Cyclic Homo and Block Copolymers Through Sequential Double Click Reactions

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ABSTRACT: Well-defined linear α-anthracene-ω-maleimide functionalized polystyrene (*l*-Anth-PS-MI) and linear α-alkyne-ω-maleimide functionalized poly(*tert*-butyl acrylate) (*l*-alkyne-P*t*BA-MI) homopolymers, and linear α-anthracene-ω-maleimide functionalized PS-*b*-P*t*BA (*l*-Anth-PS-*b*-P*t*BA-MI) and linear α-anthracene-ω-maleimide functionalized PS-*b*-poly(ε-caprolactone) (PCL) (*l*-Anth-PS-*b*-PCL-MI) block copolymers were obtained via combination of atom transfer radical polymerization (ATRP)/ring opening polymerization (ROP) and azide-alkyne click reaction strategy. Subsequently, these linear homo and block copolymers were efficiently clicked via Diels-Alder reaction to give their corresponding cyclic homo and block copolymers at reflux temperature of toluene for 48 h under 7–4 $\times$ 10^{-5} M conditions. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 5083–5091, 2010

KEYWORDS: azide-alkyne click reaction; cyclic block copolymer; cyclic homopolymer; Diels-Alder click reaction; triple detection GPC

INTRODUCTION

A wider variety of complex macromolecular structures, such as graft copolymers, star polymers, dendrimers, and cyclic polymers has emerged through the recent advances in polymer synthesis, in particular using living radical polymerization (LRP) techniques and their compatible partner click reactions.[1–13] These architectures display different properties both in bulk and solution, that is, morphology and assembly in solution and in bulk, and the solution and the melt viscosity, while compared with their linear counterparts.[1–13]

Earlier works on the synthesis of well-defined cyclic polymers were mainly addressed to the living anionic polymerization.[14–17] In these studies, the living polymer initiated by difunctional initiator was coupled with difunctional coupling agent yielding cyclic polymer. In addition, cyclic polymers could also be made using condensation,[18,19] ring opening polymerization (ROP),[14] and ring opening metathesis polymerization (ROMP)[20] methods.

In recent times, with the development of LRP techniques, Hemery's[21] and Monteiro's[22] groups first time used nitroxide-mediated radical polymerization (NMP) and radical addition fragmentation transfer (RAFT) polymerization for the preparation of cyclic polystyrene (*c*-PS) via intramolecular esterification and intramolecular thiol-thiol coupling reactions, respectively. However, former method was limited to the conversion of esterification and latter was a reversible reaction and both gave high yields of *c*-PS under dilute conditions. After the growing popularity of the click chemistry in macromolecular synthesis, Grayson and coworkers[23] first time obtained *c*-PS via combination of atom transfer radical polymerization (ATRP) and Cu(I) catalyzed azide-alkyne click reaction. The cyclization reaction was conducted by intramolecular click reaction of linear α-alkyne-ω-azide PS (*l*-alkyne-PS-N_3) under high dilution. Subsequently, they extended this strategy and methodology to produce cyclic block copolymer, *c*-poly(methyl acrylate)-*b*-PS.[24] After these pioneering works, many cyclic homopolymers ranging from PS and poly(*N*-isopropylacrylamide) have been produced using ATRP-click,[25–27] RAFT-click,[28,29] and NMP-click[30] combinations. Moreover, a variety of combinations involving ROP click,[31] living cationic polymerization click or ring closing metathesis,[32] and ATRP-RCM[33] has been used for the preparation of cyclic polymers. Although the most of these combinations described above afforded the synthesis of cyclic block copolymers only composed of styrene and acrylate type blocks, only one remarkable example by Tezuka and coworkers[33] arose differently where a cyclic block copolymer, *c*-poly(*n*-butyl acrylate)-*b*-poly(ethylene oxide) was prepared via a combination of ATRP-RCM.

The aim of this work is to apply the double click reaction strategy, azide-alkyne, and Diels-Alder reactions, to the preparation of cyclic homo and particularly block copolymers with different chemical compositions, which cannot be attained by using only a click reaction (Scheme 1).

EXPERIMENTAL

Materials

Styrene (St, 99%, Aldrich) and *tert*-butyl acrylate (*t*BA, 99%, Aldrich) were passed twice through basic alumina column to

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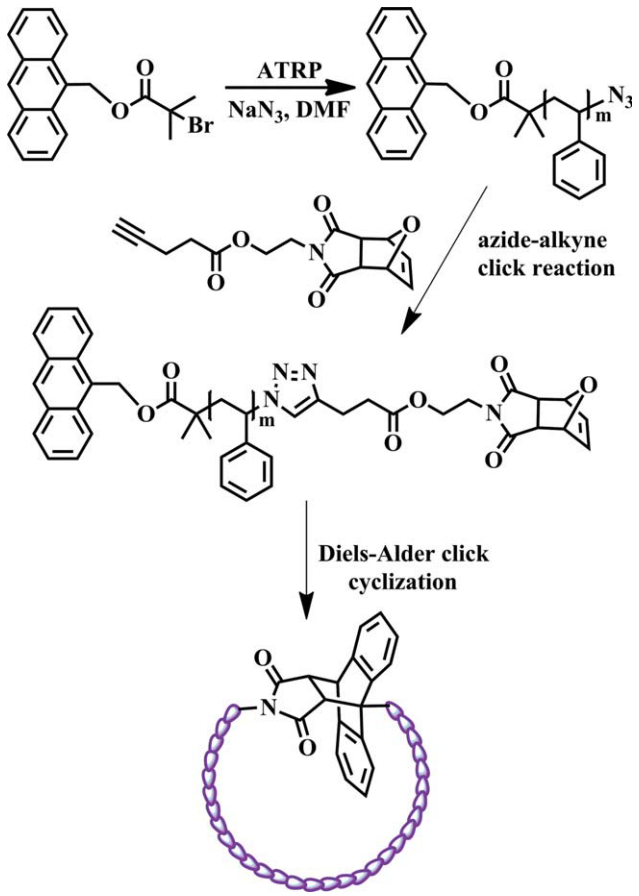


SCHEME 1 General synthetic routes showing the preparation of *l*-PS and the cyclization process via Diels-Alder click chemistry. [Color figures can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

remove inhibitor and then distilled over CaH_2 in vacuum before use. ε-Caprolactone (ε-CL, 99 %, Aldrich) was distilled from CaH_2 in vacuum. *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) was distilled over NaOH before use. Tetrabutylammonium fluoride (TBAF, 1 M in THF, Aldrich), *N,N′*-dicyclohexylcarbodiimide (DCC, 99%, Aldrich), 4-dimethylaminopyridine (DMAP, 99%, Acros), and CuBr (99.9%, Aldrich) were used as received. Dichloromethane (CH_2Cl_2, 99.9%, Aldrich) was used after distillation over P_2O_5. Tetrahydrofuran (THF, 99.8 %, J.T. Baker) was dried and distilled over benzophenone-metallic Na. Solvents unless specified here were purified by conventional procedures. All other reagents were purchased from Aldrich and used as received without further purification.

Instrumentation

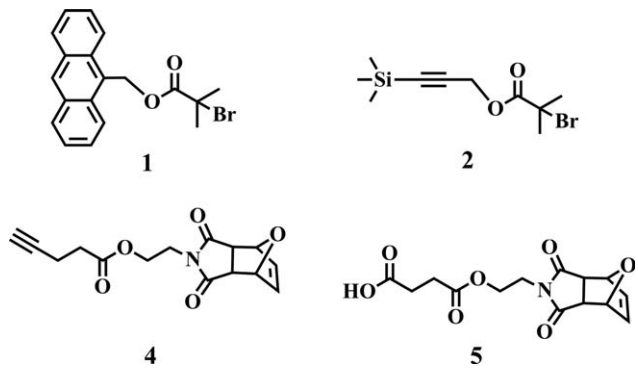
The conventional gel permeation chromatography (GPC) measurements were carried out with an Agilent instrument (Model 1100) consisting of a pump, refractive index (RI), and ultraviolet (UV) detectors and four Waters Styragel columns (guard, HR 5E, HR 4E, HR 3, and HR 2), (4.6-mm internal diameter, 300-mm length, packed with 5-μm particles). The effective molecular weight ranges are 2000–4,000,000, 50–100,000, 500–30,000, and 500–20,000, respectively. THF and toluene were used as eluent at a flow rate of 0.3 mL/min at 30 °C and as an internal standard, respectively. The apparent molecular weights ($M_{n,GPC}$ and $M_{w,GPC}$) and polydispersities (M_w/M_n) were determined with a calibration based on linear PS standards using PL Caliber Software from Polymer Laboratories. The three detection GPC (TD-GPC) set-up with an Agilent 1200 model isocratic pump, four Waters Styragel columns (guard, HR 5E, HR 4, HR 3, and HR 2), and a Viscotek TDA 302 triple detector including RI, dual laser light scattering (DLLS) ($\lambda = 670$ nm, 90° and 7°), and a differential pressure viscometer was conducted to measure the absolute molecular weights ($M_{w,TDGPC}$) in THF with a flow rate of 0.5 mL/min at 35 °C. Three detectors were calibrated with a PS standard having narrow molecular weight distribution ($M_n = 115{,}000$, $M_w/M_n = 1.02$, $[\eta] = 0.519$ dL/g at 35 °C in THF, $dn/dc = 0.185$ mL/g) provided by Viscotek company. UV spectra were recorded on a Shimadzu UV-1601 spectrophotometer in CH_2Cl_2.

Synthesis of Initiators

9-Anthyryl methyl 2-bromo-2-methyl propanoate, **1**,[34] 3-(trimethylsilyl)prop-2-ynyl 2-bromo-2-methylpropanoate, **2**,[35] 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione, **3**[36], and 4-(2-{[(3-acetyl-7-oxabicyclo[2.2.1]hept-yl) carbonyl]amino}ethoxy)-4-oxobutanoic acid, **4**[37] were prepared according to published procedures (Scheme 2).

Preparation of α-Furan-Protected Maleimide-ω-Alkyne Functionalized Precursor, 5

4-Pentynoic acid (1.12 g, 11.5 mmol, 1.2 equiv), DMAP (0.58 g, 4.78 mmol, 0.5 equiv) and **3** (2.00 g, 9.56 mmol, 1 equiv) were dissolved in 40 mL of dry CH_2Cl_2. After stirring 5 min at room temperature, DCC (2.40 g, 11.5 mmol, 1.5 equiv) dissolved in 15 mL of CH_2Cl_2 was added to the reaction mixture. The reaction mixture was stirred overnight at room temperature. After filtration, the solvent was removed, and the remaining product was extracted with CH_2Cl_2/water. The aqueous phase was again extracted with CH_2Cl_2, and the combined organic phases were dried with Na_2SO_4, and concentrated to dryness. The crude product was purified by column chromatography over silica gel eluting with ethyl acetate/hexane (1:1) to give **5** as a white solid (yield: 2.6 g; 94%).



SCHEME 2 Initiators used for the preparation of linear precursors.

^{1}H NMR ($CDCl_3$, δ) 6.5 (s, 2H, C*H*=C*H*, vinyl protons), 5.2 (s, 2H, C*H*CH=CHC*H*, bridge-head protons), 4.2 (t, 2H, J = 5Hz, $NCH_2CH_2OC{=}O$), 3.7 (t, 2H, J = 5Hz, $NCH_2CH_2OC{=}O$), 2.8 (s, 2H, C*H*—C*H*, bridge protons) 2.5 (bs, 4H, $C{=}OCH_2CH_2C{\equiv}CH$), 1.9 (s, 1H, $C{=}OCH_2CH_2C{\equiv}CH$).

LINEAR POLYMERS

Preparation of Linear α-Anthracene-ω-Maleimide Functionalized PS (*l*-Anth-PS-MI)

First linear α-anthracene-ω-bromide functionalized PS (*l*-Anth-PS-Br) was achieved by using **1** as an initiator in ATRP of St in the presence of CuBr/PMDETA at 110 °C for 35 min as described in the literature procedure.[38] ($[M]_0/[I]_0$ = 200, $[I]_0$:$[CuBr]_0$:$[PMDETA]_0$ = 1:1:1, conv. (%) = 20, $M_{n,theo}$ = 4100, $M_{n,NMR}$ = 4550, $M_{n,GPC}$ = 4400, M_w/M_n = 1.12, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 8.4 (Ar*H* of anthracene), 8.3 (Ar*H* of anthracene), 7.9 (Ar*H* of anthracene), 7.5 (Ar*H* of anthracene), 6.5–7.5 (Ar*H* of PS), 5.8 (CH_2-anthracene), 4.4 (C*H*(Ph)-Br), 2.2–0.8 (m, C*H* and CH_2 of PS and CH_3).

Second *l*-Anth-PS-Br (2.0 g, 0.44 mmol, $M_{n,NMR}$ = 4550) dissolved in *N,N*-dimethyl formamide (DMF) (15 mL) and NaN_3 (0.142 g, 2.2 mmol) was added to the flask. After stirring overnight at room temperature, CH_2Cl_2 and water were added to the mixture. The organic layer was extracted three times with water and dried over Na_2SO_4. The excess CH_2Cl_2 was evaporated under reduced pressure, and the obtained product was precipitated into an excess amount of methanol. The recovered polymer *l*-Anth-PS-N_3 was dried for 24 h in a vacuum oven at 25 °C (Yield = 1.9 g, 95 %; $M_{n,GPC}$ = 4500, M_w/M_n = 1.11, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 8.4 (Ar*H* of anthracene), 8.3 (Ar*H* of anthracene), 7.9 (Ar*H* of anthracene), 7.4 (Ar*H* of anthracene), 6.5–7.5 (Ar*H* of PS), 5.8 (CH_2-anthracene), 3.9 (m, C*H*(Ph)-N_3), 2.2–0.8 (m, C*H* and CH_2 of PS and CH_3).

Next, *l*-Anth-PS-N_3 (1.8 g, 0. 39 mmol, $M_{n,NMR}$ = 4550) dissolved in DMF (8 mL), **5** (0.342 g, 1.12 mmol), PMDETA (0.082 mL, 0.39 mmol), and CuBr (0.056 g, 0.39 mmol) were added in a 25 mL of Schlenk tube. The reaction mixture was degassed by three freeze-pump-thaw (FPT) cycles, left in vacuum and stirred at room temperature overnight. The solution was diluted with THF and filtered through a column filled with neutral alumina to remove copper complex and finally precipitated in methanol to give Anth-PS-MI (yield = 1.65 g; $M_{n,GPC}$ = 4700, M_w/M_n = 1.11, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 8.4 (Ar*H* of anthracene), 8.3 (Ar*H* of anthracene), 7.9 (Ar*H* of anthracene), 7.5 (Ar*H* of anthracene), 6.5–7.5 (Ar*H* of PS), 5.8 (CH_2-anthracene), 5.2 (s, 2H, C*H*CH=CHC*H*, bridge-head protons), 5.1 (C*H*(Ph)-triazole, end group of PS), 4.2 (m, 2H, $NCH_2CH_2OC{=}O$), 3.7 (m, 2H, $NCH_2CH_2OC{=}O$), 2.8 (br, 4H, triazole-$CH_2CH_2C{=}O$ and $CH_2NC{=}OCH$-C*H*, bridge protons), 2.6 (m, 2H, $CH_2CH_2C{=}O$), 2.0–0.8 (m, C*H* and CH_2 of PS and CH_3).

Preparation of Linear α-Alkyne-ω-Maleimide Functionalized P*t*BA (*l*-Alkyne-P*t*BA-MI)

The *l*-α-silyl alkyne-ω-bromide functionalized P*t*BA (*l*-silyl alkyne-P*t*BA-Br) was prepared by ATRP of *t*BA. The *t*BA (10.0 mL, 68.2 mmol), PMDETA (0.142 mL, 68.2 mmol), CuBr (0.098 g, 68.2 mmol), and **2** (0.189 g, 68.2 mmol) were added to a 25 mL of Schlenk tube. The reaction mixture was degassed by three FPT cycles, left in vacuum and placed in a thermostated oil bath at 80 °C for 20 min. After the specified time, the polymerization mixture was diluted with THF, passed through a column of neutral alumina to remove catalyst, and precipitated into methanol/water mixture (80/20, v/v). After decantation, the polymer was dissolved in CH_2Cl_2, extracted with water, and the water phase was again extracted with CH_2Cl_2, and combined organic phases were dried over Na_2SO_4. Finally, the organic phase was evaporated, and the polymer was dried in a vacuum oven at 40 °C ($[M]_0/[I]_0$= 100; $[I]_0$:$[CuBr]_0$:$[PMDETA]_0$ = 1:1:1; conv. (%) = 20; $M_{n,theo}$= 2850, $M_{n,NMR}$ = 2700, $M_{n,GPC}$ = 3200, M_w/M_n = 1.14, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 4.6 (s, 2H, $C{\equiv}CCH_2O$), 4.1 (m, 1H, C*H*Br end group of P*t*BA), 2.2 (bs, C*H* of P*t*BA), 2.0–1.0 (m, CH_2 and CH_3 of P*t*BA), 0.16 (s, 9H, $(CH_3)_3Si$—).

Next, *l*-silyl-alkyne-P*t*BA-Br (1.0 g, 0.37 mmol, $M_{n,NMR}$ = 2700) dissolved in DMF (10 mL) and NaN_3 (0.120 g, 1.85 mmol) was added in a Schlenk tube. After the reaction mixture was stirred overnight at 50 °C, CH_2Cl_2 and water were added, and the organic layer was extracted three times with water and dried over Na_2SO_4. Excess CH_2Cl_2 was evaporated under reduced pressure and linear α-silyl alkyne-ω-azide functionalized P*t*BA (*l*-silyl alkyne-P*t*BA-N_3) was dried for 24 h in a vacuum oven at 25 °C (yield = 0.94 g, 94%; $M_{n,GPC}$ = 3230, M_w/M_n = 1.15, relative to linear PS). ^{1}H NMR ($CDCl_3$, δ) 4.6 (s, 2H, $C{\equiv}CCH_2O$), 3.6 (m, 1H, C*H*Br end group of P*t*BA), 2.2 (bs, C*H* of P*t*BA), 2.0–1.0 (m, CH_2 and CH_3 of P*t*BA), 0.16 (s, 9H, $(CH_3)_3Si$—).

Thereafter, *l*-silyl-alkyne-P*t*BA-N_3 (0.90 g, 0. 33 mmol, $M_{n,NMR}$ = 2700) dissolved in DMF (8 mL), **5** (0.29 g, 1.0 mmol), PMDETA (0.069 mL, 0.33 mmol), and CuBr (0.048 g, 0.33 mmol) were added in a 25 mL of Schlenk tube. The reaction mixture was degassed by FPT cycles, left in vacuum and stirred overnight at room temperature. After that time, the solution was then diluted with THF and filtered through a column filled with neutral alumina to remove the copper complex. The polymer was recovered by two times precipitation in methanol/water (8/1; v/v). CH_2Cl_2 and water were added to the remaining solid, and the organic layer was extracted three times with water and dried over Na_2SO_4. Excess CH_2Cl_2 was evaporated under reduced pressure. *l*-Silyl alkyne-P*t*BA-MI was dried for 24 h in a vacuum oven at 25 °C (yield = 0.85 g, $M_{n,GPC}$ = 3600, M_w/M_n = 1.20, relative to linear PS). ^{1}H NMR ($CDCl_3$, δ) 7.5 (s, 1H, C*H* of triazole), 6.5 (s, 2H, vinyl protons), 5.2–5.0 (m, 3H, C*H*CH=CHC*H*, bridge-head protons and C*H*-triazole end group of P*t*BA), 4.6 (s, 2H, $C{\equiv}CCH_2O$), 4.2 (t, 2H, $NCH_2CH_2OC{=}O$), 3.7 (t, 2H, $NCH_2CH_2OC{=}O$), 3.0 (t, 2H, triazole-$CH_2CH_2C{=}O$), 2.9 (s, 2H, $CH_2NC{=}OCH$—C*H*, bridge protons), 2.7 (t, 2H, $CH_2CH_2C{=}O$), 2.2 (bs, C*H* of P*t*BA), 2.0–1.0 (m, CH_2 and CH_3 of P*t*BA), 0.16 (s, 9H, $(CH_3)_3Si$—).

Afterwards, the preserved α-silyl alkyne group of the polymer (0.80 g, 0.27 mmol, $M_{n,NMR}$ = 3000) was deprotected by

using TBAF (0.15 mL, 0.15 mmol) in THF (20 mL). The reaction mixture was stirred for 2 h at room temperature and precipitated in cold methanol/water (4/1; v/v). CH_2Cl_2 and water were then added to the mixture. Organic layer was extracted three times with water, dried over Na_2SO_4, and excess CH_2Cl_2 was evaporated under reduced pressure. The recovered *l*-alkyne-P*t*BA-MI was dried under vacuum at 25 °C for 24 h (yield = 0.75 g; $M_{n,GPC}$ = 3600, M_w/M_n = 1.15, relative to linear PS).^{1}H NMR ($CDCl_3$, δ) 7.5 (s, 1H, C*H* of triazole), 6.5 (s, 2H, vinyl protons), 5.2 (s, 2H, C*H*CH=CHC*H*, bridge-head protons), 5.1 (m, C*H*(C=O)—N of P*t*BA), 4.6 (s, 2H, C≡CCH_2O), 4.2 (t, 2H, NCH$_2$CH_2OC=O), 3.7 (t, 2H, NCH_2CH$_2$OC=O), 3.0 (t, 2H, triazole-CH_2CH$_2$C=O), 2.9 (s, 2H, CH$_2$NC=OC*H*—C*H*, bridge protons), 2.7 (t, 2H, CH$_2$CH_2C=O), 2.2 (bs, C*H* of P*t*BA), 2.0–1.0 (m, CH_2 and CH_3 of P*t*BA).

Preparation of Linear α-Anthracene-ω-Maleimide Functionalized PS-*b*-P*t*BA (*l*-Anth-PS-*b*-P*t*BA-MI)

The *l*-Anth-PS-N$_3$ (0.25 g, 0.055 mmol, $M_{n,NMR}$ = 4550), *l*-alkyne-P*t*BA-MI (0.20 g, 0.066 mmol, $M_{n,NMR}$ = 3000), PMDETA (0.034 mL, 0.165 mmol), CuBr (0.023 g, 0.165 mmol), and DMF (5 mL) were added in a 50 mL of Schlenk tube. The reaction mixture was degassed by three FPT cycles, left in vacuum, and then stirred overnight at room temperature. Polymer solution was passed through neutral alumina column to remove copper salt, precipitated two times in methanol, and dried in a vacuum oven at 25 °C (Yield = 0.32 g, $M_{n,theo}$ = 7550, $M_{n,NMR}$ = 7650, $M_{n,GPC}$ = 7400, M_w/M_n = 1.14, relative to linear PS standards).

Preparation of Linear α-Alkyne-ω-Maleimide Functionalized PCL (*l*-alkyne-PCL-MI)

The *l*-alkyne-PCL-MI was prepared by three step reactions. The linear α-silyl alkyne functionalized PCL (*l*-silyl-alkyne-PCL-OH) was prepared by ROP of ε-CL (5.0 mL, 0.047 mol) in bulk using tin(II) 2-ethylhexanoate as a catalyst and 3-(trimethylsilyl)prop-2-yn-1-ol (0.138 mL, 0.940 mmol) as an initiator at 110 °C for 4 h. The degassed monomer, catalyst, and initiator were added to the flamed Schlenk tube equipped with a magnetic stirring bar in that order. The tube was degassed with three FPT cycles, left under argon, and placed in a thermostated oil bath. After the polymerization, the mixture was diluted with THF and precipitated into an excess amount of cold methanol. It was isolated by filtration and dried at room temperature in a vacuum oven at 25 °C for 24 h ($[M]_0/[I]_0$ = 50, conversion (%) = 68; $M_{n,theo}$ = 4150, $M_{n,NMR}$ = 4050, $M_{n,GPC}$ = 7000, M_w/M_n = 1.06, relative to linear PS). ^{1}H NMR ($CDCl_3$, δ): 4.7 (s, 2H, C≡CCH_2O), 4.0 (2H, CH_2OC=O of PCL), 3.6 (2H, CH_2OH, end group of PCL), 2.3 (2H, C=OCH_2 of PCL), 1.7–1.3 (6H, CH_2 of PCL), 0.16 (s, 9H, (CH_3)$_3$Si—).

Then *l*-silyl-alkyne-PCL-OH (2.5 g, 0.62 mmol, M_n, NMR = 4050) was dissolved in 25 mL of dry CH_2Cl_2. **4** (0.95 g, 3.1 mmol) and DMAP (0.075 g, 0.62 mmol) were added to the reaction mixture in that order. After stirring 5 min at room temperature, DCC (0.64 g, 3.1 mmol) dissolved in 5 mL of CH_2Cl_2 was added. Reaction mixture was then stirred overnight at room temperature. Solvent was removed after filtration, and the mixture was precipitated into excess methanol. Dissolution/precipitation procedure was repeated two times for the purification of final polymer. The recovered polymer, l-silyl-alkyne-PCL-MI was dried under vacuum at 25 °C for 24 h ($M_{n,GPC}$ = 7350; M_w/M_n = 1.07, relative to linear PS). ^{1}H NMR ($CDCl_3$, δ) 6.5 (s, 2H, vinyl protons), 5.2 (s, 2H, C*H*CH=CHC*H*, bridge-head protons), 4.7 (s, 2H, C≡CCH_2O), 4.2 (m, 2H, NCH$_2$CH_2OC=O), 4.0 (2H, CH_2OC=O of PCL), 3.7 (m, 2H, NCH_2CH$_2$OC=O), 2.9 (s, 2H, CH$_2$NC=OC*H*—C*H*, bridge protons), 2.6 (s, 4H, C=OCH_2CH_2C=O), 2.3 (2H, C=OCH_2 of PCL), 1.7–1.3 (6H, CH_2 of PCL), 0.16 (s, 9H, (CH_3)$_3$Si—).

Afterward, the preserved alkyne group at the end of the polymer (2.0 g, 0.46 mmol, $M_{n,NMR}$ = 4350) was deprotected by using TBAF (0.2 mL, 0.2 mmol) in THF (20 mL). The reaction mixture was stirred for 2 h at room temperature and precipitated in cold methanol. The recovered polymer, alkyne-PCL-MI was dried under vacuum at 25 °C for 24 h ($M_{n,GPC}$ = 7100, M_w/M_n = 1.08, relative to linear PS). ^{1}H NMR ($CDCl_3$, δ) 6.5 (s, 2H, vinyl protons), 5.2 (s, 2H, C*H*CH=CHC*H*, bridge-head protons), 4.6 (s, 2H, C≡CCH_2O), 4.2 (m, 2H, NCH$_2$CH_2OC=O), 4.0 (2H, CH_2OC=O of PCL), 3.7 (m, 2H, NCH_2CH$_2$OC=O), 2.9 (s, 2H, CH$_2$NC=OC*H*—C*H*, bridge protons), 2.6 (s, 4H, CH_2CH_2C=O), 2.3 (2H, C=OCH_2 of PCL), 1.7–1.3 (6H, CH_2 of PCL).

Preparation of Linear α-Anthracene-ω-Maleimide Functionalized PS-*b*-PCL (*l*-Anth-PS-*b*-PCL-MI)

l-Anth-PS-N$_3$ (0.25 g, 0.055 mmol, M_n, NMR = 4550), *l*-alkyne-PCL-MI (0.29 g, 0.066 mmol, $M_{n,NMR}$ = 4350), PMDETA (0.034 mL, 0.165 mmol), CuBr (0.023 g, 0.165 mmol), and DMF (5 mL) were added in a 50 mL of Schlenk tube, and the reaction mixture was degassed by three FPT cycles, left in vacuum and then stirred overnight at room temperature. After the specified time, polymer solution was passed through neutral alumina column to remove copper salt, precipitated first in methanol and then diethyl ether, and dried in a vacuum oven at 25 °C (yield = 0.35 g; $M_{n,theo}$ = 8900, $M_{n,NMR}$ = 8750, $M_{n,GPC}$ = 11200, M_w/M_n = 1.05, relative to linear PS standards).

CYCLIC POLYMERS

Cyclization of *l*-Anth-PS-MI via Diels-Alder Click Reaction for *c*-PS Formation

l-Anth-PS-MI (0.10 g, 0.021 mmol, $M_{n,GPC}$ = 4700) was dissolved in toluene (300 mL). The mixture was bubbled with nitrogen for 30 min and refluxed for 48 h under nitrogen in the dark. Solvent was removed under high vacuum, and residual solid was dissolved in THF, and subsequently precipitated into methanol. The final product was dried for 24 h in a vacuum oven at 25 °C ($M_{n,GPC}$ = 4000, M_w/M_n = 1.16, relative to linear PS).

Cyclization of *l*-Anth-PS-*b*-P*t*BA-MI Copolymer via Diels-Alder Click Reaction for *c*-PS-*b*-P*t*BA Formation

l-Anth-PS-*b*-P*t*BA-MI copolymer (0.10 g, 0.013 mmol) was dissolved in toluene (300 mL). The mixture was bubbled with nitrogen for 30 min and refluxed for 48 h under

nitrogen in the dark. Solvent was removed under high vacuum, and residual solid was dissolved in THF, and subsequently precipitated into methanol. The final product was dried for 24 h in a vacuum oven at 25 °C.

Cyclization of *l*-Anth-PS-*b*-PCL-MI Copolymer via Diels-Alder Click Reaction for *c*-PS-*b*-PCL Formation

l-Anth-PS-*b*-PCL-MI (0.10 g, 0.011 mmol) was dissolved in toluene (265 mL). The mixture was bubbled with nitrogen for 30 min and refluxed for 48 h under nitrogen in the dark. Solvent was removed under high vacuum, and residual solid was dissolved in THF, and subsequently precipitated into methanol. The final product was dried for 24 h in a vacuum oven at 25 °C.

RESULTS AND DISCUSSION

Using sequential double click reaction strategy enabled us to prepare firstly linear block copolymers with anthracene and maleimide end-functionality and subsequently cyclic block copolymers, which cannot be achieved by using ATRP-azide-alkyne click reaction combination alone. Nevertheless, Diels-Alder click reaction has not been used in the synthesis of cyclic homopolymers. Therefore, it was tested whether Diels-Alder click reaction was sufficient to form cyclic homopolymers, and the same concept was further applied to create cyclic block copolymers.

Preparation of Linear Homo and Block Copolymers With α-Anthracene and ω-Maleimide Functionality via Azide-Alkyne Click Reaction

The synthesis of *l*-Anth-PS-MI required three steps: (1) *l*-Anth-PS-Br was achieved by using **1** as initiator in ATRP of St in the presence of CuBr/PMDETA at 110 °C for 35 min; (2) bromide end functionality was converted quantitatively to azido to give *l*-Anth-PS-N_3, and (3) introduction of maleimide end-group to the polymer was carried out via click reaction between linear Anth-PS-N_3 and **5**, affording *l*-Anth-PS-MI. GPC and ^{1}H NMR spectroscopy confirmed that polymers were appropriately prepared with controlled molecular weight, low polydispersity index (PDI), and desired end group functionalities.

The *l*-alkyne-P*t*BA-MI was prepared via multistep reactions similar to the synthesis of *l*-Anth-PS-MI. (1) *l*-silyl-alkyne-P*t*BA-Br was prepared by ATRP of *t*BA using **2** as initiator and CuBr/PMDETA as catalyst at 80 °C for 20 min; (2) then, bromide functionality was converted into azido group (3) *l*-silyl-alkyne-P*t*BA-N_3 was clicked with **5**, and then deprotected, thus giving the final *l*-alkyne-P*t*BA-MI. GPC and ^{1}H NMR spectroscopy confirmed that polymers were appropriately prepared with controlled molecular weight, low PDI, and desired end group functionalities.

The azide-alkyne click coupling of *l*-Anth-PS-N_3 and *l*-alkyne-P*t*BA-MI was carried out at room temperature resulting in *l*-Anth-PS-*b*-P*t*BA-MI copolymer. An excess of P*t*BA block (1.2/1) was deliberately used to ensure the reaction completion and easy removal of that segment in the final block copolymer. Moreover, ^{1}H NMR spectroscopy confirmed the incorporation of PS and P*t*BA blocks by appearance of the characteristic signals of the two blocks at 7.5–6.0 (Ar*H*) and 2.2 ppm (C*H*), respectively. The DP_n = 24 of P*t*BA block in the final block copolymer was calculated according to integrated ratio of the signals given above, while DP_n of PS block was = 40.5 and found to be comparable with the DP_n = 23 of linear alkyne-P*t*BA-MI. This also confirms the efficient click coupling so as to produce *l*-Anth-PS-*b*-P*t*BA-MI copolymer. The M_n of the block copolymer was 7400 with a PDI of 1.14 as determined by GPC relative to linear PS standards, which was comparable with $M_{n,theo}$ = 7550 and $M_{n,NMR}$ = 7650.

The preparation of *l*-alkyne-PCL-MI required three steps: (1) *l*-silyl-alkyne-PCL-OH was prepared by ROP of ε-CL using tin(II) 2-ethylhexanoate as a catalyst and 3-(trimethylsilyl)-prop-2-yn-1-ol as an initiator at 110 °C for 4 h, (2) obtained *l*-silyl-alkyne-PCL-OH was reacted with **4** affording *l*-silyl-alkyne-PCL-MI, and (3) silyl end-group was deprotected, thus yielding a *l*-alkyne-PCL-MI. ^{1}H NMR and GPC confirmed that macromolecular structures at three steps were obtained with desired architecture and molecular weight.

The *l*-Anth-PS-*b*-PCL-MI was synthesized via azide-alkyne click coupling of *l*-alkyne-PCL-MI and *l*-Anth-PS-N_3 in the presence of PMDETA/CuBr/DMF overnight at room temperature. Once again, a 20% excess of *l*-alkyne-PCL-MI was used for both reaction completion and easy removal of this segment from the final block copolymer. ^{1}H NMR spectroscopy confirmed the introduction of both PS and PCL segments into the final block copolymer structure, by the appearance of characteristic signals of those segments at 7.5–6.0 (ArH) and 4.0 and 2.3 (CH2) ppm, respectively, as well as C*H*—N of triazole signal at 5.0 ppm. In addition, DP_n = 37 of PCL segment was calculated from NMR spectrum and in good agreement with DP_n= 34 of silyl-alkyne-PCL-OH, whereas DP_n of Anth-PS-N_3 was 40.5. The M_n of the block copolymer was 11200 with a PDI of 1.05 as determined by GPC relative to linear PS standards, which was higher than $M_{n,theo}$ = 8900 and $M_{n,NMR}$ = 8750.

Preparation of Cyclic Homo and Copolymers via Diels-Alder Click Reaction

The *c*-PS was simply prepared from its linear precursor *l*-Anth-PS-MI at a concentration of 7×10^{-5} M in a reflux temperature of toluene for 48 h. After that time, polymerization mixture was evaporated, and the residue was dissolved in THF and subsequently precipitated in methanol. A GPC trace of the residue showed a clear shift to higher retention time region as compared with that of *l*-Anth-PS-MI, thus resulting in the formation of *c*-PS (Fig. 1).

Because a cyclic polymer displays a more compact topology than its linear counterpart. Moreover, a GPC trace of the residue displayed a tail at lower retention time both with respect to that of *c*-PS and its linear precursor, *l*-Anth-PS-MI. This can be described by a Diels-Alder click reaction of *l*-Anth-PS-MI so as to form multiblock linear PS chains. Multipeak splitting of the GPC trace using Gaussian function gave corresponding area fractions of *c*-PS (85%) and *l*-multiblock PS adducts (10% and 5%) (Fig. 1). Therefore, the efficiency of *c*-PS formation is in close agreement to literature values

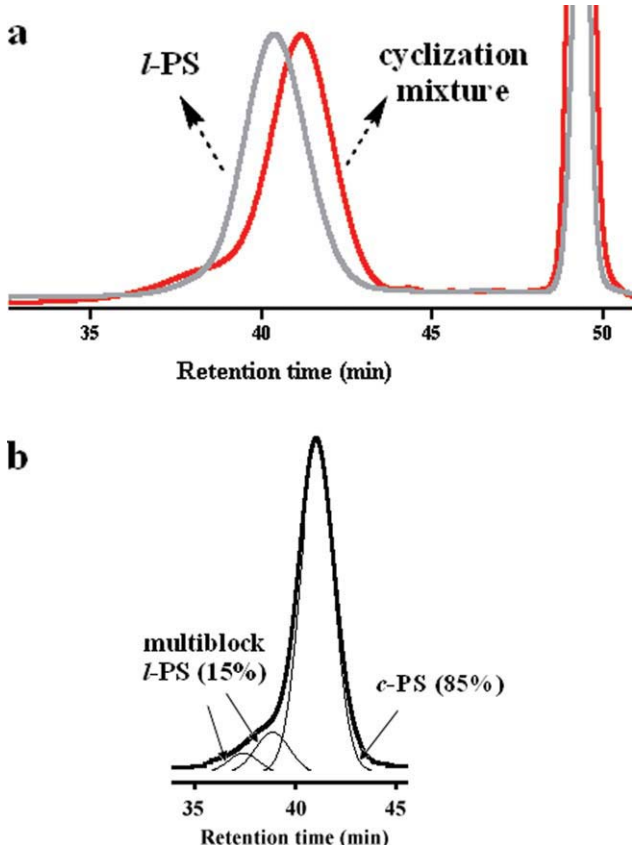


FIGURE 1 Evolution of GPC traces of cyclization product mixture (mainly *c*-PS) and *l*-Anth-PS-MI (a); area fractions of cyclization product mixture determined by multipeak splitting of GPC curve using Gaussian function (b).

under a similar molecular weight range.[9,13,15,20] Moreover, the formation of *c*-PS was primarily confirmed by disappearance of characteristic anthracene central ring signals in the range of 8.6–7.5 ppm, because of a cycloadduct formation and by the appearance of C*H* bridge-head proton at 4.7 ppm (Fig. 2).

Next, *l*-Anth-PS-*b*-P*t*BA-MI copolymer was clicked via Diels-Alder reaction to give its corresponding cyclic block copolymer, *c*-PS-*b*-P*t*BA, at a concentration of 4.3×10^{-5} M in toluene at reflux temperature for 48 h. A similar dissolution-precipitation procedure was performed affording the cyclization product mixture as given above. A GPC trace of the mixture showed a clear shift to lower molecular weight region as compared with that of its linear counterpart *l*-Anth-PS-*b*-P*t*BA-MI copolymer, thus proving the formation of *c*-PS-*b*-P*t*BA (Fig. 3).

The reduction in hydrodynamic volume arises here that when linear counterpart is arranged to form cyclic block copolymer. Once again, a tail detected at lower retention time of the GPC trace may be due to a formation of multiblock *l*-PS-*b*-P*t*BA chains. The result of multipeak splitting of the GPC trace using Gaussian deconvolution indicates that the area ratio of *c*-PS-*b*-P*t*BA and linear multiblock PS-P*t*BA

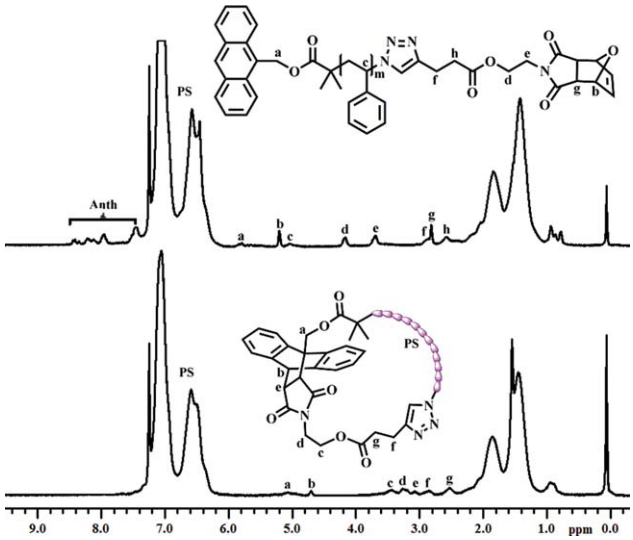


FIGURE 2 ^{1}H NMR spectra of starting *l*-Anth-PS-MI polymer (top) and its cyclization product mixture (mainly *c*-PS) (bottom) and in $CDCl_3$.

chains is 81%, and 14%, and 5%, respectively (Fig. 3). The formation of *c*-PS-*b*-P*t*BA was further confirmed by ^{1}H NMR. The disappearance of anthracene Ar*H* (8.6–7.5 ppm) and the appearance of C*H* bridge-head proton (4.7 ppm) were

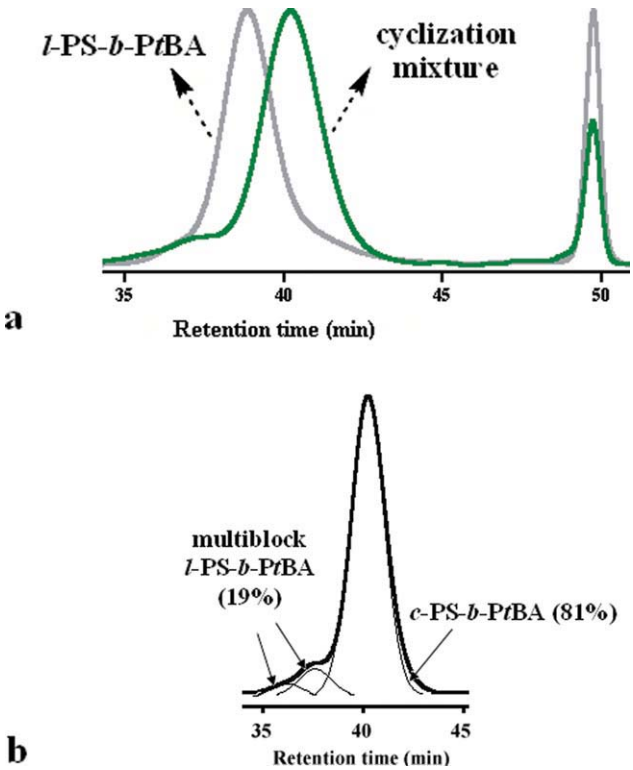


FIGURE 3 Evolution of GPC traces of cyclization product mixture (mainly *c*-PS-*b*-P*t*BA) and *l*-Anth-PS-*b*-P*t*BA-MI copolymer (a); area fractions of cyclization product mixture determined by multipeak splitting of GPC curve using Gaussian function (b).

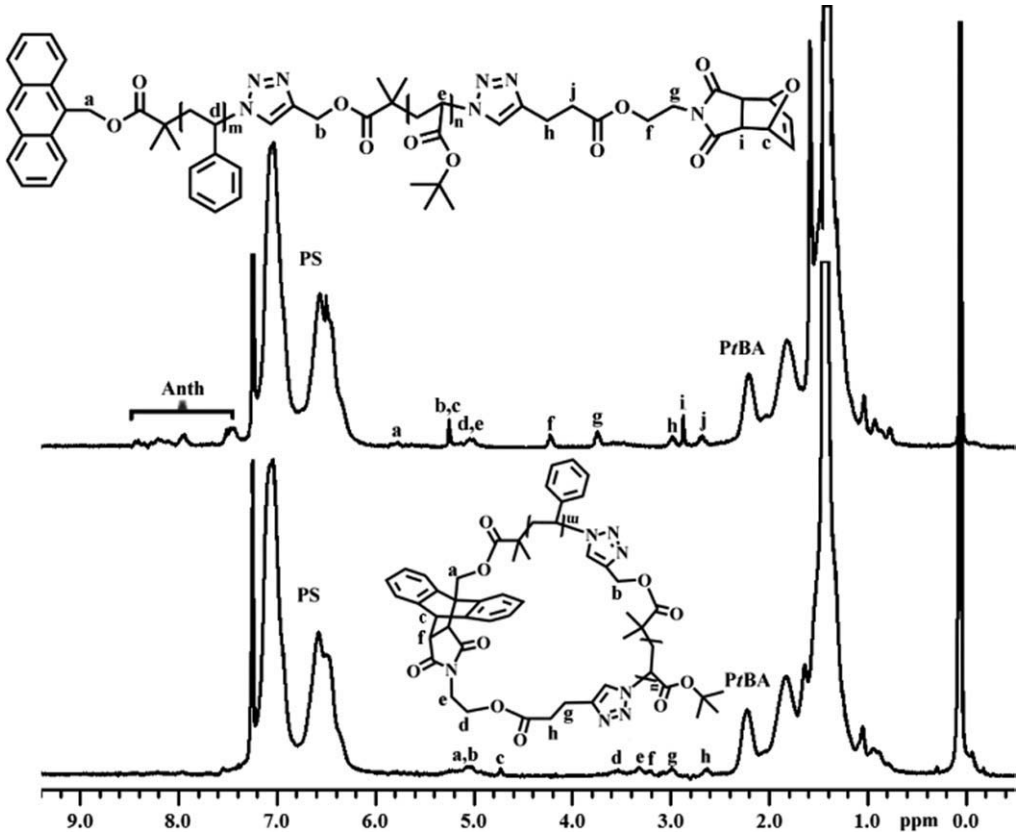


FIGURE 4 ^{1}H NMR spectra of starting *l*-Anth-PS-*b*-P*t*BA-MI copolymer (top) and its cyclization product mixture (mainly *c*-PS-*b*-P*t*BA) (bottom) and in $CDCl_3$.

primarily detected when compared with the *l*-Anth-PS-*b*-P*t*BA-MI copolymer in Figure 4.

As a second cyclic block copolymer, *c*-PS-*b*-PCL was obtained from its linear precursor *l*-Anth-PS-*b*-PCL-MI copolymer via Diels-Alder click reaction at a concentration of 4.1×10^{-5} M in toluene at reflux temperature for 48 h. The cyclization product mixture was recovered after a similar dissolution–precipitation procedure as given above. The bimodal GPC trace showed a clear shift to higher retention time with respect to its linear precursor (Fig. 5). Deconvolution of the bimodal GPC trace of the cyclization product reveals that the area ratio of *c*-PS-*b*-PCL, unreacted *l*-Anth-PS-*b*-PCL-MI copolymer and linear multiblock PS-PCL chain is approximately 77%, 10%, and 13%, respectively (Fig. 5). A deconvoluted GPC fraction (10%) fitting the retention time of the *l*-Anth-PS-*b*-PCL-MI copolymer was obtained differing from the GPC traces of previous cyclic block samples.

It is noted that efficiencies for the cyclic block copolymer formation using Diels Alder click reaction are comparable with those given in literature.[14]

Once again, ^{1}H NMR spectrum of the cyclization product demonstrated typical differences compared with its linear precursor as described above.

Linear and their corresponding cyclic products were further analyzed by TD-GPC. Molecular weights, intrinsic viscosity

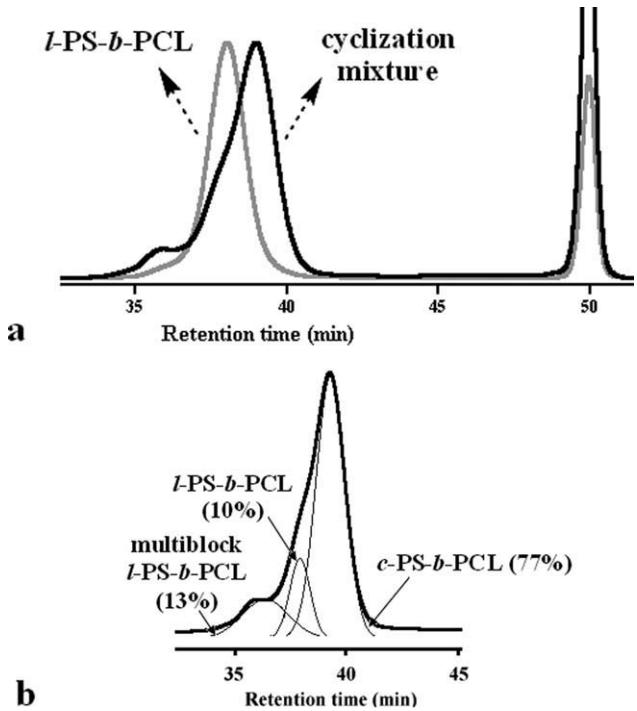


FIGURE 5 Evolution of GPC traces of cyclization mixture (mainly *c*-PS-*b*-PCL) and *l*-Anth-PS-*b*-PCL-MI copolymer (a); area fractions of cyclization product mixture determined by multipeak splitting of GPC curve using Gaussian function (b).

TABLE 1 The Characteristic Data of Cyclic Polymers and Their Linear Precursors

	GPC[a]		TD-GPC				
Polymers	M_n (g/mol)	M_w/M_n	M_n (g/mol)	M_w (g/mol)	$[\eta]$ (dL/g)	R_h (nm)	dn/dc (mL/g)
l-PS	4,700	1.10	5,400	6,150	0.069	1.86	0.185
c-PS	4,000	1.16	5,350	6,300	0.053	1.71	0.185
l-PS-*b*-P*t*BA	7,400	1.14	9,600	10,300	0.075	2.28	0.127[b,c]
c-PS-*b*-P*t*BA	5,700	1.17	10,150	11,950	0.050	2.07	0.127[b]
l-PS-*b*-PCL	11,150	1.05	9,600	10,550	0.150	2.90	0.130[b,c]
c-PS-b-PCL	9,400	1.11	9,950	15,650	0.158	3.14	0.130[b]

[a] Calibrated on the basis of linear PS standards in THF at 30 °C.
[b] Calculated according to (dn/dc) block copolymer = x(dn/dc)PS + y(dn/dc) P*t*BA/or PCL.
[c] Calculated experimentally by TD-GPC using at least three different concentrations: dn/dc (*l*-PS-*b*-P*t*BA) = 0.132 mL/g, dn/dc (*l*-PS-*b*-PCL) = 0.132 mL/g.

($[\eta]$), hydrodynamic radius (R_h), and RI increment (dn/dc) values of linear and cyclic polymers are given in Table 1 along with the molecular weights obtained from conventional GPC.

It was observed that the conventional GPC molecular weights of cyclic polymers decreased dramatically compared with those of corresponding linear counterparts because of the different topology of cyclic polymers. However, the absolute molecular weights (M_w) from TD-GPC of cyclic were consistent with those of their linear precursors, except *c*-PS-*b*-PCL sample. Again, except *c*-PS-*b*-PCL sample, the $[\eta]$ and the R_h values of cyclic polymers are lower than those of their linear counterparts with the same molecular weight, because of different topology of cyclic polymers. In the case of *c*-PS-*b*-PCL, the M_w, $[\eta]$ and R_h values are higher than their corresponding linear values. This increment may be attributed to that laser light scattering and viscosity detectors of TD-GPC are much more sensitive than RI detector for the GPC trace of *c*-PS-*b*-PCL sample with a relatively large fraction at higher molecular weight region. The dn/dc values for linear polymers were calculated both using a formula given in Table 1 and experimentally. Moreover, dn/dc values of linear and cyclic polymers were assumed to be equal for further calculations in TD-GPC.

CONCLUSIONS

Linear homo and block copolymers with α-anthracene and ω-maleimide functional groups were prepared using highly efficient azide-alkyne click reaction. Subsequently, cyclic homo and block copolymers were obtained from their corresponding linear precursors at the concentration range of 7×10^{-5} and 4×10^{-5} M in toluene via Diels-Alder click reaction. The efficiency of the cyclization reactions was determined from the GPC peak splitting method using Gaussian function and found to be in the range of 85–77% for the studied polymers in this work. Thus, double click reaction methodology provides a simple and an efficient way to produce particularly cyclic block copolymers with various compositions, which cannot be obtained by a click reaction alone.

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