oil was purified by recrystallization from petroleum ether to give a white crystalline powder. The ^1H NMR spectrum (Fig. 1B) showed the resonance signals of CH_2Br -protons (*h*) at 3.40 ppm, CH_2OCO -protons (*l*, *m*) at 2.16, 4.68 ppm and $\text{CH}=\text{CH}$ (*n*) at 5.73 ppm. Moreover, resonance signals of methylene protons *i* (1.86 ppm) and *k* (1.62 ppm), and *j* (1.43–1.28 ppm) can be also clearly observed, which correspond to the chemical structure of the alcohol. LC/MS also indicated that the product has a high purity and the exact molecular weight. All of these points affirmed the successful preparation of **3** with the expected structure.

3.3. Preparation of end-functionalized telechelic poly(butadiene)

Grubbs and co-workers have investigated many ROMP reactions of COD in presence of an appropriately difunctionalized CTA and Grubbs catalyst, and revealed that the molecular weight could be controlled through varying the initial $[\text{COD}]/[\text{CTA}]$ ratio [59–62]. In order to get PBD with the moderate molecular weight, the polymerization was initiated with second generation Grubbs catalyst using a $[\text{COD}]/[\text{CTA}]$ ratio of 25:1 and run for 48 h at 50 °C in toluene. The polymer was precipitated to an excess of slightly acidic methanol to provide the pure product.

Fig. 1C shows the ^1H NMR spectrum of PBD **4**, we can observe the appearance of two groups of new resonance signals at 5.60–5.37 ppm and 2.08–2.03 ppm, which can be ascribed to the protons of olefins (*o*, *q*) and methylene (*p*) on polymer chain. As compared to that of **3**, it was a clear observation that the signals of *n*, *m*, *h*, *l*, *i*, *k*, and *j* were still preserved, which meant telechelic PBD with dibromo-end groups was virtually formed. Additionally, the molecular weight was calculated from integration of the ^1H NMR spectrum. The integration area ratio of olefinic protons on the PBD

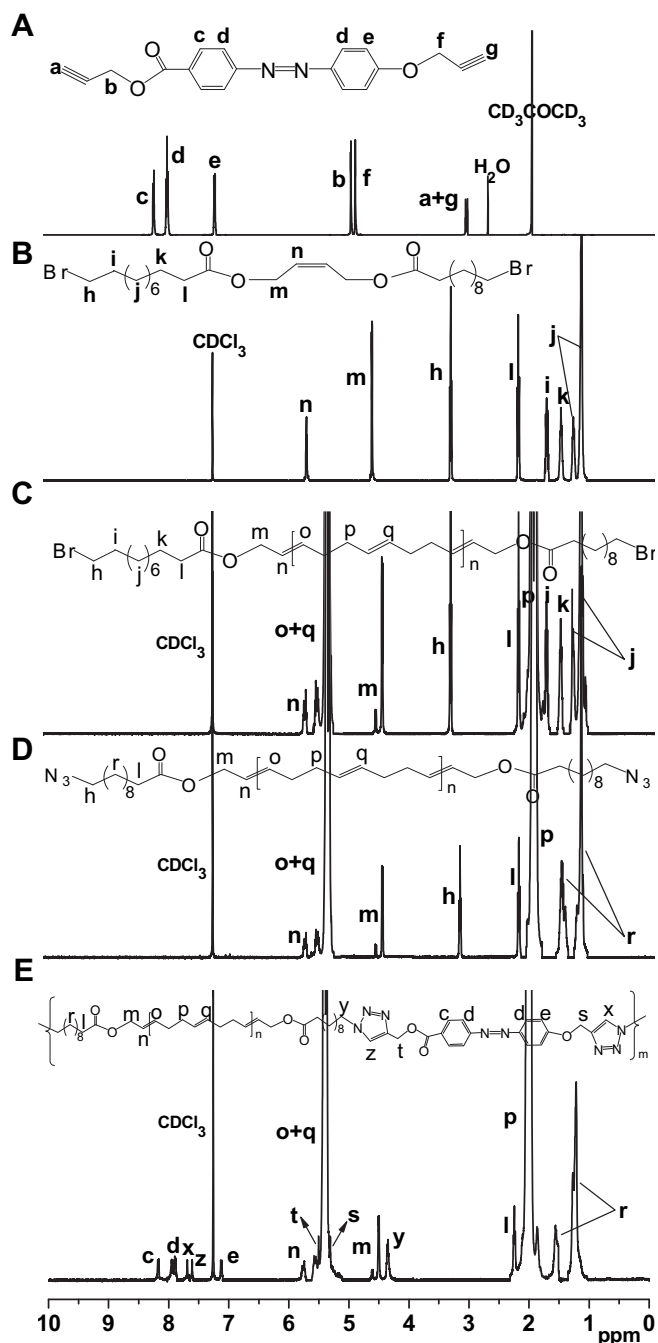


Fig. 1. ^1H NMR spectra for (A) 4-propargyl (4'-propargyloxyphenylazo) benzoate; (B) 1,4-bis(bromoundecylcarbonyloxy)-2-butene; (C) bis(bromoundecylcarbonyloxy)-functionalized telechelic poly(butadiene) (Br-PBD-Br); (D) bis(azidoundecylcarbonyloxy)-functionalized telechelic poly(butadiene) (N_3 -PBD- N_3); (E) multiblock copolymer.

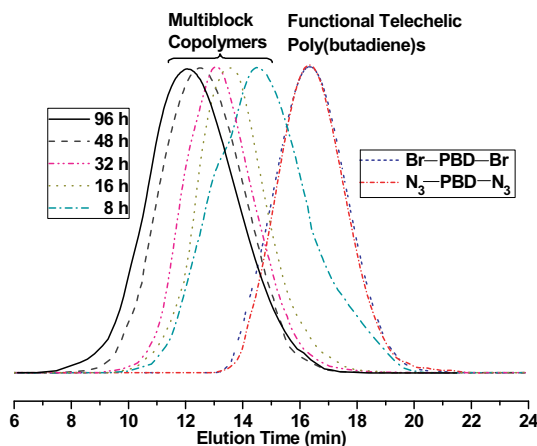


Fig. 2. Gel permeation chromatography (GPC) traces of end-functionalized telechelic poly(butadiene)s and multiblock copolymers.

Table 1
Characteristics of Polymers by ROMP of COD in the Presence of CTA **3**^a and Click Reaction^b.

Polymers	<i>t</i> (h)	Yield (%) ^c	<i>M</i> _{n,GPC} (kDa) ^d	PDI ^d	<i>M</i> _{n,NMR} (kDa) ^e	<i>m</i> ^f	<i>p</i> ^g
4	24	98.5	4.80	1.64	3.80	nd ^h	nd ^h
5	48	96.2	4.60	1.62	3.70	nd ^h	nd ^h
6a	8	96.7	13.3	2.38	nd ^h	3	0.67
6b	16	97.5	25.6	2.05	nd ^h	5	0.83
6c	32	98.3	34.5	2.01	nd ^h	7	0.86
6d	48	98.8	47.7	1.98	nd ^h	10	0.90
6e	96	99.0	57.8	2.03	nd ^h	12	0.92

^a Polymerization was run at 50 °C for 24 h with [COD]/[**3**] = 25 and was initiated with Grubbs catalyst.

^b Reaction conditions: [**2**]:[**5**]:[CuBr]:[bPy] = 1:1:2.1:4.6, polymerization temperature = 30 °C, 1,4-dioxane = 5.0 mL.

^c Obtained gravimetrically after purification from the dried polymer.

^d Number-average molecular weight (*M*_n) and polydispersity index (PDI) were determined by gel permeation chromatography (GPC) in THF relative to mono-dispersed polystyrene standards. kDa = kilo Dalton.

^e *M*_{n,NMR} = *S*_{o+q}/*S*_p × *M*_{n(COD)} + *M*_{n(CTA)} was obtained by ¹H NMR spectroscopy, where *M*_{n(COD)} = 108 and *M*_{n(CTA)} = 582 are the molar masses of COD and CTA, respectively.

^f The number of repeated blocks determined by the ratio of *M*_{n,GPC(6)}/*M*_{n,GPC(5)}.

^g Extent of click reaction (*p*) was calculated from Carothers equation.

^h Not detected.

backbone at 5.60–5.37 ppm (*H*_{o+q}, 4 protons for each unit) [*S*_{o+q}/*q* 4H] to that of methylene protons on the end of PBD backbone at 3.42–3.39 ppm (*H*_p, 4 protons for end group) [*S*_p/4H] can calculate the average degree of polymerization (*n*) and was derived from the following formula: $n = (S_{o+q}/4H):(S_p/4H) = S_{o+q}/S_p = 30$. The integrated ratio was used to determine the number-average molecular weight of PBD **4**, $M_{n,NMR} = (S_{o+q}/S_p) \times M_{n(COD)} (108) + M_{n(CTA)} (582) = 3800$. The GPC curve (Fig. 2) indicated the molecular weight (*M*_{n,GPC}) of PBD **4** was 4800 with a monomodal and a moderate polydispersity index (PDI) of 1.64, and the typical polymerization results are summarized in Table 1. But the value of *M*_{n,GPC} was higher than that of *M*_{n,NMR}, this may be the differences in hydrodynamic volume of PBD and the polystyrene standards used for calibration [61].

Moreover, in the IR spectrum of polymer **4** in Fig. 3A, the absorption bands characteristic peaks at 2921, 985 and 580 cm^{−1} were attributed to the stretching vibration of unsaturated C=C–H and saturated C–H, out-of-plane bending vibrations of C–H bond of –C=CH₂ group and C–Br, respectively, which further confirmed the successful preparation of **4**. Subsequently, dibromo-terminated PBD **4** was transformed into an azide-functional PBD using a conventional method for azide synthesis [63]. So a novel azido-functional telechelic PBD **5** was obtained.

The precise structure of **5** can be determined by ¹H NMR according to the signals of chain-end methylene proton *h* (CH₂–N₃) in the backbone. When compared PBD **5** with **4**, we can clearly detect that a clean chemical shift of proton *h* initially at 3.42 ppm in Fig. 1C to the higher field at 3.26 ppm for protons of chain-end methylene after forming the azido-linkages in Fig. 1D. The molecular weight (*M*_{n,GPC}) and PDI of PBD **5** are almost the same as **4**, and using the same method to calculate *M*_{n,NMR} shown in Table 1. Additionally, the IR spectrum (Fig. 3B) shows the typical, characteristic azido band at 2098 cm^{−1}, confirming the transformation of bromide into azide successfully.

3.4. Preparation of azo-chromophore-containing multiblock poly(butadiene)s

The click reaction of compounds **2** and **5** was proceeded using CuBr/bPy as the catalyst system in 1,4-dioxane at 30 °C for 8–96 h with an excellent yield (Table 1). The molecular weight and PDI of the multiblock copolymers were determined by GPC. It was shown that the resulting polymer **6** has a moderate molecular weight from 13.3 kDa to 57.8 kDa with reasonable PDI ranging from 2.38 to 1.98. The number of repeated blocks (*m*) on each multiblock copolymer chain can be calculated by the ratio of molecular weight of copolymer **6** to that of polymer **5**, i.e. $m = M_{n,GPC(6)}/M_{n,GPC(5)}$, and the value of *m* is within 3–12, then we calculated the extent of click reaction (*p*) by Carothers equation [64,65], i.e. $DP_n = 1/(1 - p)$. *DP*_n is the degree of polymerization, and is equal to the value of *m* in this case. Additionally, the GPC traces of the multiblock copolymers obtained from different reaction time are shown in Fig. 2. With the progress of reaction, the elution curves are gradually shifted to higher molecular weight region and PDI also becomes more narrow, indicating the increase of the number of repeated polymer blocks. As expected, longer reaction time results in the higher molecular weight, more number of repeated polymer blocks, and the lower reaction activity. Therefore, the molecular weight of the multiblock polymer increased linearly with the extension of time within 48 h, but it grew slow after 48 h. The resultant product was also characterized by ¹H NMR (Fig. 1E). As compared with the ¹H NMR spectrum of **2** (Fig. 1A), the signals at 3.16, 3.12 ppm assigned to the alkynyl groups (*a*, *g*) were obviously disappeared after the click reaction, while the protons of newly formed triazole groups (*x*, *z*) were appeared at 7.69, 7.62 ppm and the protons of methylenes (*t*, *s*) on propargyl moiety shifted downfield at 5.50, 5.31 ppm. The structure was further confirmed by IR which shows the complete disappearance of bands corresponding to azide (2098 cm^{−1}) groups after the reaction (Fig. 3C). Also present is the typical absorption at 1580 and 1186 cm^{−1} attributed to the azo and benzene ring mode of the azobenzene group, respectively.

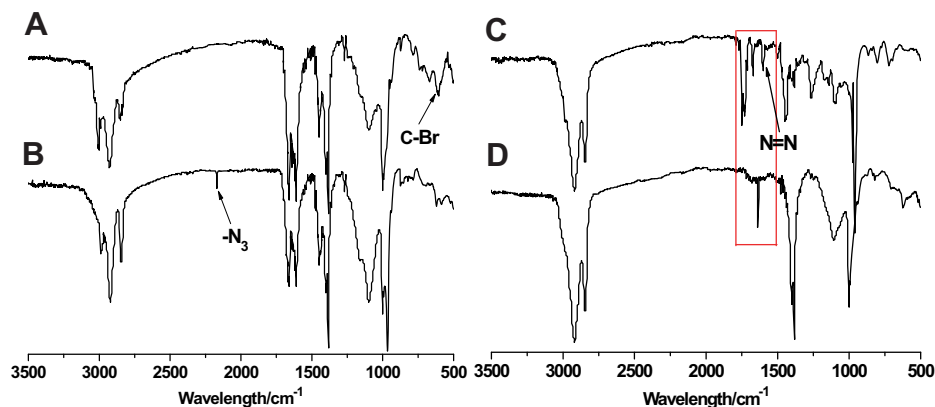


Fig. 3. FTIR spectra for (A) bis(bromoundecylcarbonyloxy)-functionalized telechelic poly(butadiene); (B) bis(azidoundecylcarbonyloxy)-functionalized telechelic poly(butadiene); (C) multiblock copolymer **6d**; (D) multiblock copolymer **6d**/DHBPh complex.

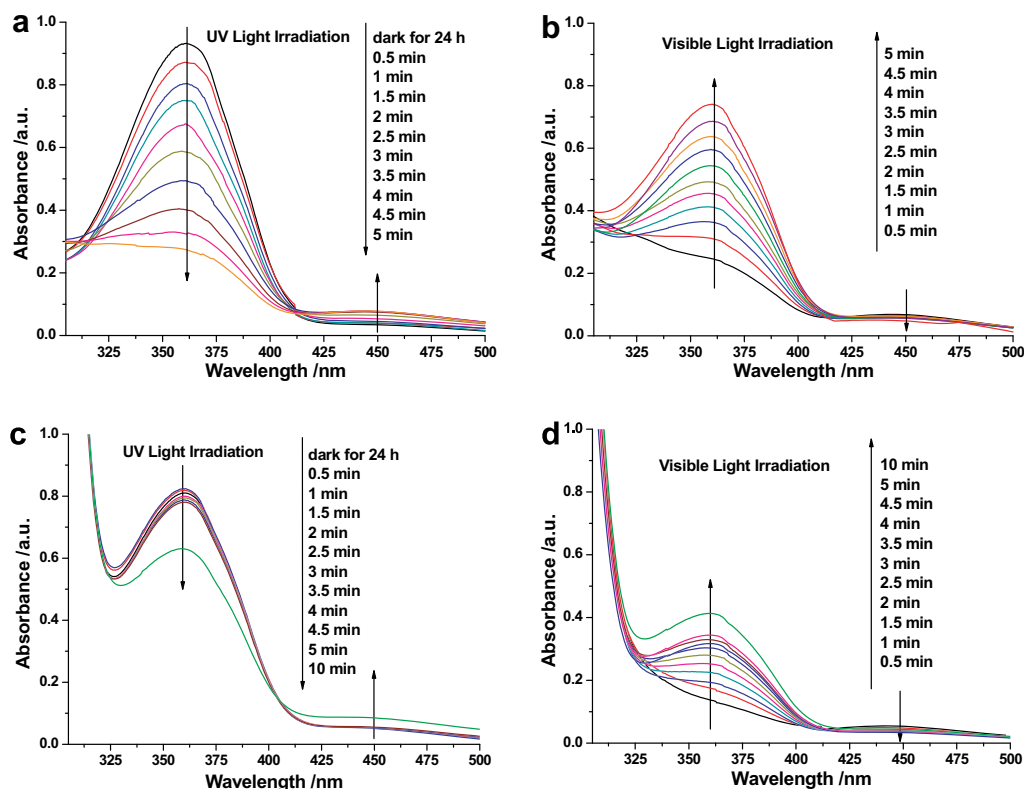


Fig. 4. UV-vis absorption spectral changes of reversible isomerization of multiblock copolymer **6d** in tetrahydrofuran solution with a concentration of 20 $\mu\text{g/mL}$. (a) Absorbance changes with UV irradiation (365 nm). At irradiation time of zero (the highest curve), the sample has been stored in dark for 24 h; (b) absorbance of the sample that has reached the photostationary state in (a) changed with visible light exposure time; (c) absorbance variation of **6d**/DHBPh complex with the repeated process of (a), then extended UV irradiation time; (d) absorbance variation of **6d**/DHBPh complex which has reached the photostationary state in (c) with the repeated process of (b), then extended visible light exposure time.

3.5. Photoisomerization in solution

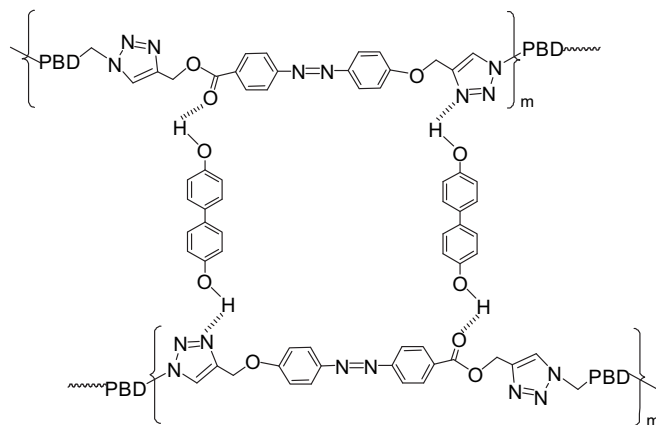
It is well-known that polymers containing azobenzene-type chromophores have the *cis* and *trans* isomers. Generally, the *cis* form of the azobenzene molecule is thermodynamically less stable than the *trans* form. Therefore, when there is a lack of the visible light, the *cis* form obtained by photoisomerization will change into the *trans* form.

UV-vis spectroscopy was generally used to characterize the process of photoisomerization of the azobenzene moiety. The photoresponsive properties of the multiblock copolymers were observed in dilute THF solution at selected time intervals in this article. As illustrated by the UV-vis spectra in Fig. 4, the solution of multiblock copolymer in THF was exposed to varying conditions of UV irradiation or visible light. The absorption band at about 361 nm is attributed to the $\pi \rightarrow \pi^*$ transition in *trans* isomer and the band at 450 nm to the $n \rightarrow \pi^*$ transition in *cis* isomer. In Fig. 4a, the initial solution of azo-chromophore-containing multiblock PBDs in THF was stored in the dark for 24 h to ensure the presence of 100% *trans* isomer. When irradiating the diluted solution by UV light of 365 nm, absorption of the $\pi \rightarrow \pi^*$ band at 361 nm decreased remarkably and at the same time, absorption of the $n \rightarrow \pi^*$ band at around 450 nm increased slightly, indicating a photochemical conversion from *trans* to *cis* isomer configuration, and the existence of a photostationary state after about 5 min of irradiation because there was not further significant change in the spectra.

It has also reported that almost all the azobenzene showed more conversion from the *cis* isomer to *trans* isomer at the photostationary state [66,67]. Fig. 4b displayed the typical spectra of reversible isomerization. When exposure to visible light, the absorption at 361 nm increases, and that at 450 nm decreases

simultaneously, with a photostationary state reached after about 5 min. The sample could also reach its initial *trans* form in 24 h at darkness though a thermal isomerization process.

Supramolecular polymers can be built on the basis of different intermolecular interactions, including coordination bond, hydrogen bond, π - π interaction, and so on. Up to date, most studies on supramolecular azo polymers based on hydrogen bonds have focused primarily on the liquid-crystallinity, nanostructures, microdomain orientation and phase behavior with a limited number of reports on their photoisomerization [68–72]. To further investigate the influence of hydrogen bond on the process of photoisomerization, a small molecule DHBPh, possessing the ability



Scheme 2. Schematic representation of possible interactions between multiblock copolymer **6d** and DHBPh.

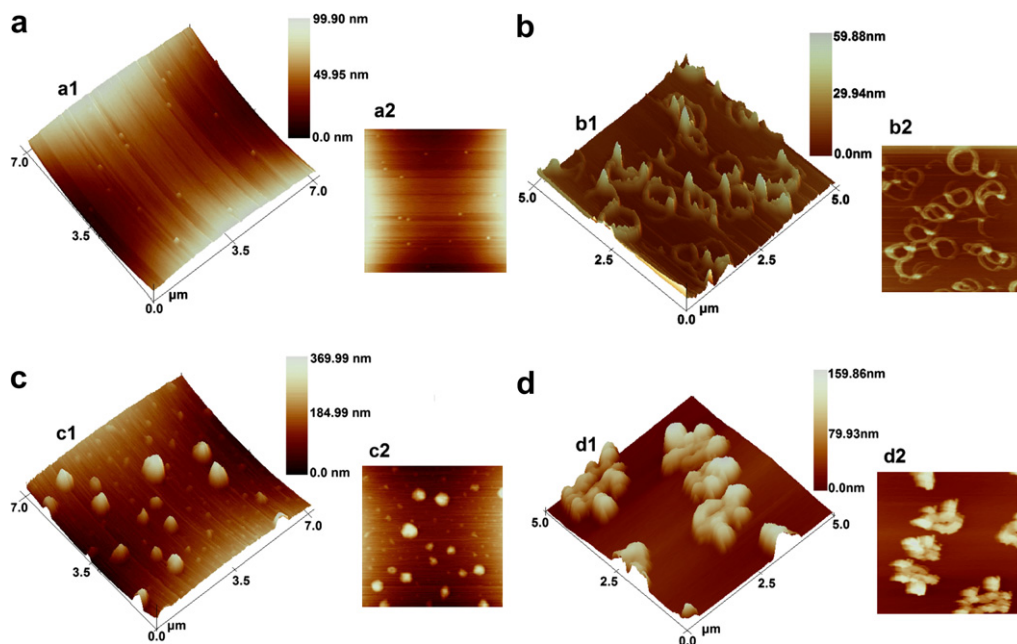


Fig. 5. AFM images of multiblock copolymer **6d** with concentration of 0.02 g/L (a), 0.2 g/L (b), and 2.0 g/L (c) in chloroform; **6d**/DHBPh complex with concentration of 0.2 g/L (d) in tetrahydrofuran (The images of a1–d1 and a2–d2 were the topography and phase images, respectively).

of hydrogen-bonding formation, was dissolved in THF solution of azo-chromophore-containing multiblock PBD. The solution was stirred at room temperature overnight in closed vials to ensure homogeneous mixing of the components. The hydroxy groups were expected to hydrogen-bond to the multiblock copolymer, as illustrated in Scheme 2.

Fig. 3D shows the IR spectrum of **6d**/DHBPh complex. When compared the IR spectrum of this complex with **6d**, we can clearly observe that the characteristic peaks of free ester, triazole, and azobenzene at 1750, 1670, and 1580 cm^{-1} in Fig. 3C for **6d** are combined and shifted to 1640 cm^{-1} in Fig. 3D for **6d**/DHBPh complex. These shifts are positive evidence that these groups are hydrogen-bonded [68,72–74]. It was also verified by UV–vis spectra that the two components of multiblock copolymer and a small molecule have indeed hydrogen-bond interreaction. As compared with Fig. 4a and b, significant changes are clearly observed in Fig. 4c and d, respectively. When repeated the process used in Fig. 4a, there were no obvious absorbance changes at 361 and 450 nm in Fig. 4c, indicating a photochemical conversion from *trans* to *cis* configuration was slight, while an evident photoisomerization process was observed after extending UV irradiation time to 10 min. Fig. 4d revealed similar change trend as that in Fig. 4b. After reaching the photostationary state in Fig. 4c, the sample repeated the process used in Fig. 4b, photoisomerization change also unobvious. However, when extended visible light exposure time, we can discover a photochemical conversion from *cis* to *trans* configuration. Therefore, all changes in these two cases meant that the photoisomerization transformations were more difficult than those in Fig. 4a and b, and these can be considered as a clear evidence that the triazole, azo, or carbonyl groups were hydrogen-bonded with DHBPh, which limited the *trans*–*cis* configuration conversion.

3.6. Morphology observation

The microphase-separated morphology of the multiblock copolymer was examined in preliminary investigations using AFM. Samples for AFM analysis were prepared firstly by dissolving the

setted amount of multiblock copolymer **6d** or **6d**/DHBPh complex in THF and stirred overnight, and then one drop of a dilute solution of **6d** or **6d**/DHBPh complex was spin-coated on a freshly cleaved mica at spinning speed of 1600 rpm/s for 30 s [73]. The AFM images of the pure multiblock copolymer **6d** with different concentrations and **6d**/DHBPh complex were given in Fig. 5. The morphology of the pure multiblock copolymer with concentration of 0.2 g/L in THF was given as image b in Fig. 5, which exhibited some characteristics of an ordered microphase-separated structure. A circular morphology with a diameter of around 0.7 μm was observed, and comparatively uniform in size. The other two samples with lower concentration of 0.02 g/L and higher concentration of 2.0 g/L in THF were investigated, and their AFM images revealed that the spherical morphologies with a diameter of around 0.3 (image a) and 1.2 μm (image c) were observed. These observations indicated that the morphologies of the multiblock copolymer changed with the variation of sample concentrations, and the spherical morphologies were usually appeared except for the specific sample concentration (0.2 g/L) which leading to the formation of an interesting circular morphology. For comparison of the morphology of the pure multiblock copolymer **6d**, a sample of **6d**/DHBPh complex was prepared with concentration of 0.2 g/L. Upon the addition of DHBPh into pure multiblock copolymer solution, cloudlike morphology with size of 1.2 μm in diameter can be observed in Fig. 5d. The formation of the strong intermolecular hydrogen-bonding between DHBPh and multiblock copolymer backbone [74–76], which collected the multiblock copolymer chain one by one randomly, causes an increase in the interfacial size and height of polymer aggregates, and thus results in the morphology change from circularity to cloudlike.

4. Conclusion

A new multiblock PBD containing azo chromophore was successfully prepared through combining of ROMP and click reaction. The dibromide terminated telechelic PBD was synthesized by ROMP of COD in the presence of a difunctional chain transfer agent using second generation Grubbs catalyst under conventional

conditions. The telechelic dibromide was then transformed into azide and reacted with a dialkynyl-containing azobenzene chromophore via click chemistry to prepare multiblock PBD. The multiblock copolymer was characterized by IR and NMR measurements. The results of GPC analysis showed the copolymer with moderate molecular weight and reasonable molecular weight distribution. The photoisomerizations of multiblock copolymers were detected by UV–vis technique in detail and some interesting results were obtained. The morphologies of copolymer aggregates were investigated by AFM measurements, and obvious variation in morphology for different samples were observed. All these results indicated that this approach may serve a valuable guideline for the synthesis of multiblock copolymers, especially for the functional multiblock polyolefins.

Acknowledgements

The authors thank the National Natural Science Foundation of China (Grant No. 20474017) for the financial support of this work.

References

- [1] Zhang Q, Ye J, Lu Y, Nie T, Xie D, Song Q, et al. *Macromolecules* 2008;41:2228–34.
- [2] Lee HS, Roy A, Lane O, Dunn S, McGrath JE. *Polymer* 2008;49:715–23.
- [3] Hong J, Wang Q, Lin YZ, Fan ZQ. *Macromolecules* 2005;38:2691–5.
- [4] Hong J, Wang Q, Fan ZQ. *Macromol Rapid Commun* 2006;27:57–62.
- [5] Ghassemi H, McGrath JE, Zawodzinski TA. *Polymer* 2006;47:4132–9.
- [6] You YZ, Zhou QH, Manickam DS, Wan L, Mao GZ, Oupicky D. *Macromolecules* 2007;40:8617–24.
- [7] Eastwood EA, Dadmun MD. *Macromolecules* 2002;35:5069–77.
- [8] Hong LZ, Zhu FM, Li JF, Ngai T, Xie ZW, Wu C. *Macromolecules* 2008;41:2219–27.
- [9] Wang WJ, Li T, Yu T, Zhu FM. *Macromolecules* 2008;41:9750–4.
- [10] Zhu FM, Ngai T, Xi ZW, Wu C. *Macromolecules* 2003;36:7405–8.
- [11] Holder SJ, Hiorns RC, Sommerdijk NAJM, Williams SJ, Jones RG, Nolte RJM. *Chem Commun* 1998;14:1445–6.
- [12] Nery L, Lefevre H, Fradet A. *J Polym Sci Part A Polym Chem* 2005;43:1331–41.
- [13] DiPasquale G, LaRosa A, Mamo A. *Macromol Rapid Commun* 1997;18:267–72.
- [14] Jeon O, Le SH, Kim SH, Lee YM, Kim YH. *Macromolecules* 2003;36:5585–92.
- [15] Acunzo Fd, Kohn J. *Macromolecules* 2002;35:9360–5.
- [16] Davis KA, Matyjaszewski K. *Macromolecules* 2001;34:2101–7.
- [17] Eastwood EA, Dadmun MD. *Macromolecules* 2001;34:740–7.
- [18] Ramakrishnan A, Dhamodharan R. *Macromolecules* 2003;36:1039–46.
- [19] Toman L, Janata M, Sikora A, Masar B. *J Polym Sci Part A Polym Chem* 2005;43:3823–30.
- [20] You YZ, Manickam DS, Zhou QH, Oupicky D. *Biomacromolecules* 2007;8:2038–44.
- [21] Jia ZF, Xu XW, Fu Q, Huang JL. *J Polym Sci Part A Polym Chem* 2006;44:6071–82.
- [22] Lei P, Wang Q, Hong J, Li YX. *J Polym Sci Part A Polym Chem* 2006;44:6600–6.
- [23] Zhang LS, Wang Q, Lei P, Wang X, Wang CY, Cai L. *J Polym Sci Part A Polym Chem* 2007;45:2617–23.
- [24] Pavlović D, Linhardt JG, Künzler JF, Shipp DA. *J Polym Sci Part A Polym Chem* 2008;46:7033–48.
- [25] Karunakaran R, Kennedy J. *J Polym Sci Part A Polym Chem* 2008;46:4254–7.
- [26] Kavassalis TA, Whitmore MD. *Macromolecules* 1991;24:5340–5.
- [27] Trifitaridou AI, Loizou E, Patrickios CS. *J Polym Sci Part A Polym Chem* 2008;46:4420–32.
- [28] Hadjiantoniou NA, Patrickios CS. *Polymer* 2007;48:7041–8.
- [29] He JL, Ni PH, Liu CC. *J Polym Sci Part A Polym Chem* 2008;46:3029–41.
- [30] Fragouli P, Iatrou H, Lohse DJ, Hadjichristidis N. *J Polym Sci Part A Polym Chem* 2008;46:3938–46.
- [31] Stavrouli N, Katsampas I, Aggelopoulos S, Tsitsilianis C. *Macromol Rapid Commun* 2008;29:130–5.
- [32] Kawabe T, Naito M, Fujiki M. *Macromolecules* 2008;41:1952–60.
- [33] Sha K, Li D, Li Y, Zhang B, Wang J. *Macromolecules* 2008;41:361–71.
- [34] Watkins DM, Fox MA. *Macromolecules* 1995;28:4939–50.
- [35] Nomura K, Schrock RR. *Macromolecules* 1996;29:540–5.
- [36] Miyamoto Y, Fujiki M, Nomura K. *J Polym Sci Part A Polym Chem* 2004;42:4248–65.
- [37] Murphy JJ, Kawasaki T, Fujiki M, Nomura K. *Macromolecules* 2005;38:1075–83.
- [38] Hilf S, Kilbinger AFM. *Macromolecules* 2009;42:1099–106.
- [39] Scherman OA, Rutenberg IM, Grubbs RH. *J Am Chem Soc* 2003;125:8515–22.
- [40] Schwab P, Grubbs RH, Ziller JW. *J Am Chem Soc* 1996;118:100–10.
- [41] Mahanthappa MK, Bates FS, Hillmyer MA. *Macromolecules* 2005;38:7890–4.
- [42] Bielawski CW, Louie J, Grubbs RH. *J Am Chem Soc* 2000;122:12872–3.
- [43] Bielawski CW, Grubbs RH. *Prog Polym Sci* 2007;32:1–29.
- [44] Owen RM, Gestwick JE, Young T, Kiessling LL. *Org Lett* 2002;4:2293–6.
- [45] Katayama H, Yonezawa F, Nagao M, Ozawa F. *Macromolecules* 2002;35:1133–6.
- [46] Lexer C, Saf R, Slugovc C. *J Polym Sci Part A Polym Chem* 2009;47:299–305.
- [47] Hillmyer MA, Nguyen ST, Grubbs RH. *Macromolecules* 1997;30:718–21.
- [48] Pinazzi CP, Campistron I, Croissandeau MC, Reyx D. *J Mol Catal* 1980;8:325–8.
- [49] Reyx D, Campistron I, Hamza M. *J Mol Catal* 1986;36:101–5.
- [50] Nubel PO, Yokelson HB, Lutman CA, Bouslog WG, Behrends RT, Runge KD. *J Mol Catal A Chem* 1997;115:43–50.
- [51] Qin AJ, Jim CKW, Lu WX, Lam JWY, Halussler M, Dong YQ, et al. *Macromolecules* 2007;40:2308–17.
- [52] Gao HF, Matyjaszewski K. *J Am Chem Soc* 2007;129:6633–9.
- [53] Zeng Q, Li ZA, Li Z, Ye C, Qin JG, Tang BZ. *Macromolecules* 2007;40:5634–7.
- [54] Vogt AP, Sumerlin BS. *Macromolecules* 2006;39:5286–92.
- [55] Binder WH, Kluger C. *Macromolecules* 2004;37:9321–30.
- [56] Kluger C, Binder WH. *J Polym Sci Part A Polym Chem* 2007;45:485–99.
- [57] Xia Y, Verdusco R, Grubbs RH, Kornfield JA. *J Am Chem Soc* 2008;130:1735–40.
- [58] Leclair S, Mathe L, Gigue M, Motalebi S, Zhao Y. *Macromolecules* 2003;36:9024–32.
- [59] Bielawski CW, Morita T, Grubbs RH. *Macromolecules* 2000;33:678–80.
- [60] Morita T, Maughon BR, Bielawski CW, Grubbs RH. *Macromolecules* 2000;33:6621–3.
- [61] Bielawski CW, Scherman OA, Grubbs RH. *Polymer* 2001;42:4939–45.
- [62] Scherman OA, Walker R, Grubbs RH. *Macromolecules* 2005;38:9009–14.
- [63] Agat T, Takeichi T. *Macromolecules* 2001;34:7257–63.
- [64] Carothers WH. *J Am Chem Soc* 1929;51:2548–59.
- [65] Flory PJ. *Chem Rev* 1946;39:137–97.
- [66] Tanchak OM, Barrett CJ. *Macromolecules* 2005;38:10566–70.
- [67] Kausar A, Nagano H, Ogata T, Nonaka T, Kurihara S. *Angew Chem Int Ed* 2009;48:2144–7.
- [68] Laforgue A, Bazuin CG, Prud'homme RE. *Macromolecules* 2006;39:6473–82.
- [69] Kautz H, Beek DJM, Sijbesma RP, Meijer EW. *Macromolecules* 2006;39:4265–7.
- [70] Cui L, Zhao Y. *Chem Mater* 2004;16:2076–82.
- [71] Medvedev AV, Barmatov EB, Medvedev AS, Shibaev VP, Ivanov SA, Kozlovsky M, et al. *Macromolecules* 2005;38:2223–9.
- [72] Gao J, He Y, Liu F, Zhang X, Wang ZQ, Wang XG. *Chem Mater* 2007;19:3877–81.
- [73] Hameed N, Liu J, Guo QP. *Macromolecules* 2008;41:7596–605.
- [74] Tung SH, Kalarickal NC, Mays JW, Xu T. *Macromolecules* 2008;41:6453–62.
- [75] Wu S, Niu LF, Shen J, Zhang QJ, Bubeck C. *Macromolecules* 2009;42:362–7.
- [76] Deffieux A, Schappacher M, Hirao A, Watanabe T. *J Am Chem Soc* 2008;130:5670–2.