Well-Defined Brush Copolymers with High Grafting Density of Amphiphilic Side Chains by Combination of ROP, ROMP, and ATRP

Meiran Xie,* Jingya Dang, Huijing Han, Weizhen Wang, Jingwei Liu, Xiaohua He, and Yiqun Zhang

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

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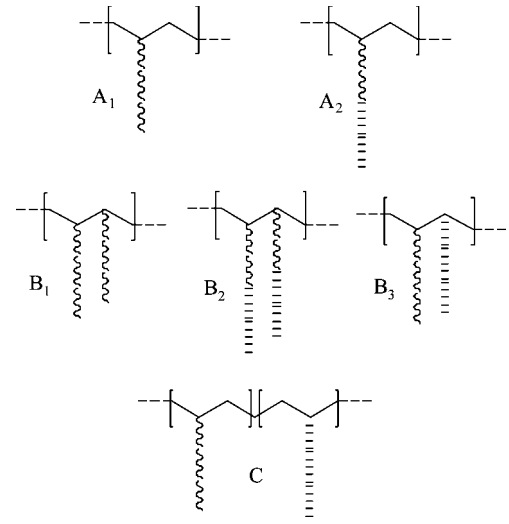
ABSTRACT: This work reports a facile strategy for the preparation of a novel well-defined brush copolymer with two different grafts distributed on the same unit along the backbone via combination of three controlled polymerization methods, ring-opening polymerization (ROP), ring-opening metathesis polymerization (ROMP), and atom transfer radical polymerization (ATRP) based on the synthesis of the heterotrifunctional inimer, 2-hydroxymethyl-3-(2-bromoisobutyryloxymethyl)-5-norbornene (NBE-OH/Br). ROP of ε-caprolactone initiated by NBE-OH/Br was carried out to generate macroinimer, norbornene-*graft*-poly(ε-caprolactone)/Br (NBE-*g*- PCL/Br). The grafting-through strategy was then employed to construct the polymer backbone, poly(norbornene)-*graft*-poly(ε-caprolactone)/Br (PNBE-*g*-PCL/Br) via ROMP of the norbornene-terminated macroinimer NBE-*g*-PCL/Br. Finally, the grafting-from route was used for the synthesis of amphiphilic grafted brush copolymer, poly(norbornene)-*graft*-poly(ε-caprolactone)/poly(2-(dimethylamino)ethyl methacrylate) (PNBE-*g*-PCL/PDMAEMA) by ATRP of 2-(dimethylamino)ethyl methacrylate using bromo-functionalized ROMP product PNBE-*g*-PCL/Br as macroinitiators, containing one hydrophobic PCL graft and one hydrophilic PDMAEMA graft on each unit of the backbone.

Introduction

Graft copolymers are regularly branched macromolecules consisting of a backbone and side chains. They can offer the unique possibility of tailoring material properties through selection of the polymer backbone and the graft chains. Brush copolymers are a special class of graft copolymers in which side chains are distributed densely on a polymer backbone, and because of their crowding arrangement, those side chains are stretched away from the backbone to form a brushlike or a wormlike cylindrical conformation.[1−7] Brush copolymers with controlled structures are expected to provide relatively precise shape and size control in each dimension and can afford unique nanoscale morphologies that are unavailable by self-assembly of block copolymers.[8,9] Usually, three synthetic routes to macromolecular brushes are utilized:[10] (i) "grafting onto" (attachment of side chains to the backbone), (ii) "grafting through" (homo- and copolymerization of macromonomers), and (iii) "grafting from" (grafting side chains from the backbone). Up to now, a variety of well-defined brush copolymers with various architectures have been synthesized by controlled/"living" polymerization methods, such as atom transfer radical polymerization (ATRP),[11] ring-opening polymerization (ROP),[12,13] nitroxide-mediated free radical polymerization (NMP),[14,15] reversible addition−fragmentation chain transfer (RAFT) polymerization,[16,17] ring-opening metathesis polymerization (ROMP),[18−25] and also a combination of these polymerization techniques via three aforementioned synthetic strategies.[26]

Generally, brush copolymers could be divided into three categories according to the number and the kind of side chains as well as the formation of backbone (Scheme 1). The first group contains one linear branch of homopolymer [A_1, Scheme 1] or diblock copolymer [A_2, Scheme 1] as the side chains distributed on each unit of the polymer backbone formed by homopolymerization of one monomer or macromonomer. They have been synthesized extensively by single method or combination of various techniques including ATRP,[27] ATRP/ROP,[28] RAFT/ATRP,[29] ROMP/ROP,[30−32] anionic polymerization/ROP,[33] anionic polymerization/ROMP,[34] and ROMP/ATRP[35−38] to yield the brush copolymers with homopolymer-based grafts (A_1), as well as by ATRP,[39−42] ATRP/ROP,[43] ROMP/NMP,[44,45] ROMP/RAFT,[46] ROMP/ATRP,[47] and anionic polymerization/ROMP[48] to afford the unique brush copolymers composed of diblock grafts (A_2).

Scheme 1. Three Representative Kinds of Architectures for Well-Defined Brush Copolymers



The second group is attachment of two linear branches of homopolymers [B_1, Scheme 1], block copolymers [B_2, Scheme 1], or heteropolymers [B_3, Scheme 1] as the side chains densely distributed on the same unit of the polymer backbone which was also formed by homopolymerization of one monomer or macromonomer. The controlled and modular preparation of such brush copolymers still remains a challenge arising from the limitation of the steric crowded two branches within each monomer unit; thus, so far few efforts have been paid to describe

* Corresponding author. E-mail: mrxie@chem.ecnu.edu.cn; fax: (+86) 21 62232414.

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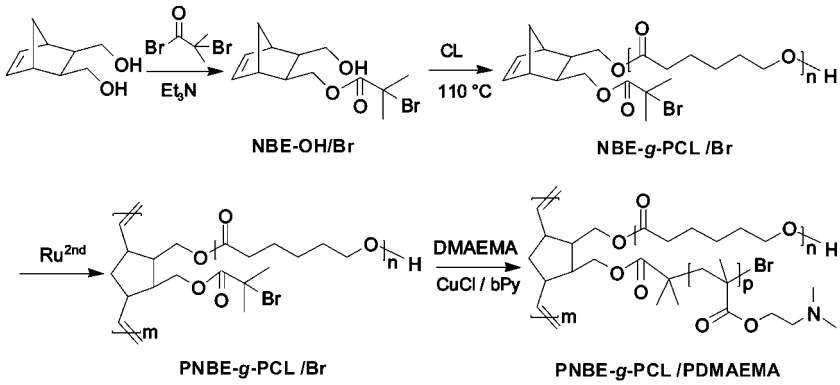
Scheme 2. Synthesis of High Density Amphiphilic Grafted Brush Copolymers



the use of well-defined polymerization methods toward the synthesis of these copolymers by ROMP/ROP[30,31] and anionic polymerization/ROMP[49] to give the brush copolymers with the same two homopolymer grafts (B_1), and by combining highly controlled polymerization methods ROMP/ATRP[50] to present the well-defined brush copolymers with the same two diblock copolymer grafts (B_2). As for the well-defined graft copolymers with two different side chains or amphiphilic grafts distributed on the same unit of the backbone (B_3), there has been few literature reports available. Huang[51] presented a strategy to prepare "asymmetric" centipede-like graft copolymer of poly-[poly(ethylene glycol) methyl ether acrylate]-*g*-polystyrene (PPEGMEA-*g*-PS) with a well-defined centipede structure via successive ATRP of poly(ethylene glycol) methyl ether acrylate and styrene. In this case, the macroinitiator of PPEGMEA-Br must be synthesized under a strict reaction condition of −78 °C with *n*-BuLi as a reagent. In another case, amphiphilic graft copolymers $EtTrp_x$/$PNIPAm_y$-PPPs with tryptophan ethyl ester (EtTrp) as hydrophobic groups and oligomer poly(*N*-isopropylacrylamide) (PNIPAm) as hydrophilic segments were synthesized by thermal ROP of hexachlorocyclotriphosphazene, and subsequent substitution reaction with EtTrp and PNIPAm,[52] where x and y indicated the average number of EtTrp and PNIPAm, respectively, in a structural repeat unit of polyphosphazene (PPP) backbone; therefore, these two grafts were connected randomly along with the PPP backbone.

The third group contains two or more different linear branches [C, Scheme 1] attached to dissimilar units of the polymer backbone formed by copolymerization of different monomers or macromonomers; only a limited number of reports are available to prepare this type of brush copolymers. Schmidt and co-workers reported the first example of experimental realization of statistical copolymer cylindrical brushes by ATRP[53] of two different macromonomers. Neugebauer and Matyjaszewski studied the copolymerization of two crystallizable monomers using ATRP[54] to offer brush macromolecules with densely heterografted amphiphilic side chains. Chen and co-workers[55] reported a simple synthetic strategy toward the rapid and easy synthesis of amphiphilic heterografted copolymer brushes with alternating hydrophobic and hydrophilic grafts through radical copolymerization of styrenic and maleimidic macromonomers. Vlček and co-workers[56] recently prepared bottlebrush-shaped copolymers with cellulose diacetate backbone and chemically different grafts by a combination of ROP and ATRP.

Such regularly brush copolymers (B_3) with two different grafts high densely distributed on the same unit along the backbone are very interesting and may undergo unusual intramolecular microphase separation.[53] This well-defined, complex architecture can meet the demand for new polymeric materials with higher levels of performance and improved control of properties for specific applications. To achieve these goals, we have synthesized a novel heterotrifunctional inimer, 2-hydroxy- methyl-3-(2-bromoisobutyryloxymethyl)-5-norbornene (NBE-OH/Br), having one polymerizable group for ROMP, and two different initiating sites for ROP and ATRP, respectively (Scheme 2). This is crucial to gain access to the expected structure and is fortunately convenient for norbornene derivative monomer bearing two different functional groups on the norbornene ring, but it is difficult for vinyl monomers to construct the complex polymer architectures unless introducing a spacer between the vinyl end and the moiety with two functional groups,[57] or yielding macroinitiator under strict reaction conditions.[51] Starting from the mixed functional norbornene inimer, three steps are needed to produce well-defined brush copolymers with high grafting density of amphiphilic side chains. First, the hydroxyl attached to norbornene ring (NBE-OH/Br) was used to initiate ROP of ε-caprolactone (CL) to generate norbornene-terminated macroinimer, norbornene-*graft*-poly(ε-caprolactone)/Br (NBE-*g*-PCL/Br) with 2-bromoisobutyryl as the side group and one side chain of poly(ε-caprolactone) (PCL) as the hydrophobic graft. Second, ROMP of the strained cyclic norbornene-terminated macroinimer was employed as the polymerization method for the construction of the primary polymer backbone containing both PCL grafts and 2-bromoisobutyryl groups regularly to form macroinitiator, poly(norbornene)-*graft*-poly(ε-caprolactone)/Br (PNBE-*g*-PCL/Br). Last, ATRP of 2-(dimethylamino)ethyl methacrylate (DMAEMA) using bromo-functionalized ROMP polymers (PNBE-*g*-PCL/Br) as polyfunctional macroinitiators gave well-defined high densely amphiphilic grafted brush copolymer, poly(norbornene)-*graft*-poly(ε-caprolactone)/poly(2-(dimethylamino)ethyl methacrylate) (PNBE-*g*- PCL/PDMAEMA) containing one hydrophobic PCL graft and one hydrophilic PDMAEMA graft on each unit of the backbone (Scheme 2).

Experimental Section

Materials. 5-Norbornene-*endo*,*endo*-2,3-dicarboxylicanhydride (>98%), lithium aluminum hydride (95%), tin(II) 2-ethylhexanoate ($Sn(Oct)_2$, 95%), α,α′-bipyridyl (bPy, 99%), 2-(dimethylamino)ethyl methacrylate (97%), 2-bromoisobutyryl bromide (97%), ε-caprolactone (99%), and benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(tricyclohexylphosphine)ruthenium (second generation Grubbs catalyst, Ru^{second}) were purchased from Alfa Aesar or Aldrich and used as received without purification. 2,3-Dihydroxymethyl-5-norbornene was synthesized according to a literature procedure.[58] Triethylamine (Et_3N) was freshly distilled and dried by sieves. Copper(I) chloride (CuCl, Alfa Aesar, 97%) was purified by washing with glacial acetic acid, followed by absolute ethanol and ethyl ether, and then dried under vacuum. Solvents were distilled over drying agents under nitrogen prior to use: methylene chloride (CH_2Cl_2) from calcium hydride, tetrahydrofuran (THF), and toluene from sodium/benzophenone.

Characterization. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded using tetramethylsilane as an internal standard in $CDCl_3$ or CD_3COCD_3 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; 10^3, 10^4, and 10^5 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. Gas chromatography (GC) was measured by Agilent 6890 series GC system instrument equipped with a flame ionization detector and a capillary column (HP-5. 0.25 mm × 30 m), using decane as an internal standard. T_{inj} 280 °C, T_{detec} 280 °C, T_{init} 50 °C (10 °C/min), carrier gas: N_2. High-resolution mass spectrometry (HRMS) data were recorded on a Waters GCT Premier mass spectrometer with electron ionization mode.

Polymerizations were carried out in Schlenk tubes under dry nitrogen atmosphere for both ROP and ROMP and under vacuum for ATRP.

Synthesis of 2-Hydroxymethyl-3-(2-bromoisobutyryloxymethyl)-5-norbornene (NBE-OH/Br). 2,3-Dihydroxymethyl-5-norbornene (6.80 g, 44.0 mmol) was dissolved in 100 mL of CH_2Cl_2, and 14 mL (10.2 g, 100 mmol) of dry Et_3N was added under nitrogen. The reaction mixture was cooled to 0 °C before 2-bromoisobutyryl bromide (4.9 mL, 40 mmol) was added dropwise over 1 h. The reaction mixture was then warmed to room temperature and stirred for further 22 h. The mixture was filtered, the filtrate was washed three times with water (3 × 60 mL), and the organic layer was dried over anhydrous Na_2SO_4. Solvent was then removed under reduced pressure, and the crude oil was purified by column chromatography, eluting with 80:1 CH_2Cl_2/MeOH on silica. Solvent removal under reduced pressure afforded 9.66 g of NBE-OH/Br as a viscous colorless liquid in 80% yield. ^{1}H NMR ($CDCl_3$): δ (ppm) 6.20−6.17 (m, 2H, olefinic protons on the norbornene ring), 4.05−3.90 (m, 2H, CH_2OCO), 3.52−3.34 (m, 2H, CH_2OH), 2.97 (s, 2H, 2 × CH on the norbornene ring), 2.60−2.47 (m, 2H, 2 × CH on the norbornene ring), 1.94 (s, 6H, 2 × CH_3), 1.54−1.26 (m, 2H, CH_2 on the norbornene ring). ^{13}C NMR ($CDCl_3$): δ (ppm) 171.47 (O COC(CH$_3$)$_2$Br), 135.50 (CH═CH), 135.15 (CH═CH), 66.50 (OCO C(CH$_3$)$_2$Br), 62.77 (CH$_2$OH), 55.88 (CH$_2$OCO), 49.16 (CH CH$_2$CH), 45.66 (CH CHCH═), 45.36 (CH CHCH═), 44.60 (CH CHCH$_2$OH), 40.37 (CH CHCH$_2$OCO), 30.78 (C(CH$_3$)$_2$Br), 30.76 (C(CH$_3$)$_2$Br). GC: single peak observed at the retention time of 13.2 min. EI/HRMS: calcd for $C_{13}H_{19}BrO_3$: 302.0518; found: 302.0518.

Preparation of Norbornene-*graft*-poly(ε-caprolactone)/Br (NBE-*g*-PCL/Br) via ROP. In a Schlenk tube 0.3 mL solution of Sn(Oct)$_2$ (12.7 mg, 31.3 μmol) in toluene was added to monohydroxyl derivatives of norbornene (NBE-OH/Br) (950 mg, 3.13 mmol). CL (8.93 g, 78.3 mmol) was then added to the alcohol/catalyst solution, and the reaction mixture was stirred at 110 °C under nitrogen for 24 h. The mixture was cooled to room temperature, dissolved in 8 mL of THF, precipitated twice from an excess of methanol, and dried overnight under reduced pressure to give the product NBE-*g*-PCL/Br macroinimer as a white solid in 96% yield. ^{1}H NMR ($CDCl_3$): δ (ppm) 6.18−6.14 (m, 2H, olefinic protons on the norbornene ring), 4.09−4.06 (t, CH_2O on PCL; CH_2OCOCBr), 3.90−3.77 (m, CH_2OCO-PCL), 3.66 (t, PCL-CH_2OH), 2.96 (s, 1H, CH on the norbornene ring), 2.89 (s, 1H, CH on the norbornene ring), 2.62−2.49 (m, 2H, 2 × CH on the norbornene ring), 2.33−2.30 (t, OCOCH_2 on PCL), 1.96 (s, 6H, 2 × CH_3), 1.70−1.63 (m, CH_2 on PCL), 1.51 (s, 1H, CH on the norbornene ring), 1.43−1.37 (m, CH_2 on PCL), 1.23 (s, 1H, CH on the norbornene ring). GPC: M_n = 4300, M_w/M_n = 1.1; NMR: M_n = 3380.

General Procedure for Synthesis of Poly(norbornene)-*graft*-poly(ε-caprolactone)/Br (PNBE-*g*-PCL/Br) via ROMP. In a nitrogen-filled Schlenk tube, a solution of second generation Grubbs catalyst (30.5 mg, 36.0 μmol) in 2 mL of degassed toluene was added to a solution of macroinimer NBE-*g*-PCL/Br ($M_{n,NMR}$ = 3380, M_w/M_n = 1.1; 600 mg, 0.18 mmol) in 8 mL of toluene, which was degassed with three freeze-vacuum-thaw cycles, to give an initial macroinimer concentration of 0.018 M. The molar ratio of macroinimer to catalyst was 5:1. After the reaction mixture was stirred for 4 h at 60 °C, the polymerization was quenched by adding ethyl vinyl ether with stirring for 30 min. The solution was precipitated into an excess of methanol, and the precipitate was isolated by filtration and dried under vacuum for 24 h to give the polymer PNBE-*g*-PCL/Br as a solid with generally high yield of 99%. ^{1}H NMR (CD_3COCD_3): δ (ppm) 7.43−7.21 (t, 5H, Ar), 5.60 (s, olefinic protons on the backbone), 4.07−4.04 (t, CH_2O on PCL; CH_2OCOCBr; CH_2OC-PCL), 3.54−3.52 (t, PCL-CH_2OH), 2.91 (m, CH on the norbornene units), 2.56 (m, CH on the norbornene units), 2.33−2.28 (t, OCOCH_2 on PCL), 1.93−1.79 (m, CH_3), 1.64 (m, CH_2 on PCL), 1.52−1.50 (s, CH on the norbornene units), 1.43−1.37 (m, CH_2 on PCL), 1.32 (s, CH on the norbornene units). GPC: M_n = 24700, M_w/M_n = 1.2; NMR: M_n = 20300.

Preparation of Poly(norbornene)-*graft*-poly(ε-caprolactone)/poly(2-(dimethylamino)ethyl methacrylate) (PNBE-*g*-PCL/PDMAEMA) via ATRP. A typical procedure is as follows. A mixture of ROMP macroinitiator PNBE-*g*-PCL/Br ($M_{n,NMR}$ = 20300, M_w/M_n = 1.2; 50.0 mg, 14.8 μmol), DMAEMA (465 mg, 2.96 mmol), CuCl (1.5 mg, 15 μmol), and bPy (4.6 mg, 30 μmol) was degassed by three freeze- pump-thaw cycles and then heated at 60 °C for 6 h under a vacuum atmosphere. The mixture was diluted in 15 mL of THF followed by passing through a column of basic alumina. The purified copolymer was precipitated in petroleum ether twice and then dried under vacuum for 24 h to give the brush copolymer PNBE-*g*-PCL/PDMAEMA as a solid with a monomer conversion of 42%. ^{1}H NMR (CD_3COCD_3): δ (ppm) 7.43−7.21 (t, 5H, Ar), 5.60 (s, olefinic protons on the backbone), 4.21−3.93 (m, COOCH_2 on PDMAEMA; CH_2O on PCL; CH_2OCO), 3.62 (t, PCL-CH_2OH), 2.58 (s, CH_2N on PDMAEMA), 2.33−2.28 (m, NCH_3 on PDMAEMA; OCOCH_2 on PCL), 1.97−1.88 (d, CH_2C on PDMAEMA; CH_3CCH_3), 1.64 (m, CH_2 on PCL), 1.42−1.41 (m, CH_2 on PCL), 1.10−0.96 (d, CH_3C on PDMAEMA). GPC: M_n = 92900, M_w/M_n = 1.8; NMR: M_n = 126800.

Results and Discussion

Synthesis of Inimer. The norbornene-based monomer with mixed functionality (NBE-OH/Br), containing one hydroxyl group for initiating ROP and one 2-bromoisobutyryl group for initiating ATRP, was designed and prepared, and the synthetic routes are illustrated in Scheme 2. In order to realize single substitution of dihydroxyl groups on the norbornene ring with the 2-bromoisobutyryl group by esterification, a little excess of 2,3-dihydroxymethyl-5-norbornene is necessary to have 2-bromoisobutyryl bromide completely consumed, and the suitable ratio of 2,3-dihydroxylmethyl-5-norbornene to 2-bromoisobutyryl bromide was 1.1:1. Under this condition, thin layer chromatography analysis showed the expected product was dominant in the reaction mixture. The crude oil was purified by column chromatography to provide pure product with good yield of 80%. The ^{1}H NMR spectrum (Figure 1A) showed the resonance signals of CHCH_2OCO protons (H_e) at 4.00 ppm and OCOC(CH_3)$_2$Br protons (H_g) at 1.94 ppm, while the signals of CHCH_2OH protons (H_f) at 3.64 ppm were still observed, and importantly the integration area ratios of these characteristic resonances of 2:6:2 were well agreed with the ratios of corresponding protons (H_e: H_g: H_f) of 2:6:2, which indicated that full esterification of one hydroxyl occurred. Furthermore, the molecular weight (M = 302.0518) of inimer from HRMS analysis was in good accordance with the calculated value, and the product also has a high purity (>99%) estimated from the single peak of GC chromatogram. All of these points affirmed the successful preparation of inimer with the expected structures.

Preparation of Copolymers. Copolymers were obtained with a three-step protocol as shown in Scheme 2. The first step was the ROP of CL initiated by Sn(Oct)$_2$ to form norbornene-

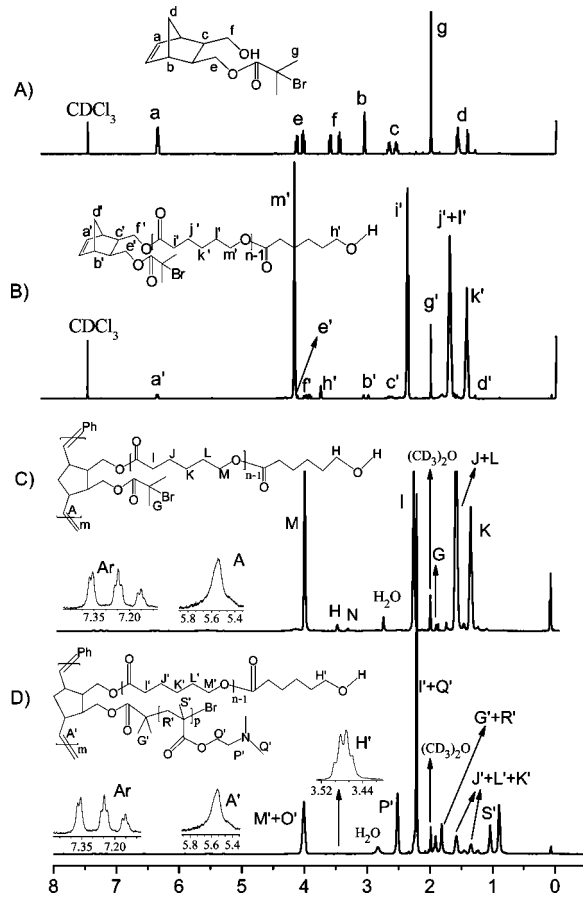


Figure 1. ^{1}H NMR spectra for (A) inimer 2-hydroxymethyl-3-(2-bromoisobutyryloxymethyl)-5-norbornene (NBE-OH/Br), (B) macroinimer norbornene-*graft*-poly(ε-caprolactone)/Br (NBE-*g*-PCL/Br), (C) macroinitiator poly(norbornene)-*graft*-poly(ε-caprolactone)/Br (PNBE-*g*-PCL/Br), and (D) brush copolymer poly(norbor-nene)-*graft*-poly(ε-caprolactone)/poly(2-(dimethylamino)ethyl methacrylate) (PNBE-*g*-PCL/PDMAEMA).

terminated PCL macroinimer (NBE-*g*-PCL/Br). The second step was the ROMP of macroinimer NBE-*g*-PCL/Br to convert into macroinitiator (PNBE-*g*-PCL/Br) via the "grafting through" technique. The last step was the ATRP of DMAEMA initiated by the macroinitiator to form densely grafted brush copolymers (PNBE-*g*- PCL/PDMAEMA) with amphiphilic side chains via the "grafting from" technique.

Synthesis of the Norbornene-Terminated PCL Macroinimer. The macroinimer NBE-*g*-PCL/Br terminated with a norbornyl group was synthesized via ROP of CL initiated by the monohydroxyl derivative of norbornene NBE-OH/Br with the feed ratio ([CL]:[OH]) of 10:1 or 25:1. $Sn(Oct)_2$ was chosen as catalyst for its efficiency and extensive use for initiating the ROP of various lactones and lactides.[31]

Two norbornene-based macroinimers with different PCL chain lengths were prepared, and their characteristics are listed in Table 1. The macroinimer with a shorter PCL chain (Table 1, entry 1) could not be separated by precipitation even from cold methanol but just precipitated from water, thus giving a mixture of the macroinimer, unreacted CL, and the residue of monoalcohol initiator NBE-OH/Br as viscous wax, which was used to estimate the molecular weight ($M_{n,GPC}$ = 940, M_w/M_n = 1.1) from one of the three peaks depicted in the higher molecular weight region in GPC curves and but was unsuitable for determination of the molecular weight by ^{1}H NMR spectroscopy. The monomer conversion of 62% determined by gravimetry was relatively low due to partial weight loss of the

Table 1. Characteristics of Macroinimer Norbornene-*graft*-poly(ε-caprolactone)/Br (NBE-*g*-PCL/Br) by Ring-Opening Polymerization (polymerization temperature =110 °C, polymerization time = 24 h)

entry	[CL]:[OH]:[Sn(Oct)$_2$]	conversion (%)[a]	$M_{n,th}$[b]	$M_{n,GPC}$[c]	M_w/M_n[c]	$M_{n,NMR}$[d]
1	1000:100:1	62	1010	940	1.1	nd[e]
2	2500:100:1	96	3040	4300	1.1	3380

[a] Obtained gravimetrically after purification from the dried polymer. [b] $M_{n,th}$ = ([CL]:[OH]) × conversion% × M_{CL} + M_{inimer}, where M_{CL} = 114 and M_{inimer} = 302 are the molar masses of CL and inimer, respectively. [c] Measured by GPC analysis in THF. [d] $M_{n,NMR}$ = ($S_{i'}/S_{a'}$) × M_{CL} + M_{inimer} was obtained by ^{1}H NMR spectroscopy, where M_{CL} and M_{inimer} are the molar masses of CL and inimer, respectively. [e] Not detected.

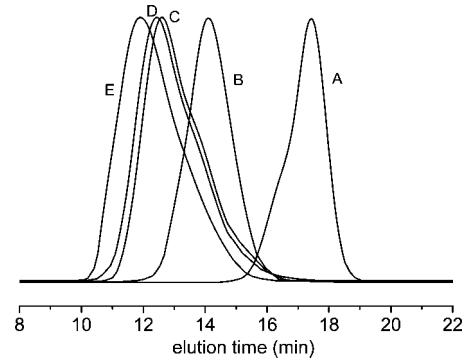


Figure 2. Gel permeation chromatography (GPC) traces of macroinimer, norbornene-*graft*-poly(ε-caprolactone)/Br (NBE-*g*-PCL/Br) (A: M_n = 4300, M_w/M_n = 1.1); macroinitiator, poly(norbornene)-*graft*-poly(ε-caprolactone)/Br (PNBE-*g*-PCL/Br) (B: M_n = 24700, M_w/M_n = 1.2); brush copolymer, poly(norbornene)-*graft*-poly(ε-capro- lactone)/poly(2-(dimethylamino)ethyl methacrylate) (PNBE-*g*-PCL/PDMAEMA) at different polymerization time for 1 h (C: M_n = 68600, M_w/M_n = 1.7), 3 h (D: M_n = 73800, M_w/M_n = 1.6), and 6 h (E: M_n = 92900, M_w/M_n = 1.8) starting from macroinitiator PNBE-*g*-PCL/Br with M_n = 24700.

oligomers which are soluble in organic solvents. The macroinimer with a longer PCL chain (Table 1, entry 2) was readily obtained as a powder by precipitation from methanol to remove the monomer residue and initiator and shown in Figure 2A to have a molecular weight ($M_{n,GPC}$) of 4300 with a monomodal GPC trace and low molecular weight distribution (M_w/M_n = 1.1). It was also characterized by ^{1}H NMR spectroscopy as shown in Figure 1B, the chemical shifts corresponding to olefinic signals on the norbornene (6.16−6.24 ppm) indicating attachment of the norbornyl group. After ROP of CL initiated by alcohol, signals corresponding to methylene protons of CHCH_2OH (3.52−3.34 ppm) disappeared, and a new signal at 3.66 ppm for protons of CH_2CH_2OH on the PCL chain was observed, which meant the side chain of PCL was virtually formed. By comparing the peak integration areas (*S*) of methylene protons of $CH_2CH_2CH_2OCO$ ($H_{i'}$, 2 protons) from PCL at 2.33−2.30 ppm with those of olefinic protons of C*H*═C*H* ($H_{a'}$, 2 protons) from the norbornyl group at 6.16−6.24 ppm, it was possible to determine PCL-to-norbornene molar ratio from the integral ratio n = ($S_{i'}$/2H):($S_{a'}$/2H) = ($S_{i'}/S_{a'}$), therefore, to calculate the average number of CL units in the PCL chain end-capped with a norbornene group. Using ^{1}H NMR analysis,[55] we confirmed that it contained 27 CL units (n = 27) with a number average molecular weight ($M_{n,NMR}$ = ($S_{i'}/S_{a'}$) × M_{CL} + M_{inimer}, M_{CL} = 114, and M_{inimer} = 302) of 3380. The value was a bit higher than the theoretical one, maybe caused by incomplete initiation of the NBE-OH/Br. The lack of agreement between the molecular weight of macroinimer measured by GPC calibrated with polystyrene standards and that calculated from ^{1}H NMR maybe arose from differences in the hydrodynamic volume of polystyrene relative to NBE-*g*-

Table 2. Ring-Opening Metathesis Polymerization of Macroinimer Norbornene-*graft*-poly(ε-caprolactone)/Br (NBE-*g*-PCL/Br) Using Second Generation Grubbs Catalyst[a]

				GPC analysis			
entry	[M]:[Cat][b]	t (h)	$M_{n,th}$[c]	M_n	M_w/M_n	no. of peaks	$M_{n,NMR}$[d]
1	5:1	4	16740	24700	1.2	1	20300
2	25:1	24	82800	128500	1.8	3	84000
3	50:1	24	165700	228000	1.7	3	165000

[a] Reaction conditions: $[M]_0$ = 0.018 mol/L, toluene = 10 mL, polymerization temperature = 60 °C. [b] Feed ratio of macroinimer NBE-*g*-PCL/Br ($M_{n,NMR}$ = 3380) to second generation Grubbs catalyst. [c] $M_{n,th}$ = ([M]:[Cat]) × $M_{n\ (macroinimer)}$ × conversion%, where $M_{n(macroinimer)}$ = 3380 is the molecular weight of macroinimer by ^{1}H NMR. [d] $M_{n,NMR} = (5S_A/2S_{Ar}) \times M_{n\ (macroinimer)}$ was obtained by ^{1}H NMR, where the molecular weight of macroinimer is $M_{n,NMR}$ = 3380.

Table 3. Atom Transfer Radical Polymerization of 2-(Dimethylamino)ethyl Methacrylate (DMAEMA) Using Poly(norbornene)-*graft*-poly(ε-caprolactone)/Br (PNBE-*g*-PCL/Br) as Macroinitiator[a] in Bulk

entry	catalyst/ligand	t (h)	yield (%)	$M_{n,GPC}$[b]	M_w/M_n[b]	$M_{n,NMR}$[c]
1	CuCl/bPy	1	19	68600	1.7	nd[d]
2	CuCl/bPy	3	33	73800	1.6	nd[d]
3	CuCl/bPy	6	42	92900	1.8	126800

[a] Reaction conditions: [Macroinitiator]:[DMAEMA]:[CuCl]:[bPy] = 1:200:1:2; polymerization temperature = 60 °C. [b] Measured by GPC analysis in THF. [c] $M_{n,NMR} = (S_{P'}/(S_{I'+Q'} - 3S_{P'})) \times n \times M_{DMAEMA} \times m + M_{n(macroinitiator)}$ was obtained by ^{1}H NMR, where n = 27 represents the average number of CL repeating units per PCL graft, m = 6 represents the average number of norbornenyl repeating units on the backbone per brush polymer, M_{DMAEMA} = 157 is the molar mass of DMAEMA, and $M_{n(macro-initiator)}$ = 20300 is the molecular weight of macroinitiator. [d] Not determined.

PCL/Br macroinimer.[31] In contrast to the relative molecular weight from GPC analysis, the data of absolute molecular weights ($M_{n,NMR}$) obtained by the end group analysis using ^{1}H NMR spectra were applied to the next polymerization and further analysis.

ROMP of Macroinimer Catalyzed by Grubbs Catalyst. Kenwright and co-workers have investigated many ROMP reactions of PCL macromonomers[31] and revealed that the lower ratio of [M]/[Cat] and the shorter side chains of macromonomer would help to complete consumption of macromonomers using second generation Grubbs catalyst, which is one of the most active ROMP initiators, but the polymerizations were usually not well controlled.[50,59]

In order to have the macromonomer entirely polymerized, norbornene-based macroinimer with one PCL chain and a really low ratio [M]/[Cat] of 5 was applied. The concentration of macroinimer was as low as 0.018 M to make the chain stretched so that the catalyst could be close to the double bond of the norbornenyl group. Therefore, we investigated the ROMP performance of macroinimer with a middle M_n of 3380 for the PCL side chain (27 CL units). It polymerized well with second generation Grubbs catalyst to greater than 99% conversion after 4 h (Table 2, entry 1). The GPC curve (Figure 2B) indicated the molecular weight ($M_{n,GPC}$) of macroinitiator PNBE-*g*-PCL/Br was 24700 with a monomodal and a low M_w/M_n of 1.2. Moreover, ^{1}H NMR spectrum of macroinitiator (Figure 1C) did not show the signals of olefinic protons on the norbornene ring, and these proton signals shifted upfield to approximately 5.45−5.75 ppm upon ring-opening and subsequent polymerization, indicating the macroinimer had entirely converted to polymer. Additionally, the molecular weight was calculated from integration of the ^{1}H NMR spectrum. The observed integration area ratio of olefinic protons on the PNBE backbone at 5.45−5.75 ppm (H_A, 2 protons for each NBE unit) [S_A/2H] to that of aromatic protons on the end of PNBE backbone at 7.43−7.21 ppm (H_{Ar}, 5 protons for one phenyl end group) [S_{Ar}/5H] was derived from the following formula: $m = (S_A/2H):(S_{Ar}/5H) = 5S_A/2S_{Ar} = 6$, which is the degree of polymerization of the norbornene-based macroinimer. The integrated ratio was used to determine the number-average molecular weight of the macroinitiator, $M_{n,NMR} = (5S_A/2S_{Ar}) \times M_{n\ (macroinimer)}$ (3380) = 20300. The ^{1}H NMR measured molecular weights matched the predicted molecular weights well. These results from GPC and NMR measurements indicated that the polymerization had successfully occurred with better control under this condition for macromonomer.

For comparison, we also investigated the other two polymerizations with the ratio [M]/[Cat] of 25 and 50. After 24 h, the reactions were terminated with ethyl vinyl ether, and the polymers were precipitated from methanol with excellent yield. In contrast to the monomodal GPC profile in the first case (Table 2, entry 1), three peaks were observed in GPC chromatograms in the next two cases (Table 2, entries 2 and 3). One of these corresponded to the trace of unreacted macromonomer which had the same retention time as that of macromonomer (approximately 1.4 or 1.5% calculated from the GPC peak areas), and the others corresponded to copolymer with bimodal and high molecular weight (98.6 or 98.5% from the GPC peak areas), which resulted in broad molecular weight distribution with a PDI of 1.8 and 1.7, respectively.[31] ^{1}H NMR spectroscopy was also used to determine the unit number of macromonomer on the backbone, and the value almost agreed with the theoretical one for each sample.

As discussed above, because of the different hydrodynamic volumes of the copolymers, relative molecular weights measured by GPC were different from those measured by ^{1}H NMR. It was noted that this catalyst had been described as uncontrolled for polymerization of low molecular weight monomer,[30,31,50] and it was hard to make a claim for controlled polymerization of macromonomer, but there has been improved polymerization performance for macromonomer under appropriate conditions because steric crowding between macromonomers affects the rate of propagation k_p more than the rate of initiation k_i and lowers the ratio of k_p/k_i, and the steric hindrance of the side chain prevents the catalyst from reacting with the olefins along the backbone.[30,50]

ATRP of DMAEMA Using PNBE-*g*-PCL/Br as Macroinitiator. To synthesize brush copolymers with amphiphilic side chains, the ATRP of hydrophilic DMAEMA was carried out by using PNBE-*g*-PCL/Br (M_n = 20300) as macroinitiator and CuCl/bPy as catalyst/ligand at 60 °C in bulk. Copper(I) complex was used as catalyst and bPy as ligand. Both of these are inexpensive and readily available, and also this catalyst/ligand system has a relatively low catalytic reactivity[27,40] which is useful to avoid the cross-linking reaction between spatially neighboring radical sites on the side chains during ATRP using polyfunctional alkyl halides as macroinitiators. The macroinitiator was soluble in DMAEMA, which facilitates the reaction undertaken in bulk. Since DMAEMA was not only the ATRP monomer but also the solvent, it was in excess to the desired length of the PDMAEMA chains. The resulting mixture was diluted with THF and then precipitated from petroleum ether to remove the excess of monomer.

With progress of the reaction, the viscosity of reaction mixture increased, and after 3 h the reaction mixture became stagnant for stirring. Adjusting the reaction time allowed a changing in the length of the PDMAEMA segment, and the yield of precipitated product (PNBE-*g*-PCL/PDMAEMA) increased from 19 to 42% with an extension of the polymerization time from 1 to 6 h (Table 3). The GPC curves in Figures 2C−E show the variation of molecular weights and molecular weight distributions of the brush copolymers prepared from the same macro-

initiator. We observed clearly that the molecular weight of the copolymers shifted to high a molecular weight position along with the extension of polymerization time, and the subtle peak attributed to the starting macroinitiator residue in Figure 2C for 1 h or Figure 2D for 3 h disappeared in Figure 2E for 6 h, which meant the macroinitiator was completely consumed after 6 h and could be considered as positive evidence for the formation of brush copolymers, which exhibited monomodal distribution in GPC curve after 6 h.

It was reported that such polyfunctional radical polymerization systems were usually carried out in solvent and also required quenching at a low conversion of the monomer to avoid significant occurrence of either termination or transfer reactions, which would be severe under higher monomer conversions.[27,37,60] Gel formation was observed during the ATRP of methyl methacrylate in bulk even though the molecule weight of macroinitiater was small and reaction time was shorter than 1 min[61,62] or the ATRP of poly(ethylene glycol) methyl ether methacrylates was conducted for a longer time.[27] However, there were no gel observations in our trials in bulk. We speculated that the PCL side chains interfered with the intermolecular cross-linking of the side chains; that is, there was no brush−brush coupling, which makes polymers soluble.

To further confirm the formation of the brush copolymers, the ^{1}H NMR spectrum of brush copolymer (Figure 1D) was measured. The signals of OCH_2CH_2N protons from the block of PDMAEMA at 2.58 ppm and signals of methyl protons of $C(CH_3)$ from the same block at 1.1−0.9 ppm appeared. An integration area ratio of these characteristic protons resonances of 2.0:2.9 agreed well with the number ratio of the corresponding protons, 2:3. By comparing the integration area ratio of methylene protons of CH_2N from the block of PDMAEMA at 2.58 ppm ($H_{P'}$, 2 protons for each DMAEMA unit) [$S_{P'}$/2H] to that of methylene protons of $OCOCH_2$ from the block of PCL at 2.33−2.28 ppm ($H_{I'}$, 2 protons for each CL unit) [$S_{I'}$/2H = ($S_{I'+Q'} - 3S_{P'}$)/2H], the average degree of polymerization of the PDMAEMA grafts (DP_n) can be written as follows: $DP_{n,NMR}$ = ([$S_{P'}$/2H]: [($S_{I'+Q'} - 3S_{P'}$)/2H]) × n (27) = ($S_{P'}$/($S_{I'+Q'} - 3S_{P'}$)) × n (27) = 113, which was designated as "p" in Scheme 2; that is, p = 113. The integrated ratio was further used to determine the number-average molecular weight of the macroinitiator, $M_{n,NMR} = p \times M_{n(DMAEMA)}$ (157) × m (6) + $M_{n(macroinitiator)}$ (20300) = 126800. The molecular weight ($M_{n,NMR}$) of the copolymers obtained by ^{1}H NMR was higher than that by GPC, it was likely due to adsorption of amino-end-groups onto the column.

The graft efficiency or initiation efficiency (f) for the ATRP process was preliminarily estimated through the ratio of the calculated DP_n value of PDMAEMA grafts ($DP_{n,th}$ = ([DMAEMA]$_0$/[macroinitiator]$_0$) × conversion%) to the experimental DP_n value of PDMAEMA grafts by ^{1}H NMR spectroscopy ($DP_{n,NMR}$), $f = DP_{n,th}/DP_{n,NMR}$ = 74%, which indicated that the initiation did not occurr quantitatively. However, incomplete initiation is hard to discern by the ^{1}H NMR spectrum (Figure 1D), because the resonances of methyl protons ($H_{G'}$) were considerably overlapped with resonances of methylene protons ($H_{R'}$) from the DMAEMA repeating units at 1.97−1.88 ppm, and the resonances of methyl protons (H_G) of unreacted initiating groups from the α-bromoisobutyrate at 1.93−1.79 ppm should appear, but they could not be ascertained from the ^{1}H NMR spectrum.

Conclusion

This work reported the preparation of a novel well-defined brush copolymer with two different grafts very densely distributed on the same unit along the backbone via combination of three highly controlled polymerization methods, ROP, ROMP, and ATRP based on the synthesis of heterotrifunctional inimer NBE-OH/Br, which has one polymerizable norbornenyl group (NBE) for ROMP and two different initiating sites (OH and Br) for ROP and ATRP, respectively. First, norbornene-terminated macroinimer NBE-*g*-PCL/Br containing the 2-bromoisobutyryl group and the hydrophobic PCL graft was generated by ROP of CL. Second, the polymer backbone with the PCL grafts and 2-bromoisobutyryl side groups (PNBE-*g*-PCL/Br) was constructed via ROMP of the strained cyclic macroinimer NBE-*g*-PCL/Br. Last, well-defined amphiphilic grafted brush copolymer PNBE-*g*-PCL/PDMAEMA containing one hydrophobic PCL graft and one hydrophilic PDMAEMA graft on each unit of the backbone regularly was obtained from ATRP of DMAEMA using bromo-functionalized PNBE-*g*-PCL/Br as macroinitiators. These well-defined, complex architectures can meet the demand for new polymeric materials with higher levels of performance and improved control of properties for specific applications.

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