Block-Brush Copolymers via ROMP and Sequential Double Click Reaction Strategy

AYDAN DAG, HATICE SAHIN, HAKAN DURMAZ, GURKAN HIZAL, UMIT TUNCA

Department of Chemistry, Istanbul Technical University, Maslak, Istanbul 34469, Turkey

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ABSTRACT: We report an efficient way, sequential double click reactions, for the preparation of brush copolymers with AB block-brush architectures containing polyoxanorbornene (poly (ONB)) backbone and poly(ε-caprolactone) (PCL), poly(methyl methacrylate) (PMMA) or poly(*tert*-butyl acrylate) (P*t*BA) side chains: poly(ONB-*g*-PMMA)-*b*-poly(ONB-*g*-PCL) and poly(ONB-*g*-P*t*BA)-*b*-poly(ONB-*g*-PCL). The living ROMP of ONB affords the synthesis of well-defined poly(ONB-anthracene)$_{20}$-*b*-poly (ONB-azide)$_5$ block copolymer with anthryl and azide pendant groups. Subsequently, well-defined linear alkyne end-functionalized PCL (PCL-alkyne), maleimide end-functionalized PMMA (PMMA-MI) and P*t*BA-MI were introduced onto the block copolymer via sequential azide-alkyne and Diels-Alder click reactions, thus yielding block-brush copolymers. The molecular weight of block-brush copolymers was measured via triple detection GPC (TD-GPC) introducing the experimentally calculated *dn*/*dc* values to the software. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 886–892, 2011

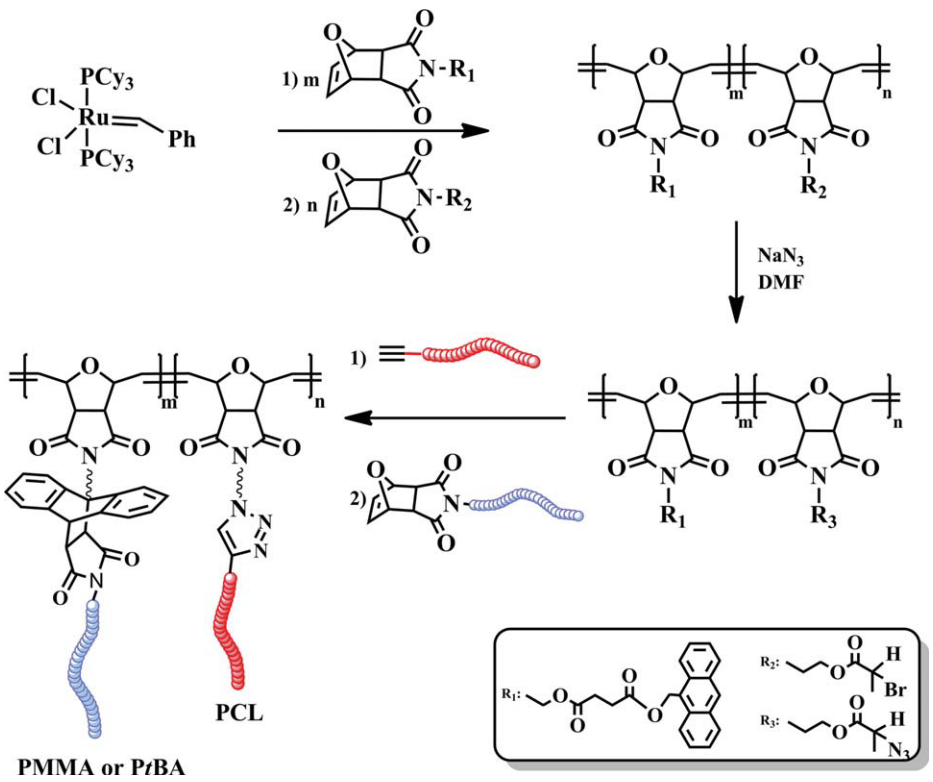
KEYWORDS: azide-alkyne click reaction; block-brush copolymers; brush copolymers; Diels-Alder click reaction; graft copolymers; Grubbs' catalyst; poly(ε-caprolactone); poly(methyl methacrylate); polyoxanorbornene; poly(tert-butyl acrylate); ring opening metathesis polymerization (ROMP); triple detection GPC (TD-GPC)

INTRODUCTION Brush copolymers are a special class of graft copolymers, in which high densely distributed side chains were covalently bonded to the backbone.[1] Those crowded side chains cause the repulsion and enhance the stiffness of the backbone to form brush-like conformation. Brush copolymers should usually contain the side chains on every monomeric unit of the backbone and the backbone significantly longer than side chains. Brush copolymers were mainly produced by three strategies; grafting onto, grafting through, and grafting from.[1,2] In each strategy, various polymerization techniques such as living ionic polymerization, living radical polymerization (LRP), ring opening metathesis polymerization (ROMP) and their compatible partner various click reactions have been employed.[1,3–6]

ROMP is a versatile and an efficient synthetic strategy for the living polymerization of cyclic olefins (norbornene, oxanorbornene, norbornadiene, dicyclopentadiene, etc.) by using metal alkylidene initiators (e.g., molybdenum and ruthenium complex catalysis).[7–25] Relatively few publications on the synthesis of brush copolymers have emerged in the literature based on combining ROMP and click reactions, whereas there have been many published papers by using a single ROMP[26–28] or a combination of ROMP and other living polymerization techniques,[29] such as ROMP-living anionic polymerization,[30,31] ROMP-atom transfer radical polymerization (ATRP),[32–35] ROMP-nitroxide mediated radical polymerization (NMP),[36] ROMP-reversible addition fragmentation chain transfer polymerization (RAFT),[37,38] ROMP-ring opening polymerization (ROP)[39,40] and ROMP-ROP-ATRP[41] combinations.

Grubbs first time employed a ROMP-click combination for the synthesis of brush copolymers using grafting-through strategy.[42] Various macromonomers were efficiently synthesized through azide-alkyne click reaction of a norbornene-alkyne with azido terminal group of polystyrene (PS), poly (methyl methacrylate (PMMA), and poly(*tert*-butyl acrylate) (P*t*BA) that were prepared by ATRP. ROMP of these macromonomers were carried out using the ruthenium catalyst, $(H_2IMes)(pyr)_2(Cl)_2RuCHPh$ in tetrahydrofuran (THF) at room temperature to give graft copolymers with narrow polydispersity and high molecular weights. Later, Fontaine and coworkers used same strategy by reacting alkyne-functionalized oxanorbornene with azido-terminated poly(ethylene glycol) (PEG) so as to give ω-oxanorbornenyl PEG macromonomers.[43] Subsequent ROMP of those macromonomers yield poly(oxanorbornene)-*g*-PEG with narrow polydispersity and moderate molecular weights employing third generation Grubbs' catalyst in dichloromethane at room temperature via grafting-through method. More recently, our group for the first time demonstrated that Diels-Alder reaction[44–49] is an efficient coupling methodology for the preparation of ROMP based brush copolymers.[50] Anthracene-functionalized oxanorbornene monomer and oxanorbornenyl PS

Correspondence to: U. Tunca (E-mail: tuncau@itu.edu.tr) or G. Hizal (E-mail: hizal@itu.edu.tr)



SCHEME 1 General synthetic pathway for the preparation of brush and block-brush copolymers: ROMP followed by azide-alkyne and Diels-Alder click reactions.

with ω-anthracene end-functionalized macromonomer were first polymerized via ROMP using the first generation Grubbs' catalyst in dichloromethane at room temperature and then clicked with maleimide end-functionalized polymers, PEG-MI, PMMA-MI, and P*t*BA-MI, in a Diels-Alder reaction to produce corresponding graft copolymers in toluene at 120 °C.

In this article, we report an efficient way, sequential double click reactions, for the preparation of brush copolymers with AB block-brush architectures containing polyoxanorbornene (poly(ONB)) backbone and poly(ε-caprolactone) (PCL), PMMA or P*t*BA side chains: poly(ONB-*g*-PMMA)-*b*-poly(ONB-*g*-PCL) and poly(ONB-*g*-P*t*BA)-*b*-poly(ONB-*g*-PCL) (Scheme 1).

EXPERIMENTAL

Materials

Methyl methacrylate (MMA, 99%, Aldrich) and *tert*-butyl acrylate (*t*BA, 99%, Aldrich) were passed twice through basic alumina column to 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. *N,N′*-dicyclohexylcarbodiimide (DCC, 99%, Aldrich), propargyl alcohol (99%, Aldrich),4-dimethylaminopyridine (DMAP, 99%, Acros), CuCl (99.9%, Aldrich), 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 ^{1}H NMR spectra were recorded on a Bruker AC250 spectrometer (250 MHz for proton). 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) (λ = 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, [η] = 0.519 dL/g at 35 °C in THF, *dn/dc* = 0.185 mL/g) provided by Viscotek company. The *dn/dc*

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values for the polymers obtained in this study were determined experimentally via using at least four different concentrations of polymers. UV-Vis spectra were recorded on a Shimadzu UV-1601 spectrophotometer in CH_2Cl_2.

Synthesis of ROMP Monomers and Initiators

Oxanorbornenyl anthracene (ONB-anthracene), **1**[50] and oxanorbornenyl bromide (ONB-bromide) (2-bromo-propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-en-4-yl)-ethyl ester), **2**[51] were prepared according to published procedures.

Synthesis of Poly(ONB-Anthracene)$_{20}$-*b*-Poly(ONB-Azide)$_5$ Copolymer via ROMP of Monomers 1 and 2

The first generation Grubbs' catalyst $(PCy_3)_2(Cl)_2$-RuCHPh (0.082 g, 0.10 mmol) was placed in a Schlenk tube and dissolved in 2 mL of anhydrous CH_2Cl_2 in a glove box. The first ROMP monomer **1** (1.0 g, 2.0 mmol) was dissolved in 8 mL of anhydrous CH_2Cl_2 in another Schlenk tube and added to the catalyst solution via syringe. The flask was capped with a septum and removed from glove box. The polymerization was allowed to stir at room temperature for 20 min, and then the second ROMP monomer **2** (0.172 g, 0.500 mmol) in 2 mL of anhydrous CH_2Cl_2 was added to the polymerization mixture and stirred additional for 20 min. The polymerization was then terminated by the addition of butyl vinyl ether, and stirred for additional 1 h at room temperature. Finally, the polymer solution was precipitated in methanol and the obtained polymer was dried for 24 h in a vacuum oven at 40 °C (**1**/**2**/catalyst = 20/5/1; conv. (%) = 100%; $M_{n,theo}$ = 11700; $M_{n,GPC}$ = 7300; M_w/M_n = 1.06, RI detector, relative to PS standards).

^{1}H NMR ($CDCl_3$, δ) 8.3 (bs, 1H, Ar*H* of anthracene), 8.2 (bs, 2H, Ar*H* of anthracene), 7.9 (bs, 2H, Ar*H* of anthracene), 7.5–7.4 (bs, 4H, Ar*H* of anthracene), 6.0 (s, 2H, CH_2-anthracene), 5.9 (s, 2H, C*H*=C*H*, trans), 5.6 (bs, 2H, C*H*=C*H*, cis), 4.9 (bs, 2H, =CH—C*H*—O, cis), 4.3 (bs, 3H, =CH—C*H*—O, trans and C*H*(Br)CH_3), 4.1 (bs, 4H, C=OOC$H_2$$CH_2$N), 3.5 (bs, 4H, C=OOC$H_2CH_2$N), 3.1 (bs, 4H, C*H*—C*H*), 2.5 (s, 4H, C=OCH_2CH_2C=O) 1.8 (bs, 3H, CH(Br)CH_3).

The previously obtained polymer (1.0 g, 0.085 mmol, $M_{n,theo}$ = 11,700) was dissolved in DMF (10 mL) and NaN_3 (0.11 g, 1.7 mmol) was added to the reaction mixture. After stirring the reaction mixture overnight at room temperature, the product was precipitated in an excess amount of methanol. The crude product was dissolved in THF and reprecipitated in methanol. The dissolution-precipitation was repeated two times. The obtained polymer was dried for 24 h in a vacuum oven at 40 °C ($M_{n,GPC}$ = 7500; M_w/M_n = 1.06, RI detector, relative to PS standards). FTIR (cm^{-1}): 2113 (s) (azide stretching).

^{1}H NMR ($CDCl_3$, δ) 8.3 (bs, 1H, Ar*H* of anthracene), 8.2 (bs, 2H, Ar*H* of anthracene), 7.9 (bs, 2H, Ar*H* of anthracene), 7.5–7.4 (bs, 4H, Ar*H* of anthracene), 6.0 (s, 2H, CH_2-anthracene), 5.9 (s, 2H, C*H*=C*H*, trans), 5.6 (bs, 2H, C*H*=C*H*, cis), 4.9 (bs, 2H, =CH—C*H*—O, cis), 4.3 (bs, 2H, =CH—C*H*—O, trans), 4.1 (bs, 4H, C=OOC$H_2$$CH_2$N and 3.5 (bs, 5H, C=OOC$H_2CH_2$N and C*H*($N_3$)$CH_3$),), 3.0 (bs, 4H, C*H*—C*H*), 2.5 (s, 4H, C=OCH_2CH_2C=O) 1.4 (bs, 3H, CH(N_3)CH_3).

Preparation of Poly(ONB-Anthracene)$_{20}$-*b*-Poly(ONB-*g*-PCL)$_5$ via Click Reaction of Poly(ONB-Anthracene)$_{20}$-*b*-Poly(ONB-Azide)$_5$ with PCL-Alkyne

Poly(ONB-anthracene)$_{20}$-*b*-poly(ONB-azide)$_5$ (0.50 g, 0.043 mmol, $M_{n,theo}$ = 11,700, 1 equiv) and PCL-alkyne (0.722 g, 0.258 mmol, based on $M_{n,NMR}$ = 2800, 6 equiv) were dissolved in nitrogen purged DMF (5 mL) in a Schlenk tube equipped with magnetic stirring bar. CuBr (0.031 g, 0.215 mmol) and PMDETA (0.045 mL, 0.215 mmol) were added and the reaction mixture was degassed by three freeze-pump-thaw (FPT) cycles and left in vacuum and stirred at room temperature for 24 h. Reaction mixture was passed through alumina column to remove copper salt and precipitated in methanol. The crude product was dissolved in THF and precipitated in methanol. The dissolution-precipitation procedure was repeated two times and recovered polymer was dried in vacuum oven for 24 h at 40 °C ($M_{n,GPC}$ = 20200; M_w/M_n = 1.29, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ) 8.3 (bs, 1H, Ar*H* of anthracene), 8.2 (bs, 2H, Ar*H* of anthracene), 7.9 (bs, 2H, Ar*H* of anthracene), 7.8 (s, 1H, C*H* of triazole), 7.5-7.4 (bs, 4H, Ar*H* of anthracene), 6.0 (s, 2H, CH_2-anthracene), 5.9 (s, 2H, C*H*=C*H*, trans), 5.6 (bs, 2H, C*H*=C*H*, cis), 5.4 (s, 1H, C=OC*H*(CH_3)-triazole), 5.2 (s, 2H, triazole-CH_2O), 4.9 (bs, 2H, =CH—C*H*—O, cis), 4.3 (s, 2H, =CH—C*H*—O, trans), 4.2-3.9 (bs, 2H, CH_2O of PCL and C=OOC$H_2$$CH_2$N), 3.7-3.5 (m, 4H, C$H_2$OH, end-group of PCL and C=OOCH_2CH_2N), 3.1 (bs, 2H, C*H*—C*H*), 2.5 (bs, 4H, C=OCH_2CH_2C=O), 2.3 (bs, 2H, C=OCH_2 of PCL), 1.8-1.2 (m, 6H, CH_2 of PCL).

Preparation of Poly(ONB-*g*-PMMA)$_{20}$-*b*-Poly(ONB-*g*-PCL)$_5$ via Diels-Alder Click Reaction of Poly(ONB-Anthracene)$_{20}$-*b*-Poly(ONB-*g*-PCL)$_5$ with PMMA-MI

A solution of PMMA-MI (0.32 g, 0.097 mmol, $M_{n,NMR}$ = 3300) in 30 mL of toluene was added to a 15 mL dioxane solution of poly(ONB-anthracene)-*b*-poly(ONB-*g*-PCL) (0.10 g, 0.0039 mmol, $M_{n,theo}$= 25,700). The mixture was bubbled with nitrogen for 30 min and refluxed for 48 h at 110 °C in the dark. After that time, the solution was evaporated to dryness, and the residual solid was dissolved in THF, and subsequently precipitated in methanol. This dissolution-precipitation procedure was repeated two times. The obtained product was dried in a vacuum oven at 40 °C for 24 h ($M_{n,GPC}$ = 38,500, M_w/M_n = 1.18, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ) 7.8 (s, 1H, C*H* of triazole), 7.4–7.0 (m, 8H, Ar*H*), 6.0 (s, 2H, C*H*=C*H*, trans), 5.7 (bs, 2H, C*H*=C*H*, cis), 5.4 (bs, 3H, CH_2-adduct and C=OC*H*(CH_3)-triazole), 5.2 (s, 2H, triazole-CH_2O), 5.0 (bs, 2H, =CH—C*H*—O, cis), 4.7 (s, 1H, CH, bridge head proton), 4.4 (s, 2H, =CH—C*H*—O, trans), 4.2-3.9 (bs, 6H, C=OOC$H_2$$CH_2$N and C$H_2$O of PCL), 3.9-3.0 (OC$H_3$ of PMMA, C*H*—C*H*, and C=OOCH_2CH_2N), 2.6 (bs, 4H, C=OCH_2CH_2C=O), 2.3 (bs, 2H, C=OCH_2 of PCL), 2.0-0.6 (m, CH_2 of PCL and CH_2, CH_3 of PMMA).

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TABLE 1 The Characterization of Brush and Block-Brush Copolymers

Entry	Polymer	DA eff. (%)	$M_{n,theo}$ (g/mol)	TD-GPC M_n (g/mol)	TD-GPC M_w (g/mol)	TD-GPC dn/dc[d] (mL/g)	TD-GPC $[\eta]$ (dL/g)	TD-GPC R_h (nm)
1	Poly(ONB-anthracene)$_{20}$-*b*-poly(ONB-bromide)$_5$	–	11,700[a]	13,000	16,900	0.154	0.050	2.32
2	Poly(ONB-anthracene)$_{20}$-*b*-poly(ONB-*g*-PCL)$_5$	–	25,700[b]	24,300	29,300	0.113	0.078	3.20
3	Poly(ONB-*g*-PMMA)$_{20}$-*b*-poly(ONB-*g*-PCL)$_5$	95	88,400[c]	90,300	115,000	0.081	0.145	6.10
4	Poly(ONB-*g*-P*t*BA)$_{20}$-*b*-poly(ONB-*g*-PCL)$_5$	91	67,600[c]	79,000	93,000	0.087	0.156	5.93

[a] $M_{n,theo}$ = (20 × MW of **1** + 5 × MW of **2**) × conv. %.
[b] $M_{n,theo}$ = 11,700 + (5 × $M_{n,NMR}$ of PCL).
[c] $M_{n,theo}$ = 25,700 + (Diels-Alder efficiency %) × 20 × $M_{n,NMR}$ of PMMA or P*t*BA.
[d] Determined from TD-GPC.

Preparation of Poly(ONB-*g*-P*t*BA)-*b*-Poly(ONB-*g*-PCL) via Diels-Alder Click Reaction of Poly(ONB-Anthracene)-*b*-Poly(ONB-*g*-PCL) with P*t*BA-MI

A solution of P*t*BA-MI (0.22 g, 0.096 mmol, $M_{n,NMR}$ = 2300) in 30 mL of toluene was added to a 15 mL dioxane solution of poly(ONB-anthracene)-*b*-poly(ONB-*g*-PCL) (0.10 g, 0.0039 mmol, $M_{n,theo}$ = 25,700). The mixture was bubbled with nitrogen for 30 min and refluxed for 48 h at 110 °C in the dark. After the specified time, toluene was evaporated under vacuum. The residual solid was dissolved in THF, and subsequently precipitated in methanol. This dissolution-precipitation procedure was repeated two times. The obtained product was dried in a vacuum oven at 40 °C for 24 h ($M_{n,GPC}$ = 31,700, M_w/M_n = 1.20, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ) 7.7 (s, 1H, C*H* of triazole), 7.4–7.0 (m, 8H, Ar*H*), 6.0 (s, 2H, C*H*=C*H*, trans), 5.8 (bs, 2H, C*H*=C*H*, cis), 5.4 (bs, 3H, CH_2-adduct and C=OC*H*(CH_3)-triazole), 5.2 (s, 2H, triazole-CH_2O), 5.0 (bs, 2H, =CH—C*H*—O, cis), 4.7 (s, 1H, C*H*, bridge head proton), 4.4 (s, 2H, =CH—C*H*—O, trans), 4.2-3.9 (bs, 6H, C=OOCH_2CH_2N and CH_2O of PCL), 3.9-3.0 (m, 14H, C=OOCH_2CH_2N, and C*H*—C*H*), 2.6 (bs, 4H, C=OCH_2CH_2C=O), 2.4-2.0 (br, C=OCH_2 of PCL and C*H* of P*t*BA), 2.0-0.6 (CH_2 of PCL and CH_2, CH_3 of P*t*BA).

RESULTS AND DISCUSSION

We exploited both living ROMP technique and sequential click chemistry strategy for the synthesis of AB block-brush copolymers. The preparation of these polymers required three steps: (1) synthesis of well-defined poly(ONB-anthracene)-*b*-poly(ONB-azide) copolymer with both pendant anthracene and azide units, (2) azide-alkyne click reaction of this block copolymer with alkyne end-functionalized PCL (PCL-alkyne) leading to the production of poly(ONB-anthracene)-*b*-poly(ONB-*g*-PCL), and (3) subsequent Diels-Alder click reaction of this polymer with either maleimide end-functionalized PMMA or P*t*BA (PMMA-MI or PtBA-MI) yields the final poly(ONB-*g*-PMMA)-*b*-poly(ONB-*g*-PCL) or poly (ONB-*g*-P*t*BA)-*b*-poly(ONB-*g*-PCL).

The monomers **1** and **2** were sequentially employed in ROMP to yield poly(ONB-anthracene)-*b*-poly(ONB-bromide) using first generation Grubbs catalyst in CH2Cl2 at room temperature for a specified time. ^{1}H NMR spectrum confirmed the structure of target block copolymer, displaying characteristic signals of anthryl hydrogens and CH_3 linked to bromide at 8.3-7.4 and 1.8 ppm, respectively (Supporting Information Fig. S1). A GPC trace of the polymer showed monomodal and narrow polydispersity index ($M_{n,GPC}$ = 7300, M_w/M_n = 1.06, relative to linear PS standards). The $M_{n,TDGPC}$ of 13,000 and M_w/M_n = 1.29 were obtained from a triple detection GPC (TD-GPC) equipped with RI, light scattering and viscometer detectors by introducing experimentally determined dn/dc = 0.154 mL/g into the software.[52,53] Moreover, the obtained $M_{n,TDGPC}$ value was comparable to the theoretical number average molecular weight ($M_{n,theo}$ = (20 × MW of **1** + 5 × MW of **2**) × conv. % = 11,700) (Table 1).

The poly(ONB-anthracene)$_{20}$-*b*-poly(ONB-bromide)$_5$ was readily converted into the azide by reacting this polymer with NaN_3 in DMF at room temperature. The ^{1}H NMR and IR spectra of poly(ONB-anthracene)$_{20}$-*b*-poly(ONB-azide)$_5$

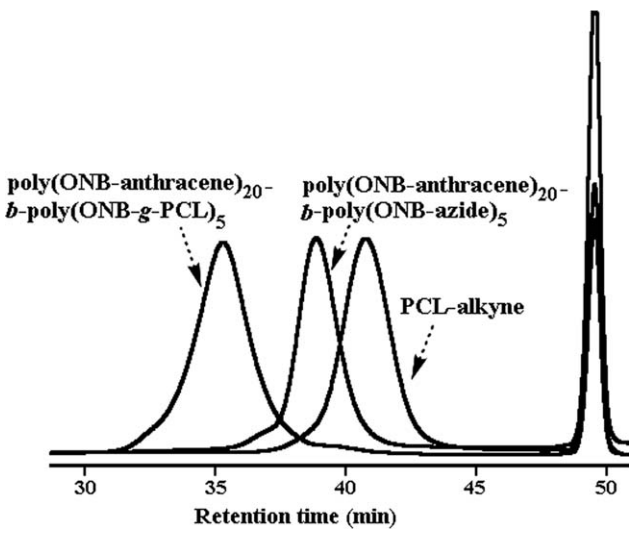

FIGURE 1 GPC traces during the synthesis of brush copolymer: PCL-alkyne, poly(ONB-anthracene)$_{20}$-*b*-poly(ONB-azide)$_5$ block-copolymer, and poly(ONB-anthracene)$_{20}$-*b*-poly(ONB-*g*-PCL)$_5$ brush copolymer.

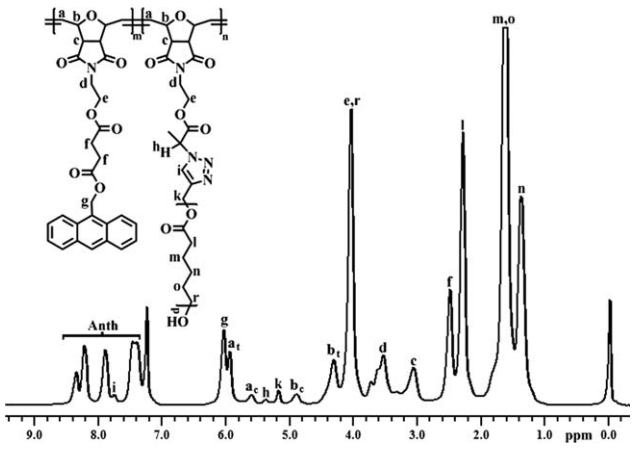

FIGURE 2 ^{1}H NMR spectrum of poly(ONB-anthracene)$_{20}$-*b*-poly(ONB-*g*-PCL)$_5$ brush copolymer in $CDCl_3$.

confirmed quantitative conversion by displaying a new signal of CH_3 linked to azide and an azide stretching band at 2113 cm^{-1}, thus confirming the proposed structure (Supporting Information Fig. S2).

A 1 mol equiv of this polymer was clicked with 6 mol equiv of PCL-alkyne in DMF in the presence of PMDETA/CuBr at room temperature to yield poly(ONB-anthracene)$_{20}$-*b*-poly(ONB-*g*-PCL)$_5$. Purification of the polymer from PCL-alkyne residue can be achieved using a simple dissolution-precipitation cycle in THF/methanol, due to the solubility of PCL precursor in methanol at room temperature within the studied molecular weight range. GPC traces showed a shift in elution volume of poly(ONB-anthracene)$_{20}$-*b*-poly(ONB-*g*-PCL)$_5$ from those of PCL-alkyne and poly(ONB-anthracene)$_{20}$-*b*-poly(ONB-azide)$_5$, indicating successful grafting (Fig. 1).

^{1}H NMR spectrum confirmed the incorporation of PCL into the block copolymer by appearance of the characteristic signals of the PCL segment at 4.0, 2.3 and 1.8–1.2 ppm, as well as a signal of the triazole at 7.8 ppm (Fig. 2). The dn/dc = 0.113 mL/g for poly(ONB-anthracene)$_{20}$-*b*-poly(ONB-*g*-PCL)$_5$ was determined by experimentally and introduced into the OmniSec software to yield molecular weights, intrinsic viscosity ([η]) and hydrodynamic radius (R_h). The $M_{n,theo}$ = 25,700 was calculated by following equation $M_{n,theo}$ = 11,700 + (5 x $M_{n,NMR}$ of PCL) and were close to $M_{n,TDGPC}$ = 24,300 (Table 1).

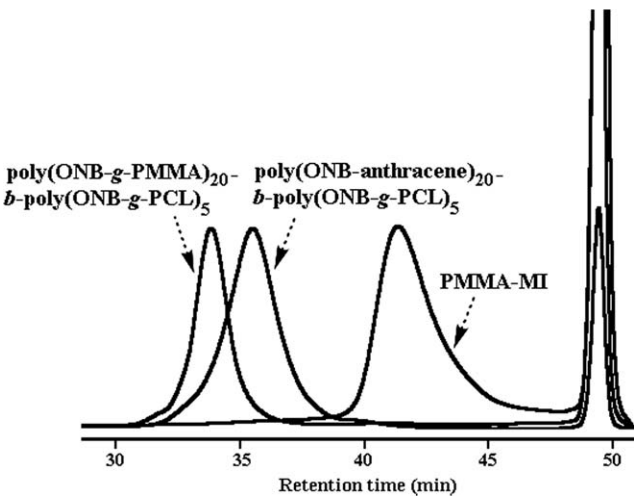

FIGURE 3 GPC traces during the synthesis of block-brush copolymer: PMMA-MI, poly(ONB-anthracene)$_{20}$-*b*-poly(ONB-*g*-PCL)$_5$ brush copolymer and poly(ONB-*g*-PMMA)$_{20}$-*b*-poly(ONB-*g*-PCL) block-brush copolymer.

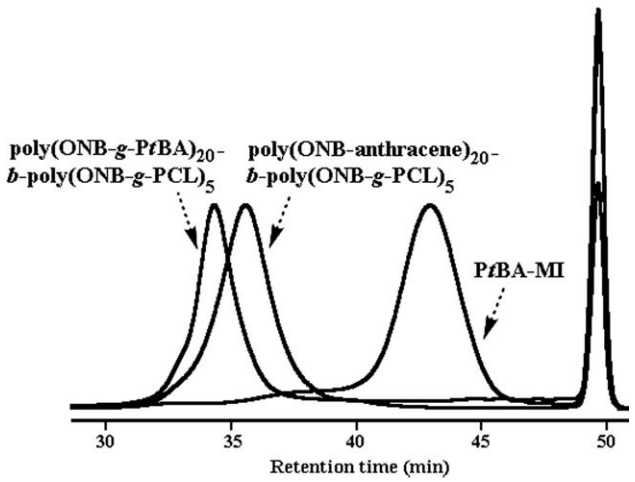

FIGURE 4 GPC traces during the synthesis of block-brush copolymer: P*t*BA-MI, poly(ONB-anthracene)$_{20}$-*b*-poly(ONB-*g*-PCL)$_5$ brush copolymer, and poly(ONB-*g*-P*t*BA)$_{20}$-*b*-poly(ONB-*g*-PCL) block-brush copolymer.

Next, the poly(ONB-anthracene)$_{20}$-*b*-poly(ONB-*g*-PCL)$_5$ was reacted with either a 25 times molar excess of PMMA-MI or P*t*BA-MI in a Diels-Alder click reaction at 110 °C for 48 h, and any unreacted PMMA-MI or P*t*BA-MI was then easily removed by dissolution-precipitation in THF-methanol. Diels-Alder click reaction efficiencies were monitored by UV-Vis spectrophotometer as a signal of anthracene at 368 nm disappeared and were found to be over 91%. GPC traces for both cases indicated a clear shift to higher molecular weight

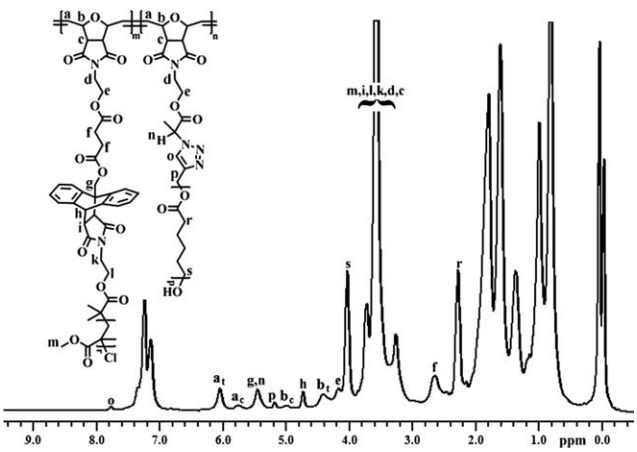

FIGURE 5 ^{1}H NMR spectrum of poly(ONB-*g*-PMMA)$_{20}$-*b*-poly(ONB-*g*-PCL)$_5$ block-brush copolymer in $CDCl_3$.

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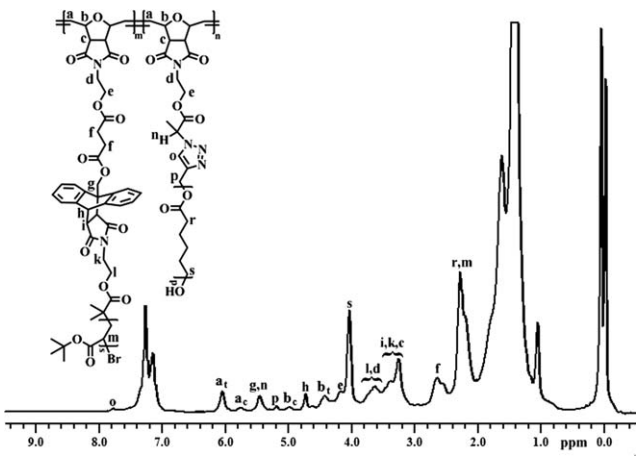

FIGURE 6 ^{1}H NMR spectrum of poly(ONB-*g*-P*t*BA)$_{20}$-*b*-poly (ONB-*g*-PCL)$_5$ block-brush copolymer in $CDCl_3$.

region, confirming the introduction of either PMMA or P*t*BA precursor into the poly(ONB-anthracene)$_{20}$-*b*-poly(ONB-*g*-PCL)$_5$ brush copolymer to yield corresponding poly(ONB-*g*-PMMA)$_{20}$-*b*-poly(ONB-*g*-PCL)$_5$ or poly(ONB-*g*-P*t*BA)$_{20}$-*b*-poly (ONB-*g*-PCL)$_5$ block-brush copolymer (Figs. 3 and 4).

Moreover, ^{1}H NMR spectra of block-brush copolymers confirmed the presence of PMMA and P*t*BA precursors in the final block-brush copolymers by appearance of characteristic signals of PMMA and P*t*BA, as well as the C*H* signal of triazole ring at 7.8 ppm (Figs. 5 and 6).

The *dn/dc* values for poly(ONB-*g*-PMMA)$_{20}$-*b*-poly(ONB-*g*-PCL)$_5$ and poly(ONB-*g*-P*t*BA)$_{20}$-*b*-poly(ONB-*g*-PCL)$_5$ block brush copolymers were experimentally determined to have 0.081 and 0.087 mL/g, respectively, and subsequent introduction of these values into the OmniSec software yielded related molecular weights, $[\eta]$ and R_h of block-brush copolymers (Table 1). $M_{n,TDGPC}$ values are similar to $M_{n,theo}$ of block-brush copolymers calculated from the equation $M_{n,theo}$ = 25,700 + (Diels-Alder efficiency %) × 20 × $M_{n,NMR}$ of PMMA or P*t*BA.

CONCLUSIONS

In this study we exploited the living nature of ROMP and subsequently highly efficient azide-alkyne and Diels-Alder click reactions for the preparation of well-defined block-brush copolymers. The living ROMP carried out at room temperature within relatively short times enables the synthesis of block copolymer structure with pendant anthryl and azide groups. The linear precursors were introduced onto the block copolymer backbone via sequential azide alkyne and Diels-Alder reactions, which are both highly efficient (over 91%). The absolute molecular weights, $[\eta]$ and R_h of polymers were measured by introducing their experimentally determined *dn/dc* values into the TD-GPC software. Moreover, it should be pointed out that theoretical molecular weights of the polymers are similar to those from TD-GPC.

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