

Synthesis of Amphiphilic Copolymer Brushes Possessing Alternating Poly(methyl methacrylate) and Poly(*N*-isopropylacrylamide) Grafts via a Combination of ATRP and Click Chemistry

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ABSTRACT: We report on the synthesis of well-defined amphiphilic copolymer brushes possessing alternating poly(methyl methacrylate) and poly(*N*-isopropylacrylamide) grafts, poly(PMMA-*alt*-PNIPAM), via a combination of atom transfer radical polymerization (ATRP) and click reaction (Scheme 1). Firstly, the alternating copolymerization of *N*-[2-(2-bromoisobutyryloxy)ethyl]maleimide (BIBEMI) with 4-vinylbenzyl azide (VBA) affords poly(BIBEMI-*alt*-VBA). Bearing bromine and azide moieties arranged in an alternating manner, multifunctional poly(BIBEMI-*alt*-VBA) is capable of initiating ATRP and participating in click reaction. The subsequent ATRP of methyl methacrylate (MMA) using poly(BIBEMI-*alt*-VBA) as the macroinitiator leads to poly(PMMA-*alt*-VBA) copolymer brush. Finally, amphiphilic poly(PMMA-*alt*-PNIPAM) copolymer brush bearing alternating PMMA and PNIPAM grafts is synthesized via the click reaction of poly(PMMA-*alt*-VBA) with an excess of alkynyl-terminated PNIPAM (*alkynyl*-PNIPAM). The click coupling efficiency of PNIPAM grafts is determined to be ~80%. Differential scanning calorimetry (DSC) analysis of poly(PMMA-*alt*-PNIPAM) reveals two glass transition temperatures (T_g). In aqueous solution, poly(PMMA-*alt*-PNIPAM) supramolecularly self-assembles into spherical micelles consisting of PMMA cores and thermoresponsive PNIPAM coronas, which were characterized via a combination of temperature-dependent optical transmittance, micro-differential scanning calorimetry (micro-DSC), dynamic and static laser light scattering (LLS), and transmission electron microscopy (TEM). © 2009 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 47: 2608–2619, 2009

Keywords: atom transfer radical polymerization (ATRP); colloids; graft copolymers; micelles

INTRODUCTION

Possessing a high density of side chains covalently attached to linear backbones, polymer brushes have been the subject of continually

increasing interest because of their unique extended cylindrical conformation in a good solvent, which is drastically different from the random coil conformation adopted by conventional polymers.^{1,2} In general, comb-shaped polymer brushes can be categorized into homopolymer brushes and copolymer brushes. Since the pioneering work reported by Tsukahara et al.^{3,4} in 1989, extensive investigations have been devoted to the synthesis of homopolymer brushes mainly

Additional Supporting Information may be found in the online version of this article.

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via three approaches including grafting-through,^{5–20} grafting-from,^{21–39} and grafting-onto.^{40–46} In the past decade, the advent of controlled polymerization techniques, such as ring-opening polymerization (ROP),^{5,24,25,30,37,43} nitroxide-mediated polymerization (NMP),^{47–49} atom transfer radical polymerization (ATRP),^{16,31–33,35,39} and reversible addition-fragmentation chain transfer (RAFT) polymerization,^{50,51} have rendered the grafting-from approach more appealing, starting with macroinitiators with the initiating sites distributed on every repeating unit.

On the other hand, copolymer brushes typically consist of more than one type of polymer side chains. When two types of polymer grafts are involved, they can be arranged in a random,^{43,46,47} alternating,^{5,12–14,18,19,25,34} block,^{22,26,51,52} or “centipede” manner.^{33,37,53} Compared to homopolymer brushes, the incorporation of another type of polymer graft endows copolymer brushes with extra structural versatility and unique aggregation properties, resulting from the intrinsic immiscibility between two types of polymer grafts.

In the context of alternating copolymer brushes, previous literature reports mainly employed two approaches for their synthesis, namely the alternating copolymerization of two types of macromonomers, and the postmodification or grafting from homopolymer brushes bearing reactive sites. In the presence of a Lewis acid (SnCl₄), Ishizu et al.^{12–14} achieved the free radical alternating copolymerization of methacryloyl-terminated poly(ethylene oxide) (PEO) with vinylbenzyl-terminated polystyrene (PS) or poly(propylene oxide) (PPO) and investigated the aggregation behavior of the obtained alternating copolymer brushes. In a more facile manner, Chen and coworkers⁵ succeeded in the alternating copolymerization of maleimide-terminated poly(ϵ -caprolactone) (MI-PCL) and vinylbenzyl-terminated PEO, taking advantage of the well-established charge-transfer complex formation between vinylbenzyl and maleimide moieties. Starting from dendronized polymer brushes, Chen and coworkers^{18,19} also synthesized alternating copolymer brushes via postmodification. Most recently, Ishizu Yamada³⁴ reported the synthesis of alternating copolymer brushes via the combination of grafting-through (macromonomer copolymerization) and grafting-from (atom transfer radical polymerization, ATRP) techniques.

Recently, the concept of click chemistry invented by Sharpless and coworkers^{54–56} has also been introduced into the synthesis of polymeric

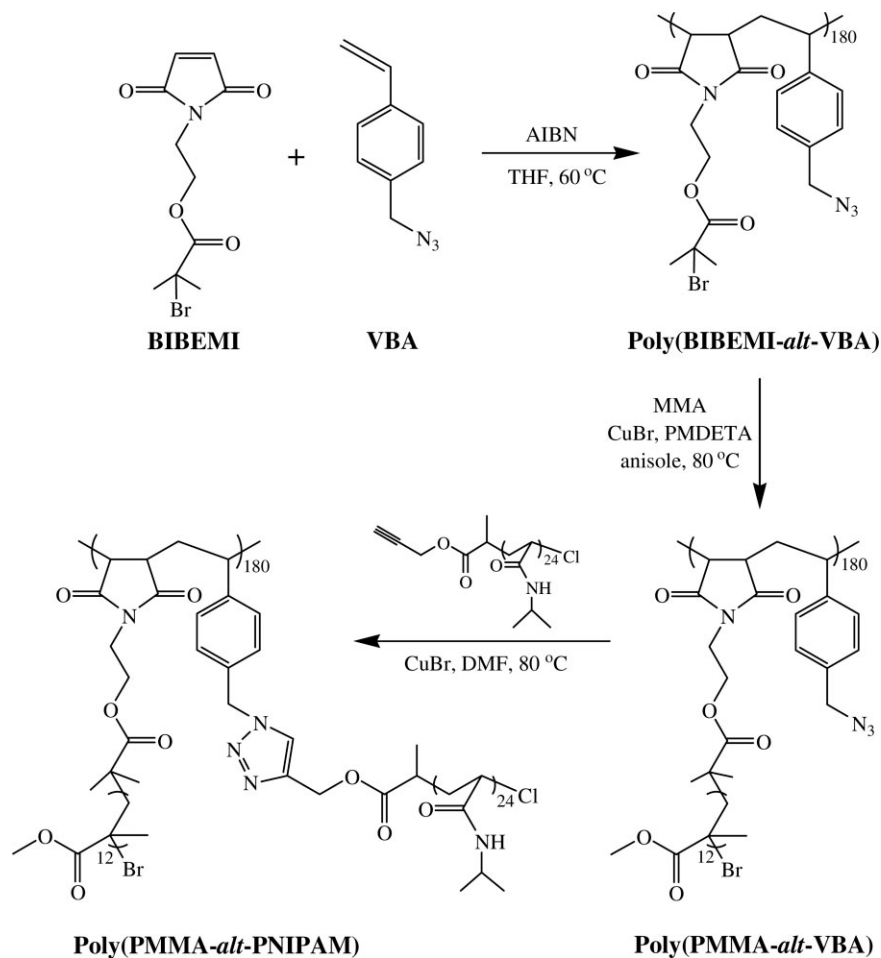
materials with well-defined and complex chain architectures.^{57–71} Gao and Matyjaszewski⁴⁰ synthesized linear poly(2-hydroxyethyl methacrylate) (PHEMA) by ATRP at first. After esterification with pentynoic acid, click reaction of the obtained PHEMA-alkyne with azide-terminated PEO afforded homopolymer brushes with a grafting efficiency up to 88%. Gao and coworkers⁴¹ fabricated amphiphilic copolymer brush-functionalized carbon nanotubes by coupling ATRP grafting-from and click grafting-to techniques.

To the best of our knowledge, click chemistry has not been employed in the synthesis of alternating copolymer brushes yet. In this work, we report on the synthesis of well-defined amphiphilic copolymer brush possessing alternating poly(methyl methacrylate) and poly(*N*-isopropylacrylamide) grafts, poly(PMMA-*alt*-PNIPAM), via a combination of ATRP and click reaction (Scheme 1). The synthesis started with the alternating copolymerization of *N*-[2-(2-bromoisobutyryloxy)ethyl]maleimide (BIBEMI) with 4-vinylbenzyl azide (VBA). Using the obtained poly(BIBEMI-*alt*-VBA) as a multifunctional initiator, the subsequent ATRP of methyl methacrylate (MMA) followed by click reaction with alkynyl-terminated PNIPAM (*alkynyl*-PNIPAM) afforded amphiphilic alternating copolymer brush, poly(PMMA-*alt*-PNIPAM). Moreover, we also investigated the supramolecular self-assembling behavior of this polymer brush in aqueous solution.

EXPERIMENTAL

Materials

N-Isopropylacrylamide (NIPAM, 97%, Tokyo Kasei Kogyo Co.) was purified by recrystallization from a mixture of benzene and *n*-hexane (1/3, v/v). Methyl methacrylate (MMA, 98%, Sinopharm Chemical Reagent Co. Ltd.) was distilled under reduced pressure and stored at –20 °C prior to use. Copper(I) bromide (CuBr, 99.99%), copper(I) chloride (CuCl, 99.99%), 2-bromoisobutyryl bromide (97%), and *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) were purchased from Fluka and used as received. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Sodium azide (NaN₃, 99%) was purchased from Alfa Aesar and used without further purification. Triethylamine (TEA) and 2-aminoethanol were vacuum-distilled over CaH₂. Maleic anhydride, acetic anhydride, sodium acetate, and *p*-toluenesulfonic acid (TsOH) were used as received. 2-



Scheme 1. Reaction schemes employed for the preparation of well-defined amphiphilic copolymer brushes possessing alternating poly(methyl methacrylate) (PMMA) and poly(*N*-isopropylacrylamide) (PNIPAM) grafts via a combination of ATRP and click chemistry.

Propanol, *N,N*-dimethylformamide (DMF), methanol, ethyl ether, acetone, dichloromethane, and all other chemicals were purchased from Sino-pharm Chemical Reagent Co. Ltd. and used as received. Merrifield Resin was purchased from GL Biochem (Shanghai) Ltd. and used as received. Tris(2-(dimethylamino)ethyl)amine (Me₆TREN),⁷² propargyl 2-chloropropionate (PCP),⁷¹ and azide-functionalized Merrifield resin⁵⁸ were prepared according to literature procedures.

Synthetic schemes employed for the synthesis of amphiphilic alternating copolymer brushes, poly(PMMA-*alt*-PNIPAM), were shown in Scheme 1. Detailed procedures employed for the preparation of *N*-[2-(2-bromoisobutyryloxy)ethyl]maleimide (BIBEMI) and 4-vinylbenzyl azide (VBA) were described in the Supporting Information.

Synthesis of Poly(BIBEMI-*alt*-VBA)

To a Schlenk tube equipped with a magnetic stirring bar, BIBEMI (2.65 g, 9.1 mmol), VBA (1.45 g, 9.1 mmol), AIBN (15 mg, 0.091 mmol), and 5 mL dry THF were added. After degassing via three freeze-pump-thaw cycles, the reaction tube was sealed under vacuum and placed in an oil bath thermostated at 60 °C. After stirring for 10 h, the tube was quenched into liquid nitrogen to stop the polymerization. The reaction mixture was diluted with THF and precipitated into an excess of methanol. This purification cycle was repeated twice. After drying in a vacuum oven overnight at room temperature, poly(BIBEMI-*alt*-VBA) was obtained as a slightly yellowish powder (3.55 g, yield: 86.6%). The obtained crude product was fractionated from a mixture of cyclohexane and *n*-hexane at 50 °C, yielding poly(BIBEMI-*alt*-

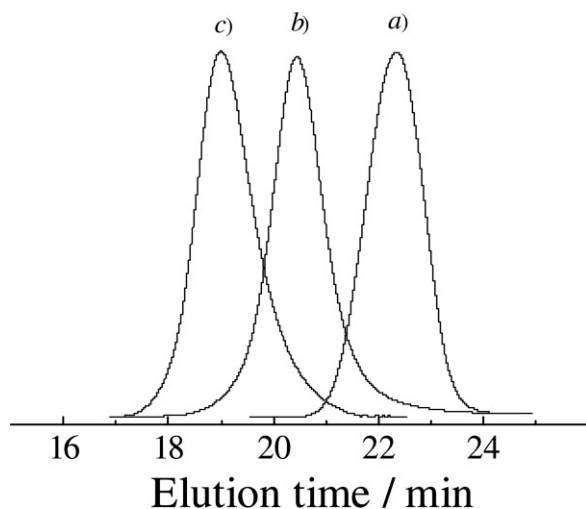


Figure 1. GPC traces recorded for (a) poly(BIBEMI-*alt*-VBA) multifunctional initiator, (b) poly(PMMA-*alt*-VBA), and (c) poly(PMMA-*alt*-PNIPAM) alternating copolymer brushes.

VBA) as a yellowish powder [0.5 g, yield: 14%; $M_{n,GPC} = 43.1$ kDa, $M_w/M_n = 1.10$, Fig. 1(a)]. The degree of polymerization (DP) of the alternating copolymer was then calculated to be 180 based on GPC results. The polymer was denoted as poly(BIBEMI-*alt*-VBA)₁₈₀.

Synthesis of Poly(PMMA-*alt*-VBA) Polymer Brush

Poly(PMMA-*alt*-VBA) was obtained by the ATRP of MMA monomer using poly(BIBEMI-*alt*-VBA) as the macroinitiator. In a typical procedure, poly(BIBEMI-*alt*-VBA)₁₈₀ (0.1 g, 0.21 mmol Br initiating sites), MMA (2.1 g, 21 mmol), PMDETA (17 mg, 0.1 mmol), and anisole (8 mL) were added into a Schlenk tube. The mixture was degassed by two freeze-pump-thaw cycles. CuBr (14 mg, 0.1 mmol) was then introduced under the protection of N₂ flow. The reaction tube was carefully degassed via three freeze-pump-thaw cycles, sealed under vacuum, and placed in an oil bath thermostated at 60 °C. After stirring for 1 h, monomer conversion was determined to be 11.6% by ¹H NMR analysis. The reaction mixture was exposed to air, diluted with THF, and passed through a silica gel column to remove copper catalysts. After removing the solvents, the residues were dissolved in THF and precipitated into an excess of methanol. The above dissolution-precipitation cycle was repeated for three times. After drying in a vacuum oven overnight at room temperature, poly(PMMA-*alt*-VBA)₁₈₀ was obtained

as a white solid [0.31 g, yield: 14.1%; $M_{n,GPC} = 128.7$ kDa, $M_w/M_n = 1.11$, Fig. 1(b)].

Synthesis of Alkynyl-Terminated Poly(N-isopropylacrylamide) (Alkynyl-PNIPAM)

General procedures employed for the preparation of *alkynyl*-PNIPAM were as follows.⁷¹ PCP (0.439 g, 3.0 mmol), NIPAM (10.18 g, 90 mmol), and Me₆TREN (0.691 g, 3.0 mmol) were dissolved in 18 mL of 2-propanol. The mixture was degassed by three freeze-pump-thaw cycles. After heating to 40 °C, CuCl (0.297 g, 3.0 mmol) was introduced under the protection of N₂ flow to start the polymerization. The reaction mixture became dark green and more viscous as polymerization proceeded. After 5 h, the mixture was exposed to air and diluted with CH₂Cl₂. After passing through a column of silica gel to remove copper catalysts, all the solvents were removed. The residues were dissolved in CH₂Cl₂ and precipitated into an excess of diethyl ether. After drying in a vacuum oven, *alkynyl*-PNIPAM was obtained as a white powder (7.67 g, yield: 72.2%; $M_{n,GPC} = 2.8$ kDa, $M_w/M_n = 1.12$). The actual DP of PNIPAM was determined to be 24 by ¹H NMR analysis in CDCl₃. Thus, the polymer was denoted as *alkynyl*-PNIPAM₂₄.

Synthesis of Poly(PMMA-*alt*-PNIPAM) Alternating Copolymer Brush

The synthesis of poly(PMMA-*alt*-PNIPAM) alternating copolymer brush was accomplished via the click reaction of poly(PMMA-*alt*-VBA) with an excess of *alkynyl*-PNIPAM, and a typical procedure was as follows. *Alkynyl*-PNIPAM₂₄ (0.86 g, 0.3 mmol alkynyl moieties) and poly(PMMA-*alt*-VBA)₁₈₀ (0.31 g, 0.18 mmol azide moieties) were dissolved in 5 mL of DMF. After one brief freeze-thaw cycle, CuBr (26 mg, 0.18 mmol) was introduced under the protection of N₂ flow. The reaction tube was carefully degassed by three freeze-pump-thaw cycles and then placed in an oil bath thermostated at 80 °C. After stirring for 24 h, azide-functionalized Merrifield resin (0.375 g, 0.3 mmol azide moieties) was then added. The suspension was kept stirring for another 8 h at 80 °C. After suction filtration, the filtrate was diluted with THF and passed through a basic alumina column to remove copper catalysts. After removing all the solvents at reduced pressure, the residues were dissolved in THF and precipitated into an excess of diethyl ether. The final product was dried in a vacuum oven overnight at room

temperature, yielding poly(PMMA-*alt*-PNIPAM)₁₈₀ as a white solid [0.73 g, yield: 88.4%; $M_{n, GPC} = 307.2$ kDa, $M_w/M_n = 1.18$, Fig. 1(c)].

Preparation of Micellar Solutions

Fifty milligrams of poly(PMMA-*alt*-PNIPAM)₁₈₀ alternating copolymer brush was dissolved in 5 mL of DMF. Under vigorous stirring, 45 mL of deionized water was added via a syringe pump at a flow rate of 0.2 mL/min. After the addition was completed, the dispersion was left stirring for another 5 h. DMF was then removed by dialysis (MW cutoff, 14.0 kDa) against deionized water for 24 h. Fresh deionized water was replaced approximately every 6 h. The obtained dispersion with a bluish tinge characteristic of colloidal aggregates did not exhibit any macroscopic phase separation upon standing at room temperature for more than 3 months, suggesting the formation of stable aggregates.

Characterization

Nuclear Magnetic Resonance Spectroscopy (NMR)

All NMR spectra were recorded on a Bruker AV300 NMR spectrometer (resonance frequency of 300 MHz for ¹H) operated in the Fourier transform mode. CDCl₃, D₂O, DMSO-*d*₆ were used as the solvents.

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectra were recorded on a Bruker VECTOR-22 IR spectrometer. The spectra were collected at 64 scans with a spectral resolution of 4 cm⁻¹.

Gel Permeation Chromatography (GPC)

Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) equipped with Waters 1515 pump and Waters 2414 differential refractive index detector (set at 35 °C). It used a series of three linear Styragel columns HT2, HT4, and HT5 at an oven temperature of 40 °C. The eluent was THF at a flow rate of 1.0 mL/min. A series of low polydispersity polystyrene (PS) standards were employed for the GPC calibration.

Differential Scanning Calorimetry (DSC) Characterization

DSC was carried on a DSC TA-60WS thermal analysis system (Shimadzu, Japan). Samples

were first heated from 20 to 200 °C at a heating rate of 10 °C/min under nitrogen atmosphere, followed by cooling to 20 °C at 10 °C/min after stopping at 200 °C for 3 min, and finally heating to 200 °C again at 10 °C/min. Glass transition temperature (T_g) was determined as the midpoint of the transition of the second heating sequence.

Temperature-Dependent Turbidimetry

The optical transmittance of aqueous solutions at a wavelength of 700 nm was acquired on a Unico UV/vis 2802PCS spectrophotometer. A thermostatically controlled cuvette was employed and the heating rate was 0.2 °C min⁻¹. The critical phase transition temperature (T_c) was defined as the temperature corresponding to ~1% decrease of optical transmittance.

Micro-Differential Scanning Calorimetry (Micro-DSC) Characterization

Micro-DSC measurements were carried on a VP DSC from MicroCal. The volume of the sample cell was 0.509 mL. The reference cell was filled with deionized water. The sample solution with a concentration of 1.0 g/L was degassed at 25 °C for half an hour and equilibrated at 10 °C for 2 h before heating at a rate of 1.0 °C/min.

Laser Light Scattering (LLS)

A commercial spectrometer (ALV/DLS/SLS-5022F) equipped with a multi-tau digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He-Ne laser ($\lambda_0 = 632$ nm) as the light source was employed for dynamic and static LLS measurements. Scattered light was collected at a fixed angle of 90° for duration of ~10 min. Distribution averages and particle size distributions were computed using cumulants analysis and CONTIN routines. All data were averaged over three measurements.

Transmission Electron Microscopy (TEM)

TEM observations were conducted on a Hitachi H-800 electron microscope at an acceleration voltage of 200 kV. The sample for TEM observations was prepared by placing 10 μL of micellar solution on copper grids coated with thin films of Formvar and carbon successively.

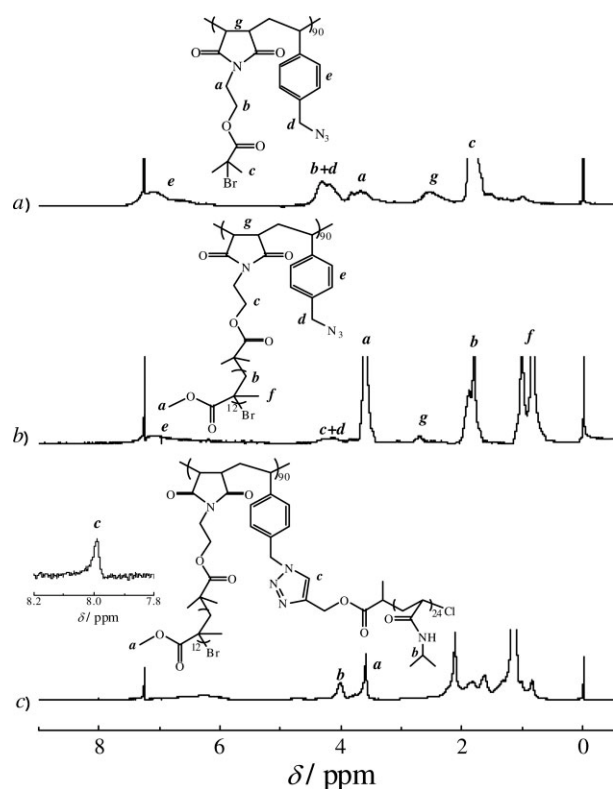


Figure 2. ^1H NMR spectra recorded in CDCl_3 for (a) poly(BIBEMI-*alt*-VBA) multifunctional initiator, (b) poly(PMMA-*alt*-VBA), and (c) poly(PMMA-*alt*-PNIPAM) alternating copolymer brush.

RESULTS AND DISCUSSION

Synthesis of Poly(PMMA-*alt*-PNIPAM) Alternating Copolymer Brush

Synthetic routes employed for the preparation of poly(PMMA-*alt*-PNIPAM) alternating copolymer brush were shown in Scheme 1. Free radical copolymerization of maleimide derivative (BIBEMI) and VBA afforded poly(BIBEMI-*alt*-VBA) with bromine and azide moieties arranged in an alternate manner. After fractionation, the obtained narrow-disperse poly(BIBEMI-*alt*-VBA) was employed as macroinitiator for the ATRP of MMA monomer. The subsequent click reaction of the obtained poly(MMA-*alt*-VBA) polymer brush with an excess of *alkynyl*-PNIPAM led to the facile preparation of amphiphilic and thermoresponsive alternating copolymer brush, poly(PMMA-*alt*-PNIPAM).

It is well-established that the free radical alternating copolymerization of maleimide derivative (BIBEMI) and 4-vinylbenzyl (VBA) monomers can be conducted in a well-defined manner because of

the formation charge-transfer complex.^{5,9,18} GPC analysis of fractionated poly(BIBEMI-*alt*-VBA) revealed a monomodal and quite symmetric elution peak, yielding an M_n of 43.1 kDa and an M_w/M_n of 1.10 [Fig. 1(a)]. The actual DP of poly(BIBEMI-*alt*-VBA) was then calculated to be 180 based on GPC results. ^1H NMR spectrum of poly(BIBEMI-*alt*-VBA) was shown in Figure 2(a). By comparing integration areas of peaks *b* and *d* to those of peaks *a* and *g*, the ratio of BIBEMI and VBA repeating units was determined to be 1:1, confirming the nature in alternating copolymerization between these two monomers. Moreover, FTIR spectrum of poly(BIBEMI-*alt*-VBA) clearly revealed the presence of absorbance peaks at 2100 and 1700 cm^{-1} , which are characteristic of azide and maleimide residues, respectively, [Fig. 3(a)].

The grafting-from approach has been frequently employed to the preparation of polymer brushes, taking advantage of the recent boom in controlled radical polymerizations. Muller and coworkers²² successfully applied ATRP to the synthesis of amphiphilic cylindrical core-shell brushes via sequential “grafting from” strategy, using poly(2-(2-bromoisobutyryloxy)ethyl methacrylate (PBIEM) as the macroinitiator. They also presented the synthesis of poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) cylindrical brushes via ATRP grafting-from technique. Recently, Matyjaszewski and coworkers²⁶ reported

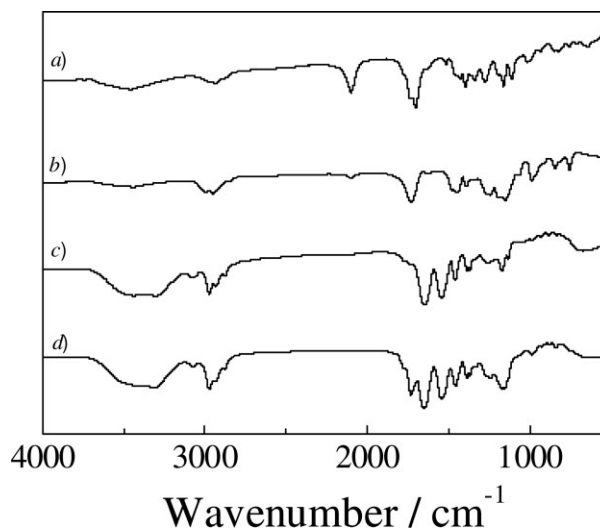


Figure 3. FTIR spectra recorded for (a) poly(BIBEMI-*alt*-VBA) multifunctional initiator, (b) poly(PMMA-*alt*-VBA), (c) *alkynyl*-PNIPAM₂₄, and (d) poly(PMMA-*alt*-PNIPAM) alternating copolymer brush.

the synthesis of thermally responsive homopolymer and random copolymer brushes.²³ Huang and coworkers³³ synthesized well-defined asymmetric centipede-shaped copolymer brushes.

Poly(PMMA-*alt*-VBA) brush was prepared by the ATRP of MMA monomer in anisole, using poly(BIBEMI-*alt*-VBA) as the macroinitiator and CuBr/PMDETA as the catalyst. Typical GPC trace of poly(PMMA-*alt*-VBA) was shown in Figure 1(b), exhibiting a monomodal and symmetric elution peak. When compared with the GPC trace of poly(BIBEMI-*alt*-VBA) macroinitiator [Fig. 1(a)], the elution peak of poly(PMMA-*alt*-VBA) exhibited a clear shift to the higher MW region, indicating the successful preparation of poly(PMMA-*alt*-VBA) brush. GPC analysis revealed an M_n of 128.7 kDa and an M_w/M_n of 1.11. ¹H NMR spectrum of poly(PMMA-*alt*-VBA) was shown in Figure 2(b), and all signals characteristic of PMMA grafts and VBA repeating units can be clearly discerned. The actual DP of PMMA grafts in poly(PMMA-*alt*-VBA) was calculated to be 12 by comparing integration areas of peaks *a* and *g*, assuming a quantitative initiating efficiency. Thus, the obtained polymer was denoted as poly(PMMA₁₂-*alt*-VBA)₁₈₀. FTIR spectrum of poly(PMMA-*alt*-VBA) revealed the presence of absorbance peaks at 2100 and 1730 cm⁻¹, which are characteristic of azide and ester carbonyl residues in poly(PMMA-*alt*-VBA), respectively, [Fig. 3(b)].

Finally, the synthesis of poly(PMMA-*alt*-PNIPAM) copolymer brush was accomplished by the click reaction of poly(PMMA₁₂-*alt*-VBA)₁₈₀ with *alkynyl*-PNIPAM₂₄ in DMF at 80 °C using CuBr as catalyst. An excess of *alkynyl*-PNIPAM₂₄ was employed to ensure the highest extent of consumption of azide moieties in poly(PMMA-*alt*-VBA). The removal of unreacted *alkynyl*-PNIPAM₂₄ was facilely achieved by clicking onto azide-functionalized Merrifield resin and a subsequent simple filtration step.^{73,74} GPC analysis supported the successful preparation of poly(PMMA-*alt*-PNIPAM) alternating copolymer brush. The elution peak was monomodal and clearly shifted to the higher MW region [Fig. 1(c)], when compared with that of poly(PMMA-*alt*-VBA) precursor [Fig. 1(b)]. GPC analysis revealed an M_n of 307.2 kDa and an M_w/M_n of 1.18. From ¹H NMR spectrum of poly(PMMA₁₂-*alt*-PNIPAM₂₄)₁₈₀ [Fig. 2(c)], we could discern all characteristic signals of PMMA and PNIPAM sequences, as well as the new resonance signal (peak *c*) at 8.0 ppm characteristic of protons in 1,2,3-triazole rings.

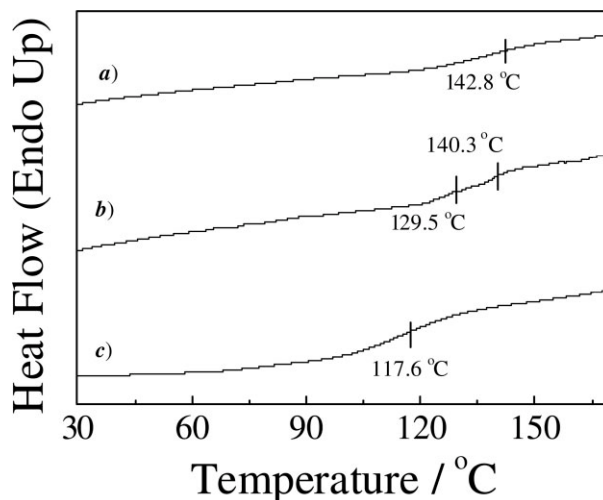


Figure 4. DSC curves recorded for (a) *alkynyl*-PNIPAM₂₄, (b) poly(PMMA-*alt*-PNIPAM), and (c) poly(PMMA-*alt*-VBA) alternating copolymer brushes.

A comparison of integration areas of peaks *a* and *b* further revealed a grafting efficiency of 80% for PNIPAM side chains, that is, ~48% of *alkynyl*-PNIPAM₂₄ participated in the “click” grafting-to reaction. Figure 3(d) shows the FTIR spectrum of poly(PMMA-*alt*-PNIPAM), clearly indicating the presence of PMMA and PNIPAM characteristic absorbance peaks. Compared to that of poly(PMMA-*alt*-VBA), IR spectrum of poly(PMMA-*alt*-PNIPAM) revealed the nearly complete disappearance of characteristic azide absorbance peak at ~2100 cm⁻¹. This apparently indicated that most of the azide moieties were consumed and participated in the click reaction with terminal *alkynyl* group of *alkynyl*-PNIPAM₂₄, though ¹H NMR analysis only revealed a grafting efficiency of ~80%. Previously, Gao and Matyjaszewski⁴⁰ investigated the click grafting-to reaction between azide-terminated PEO ($M_n = 0.77$ kDa) with *alkynyl*-functionalized homopolymers, and a grafting efficiency up to 88.4% was achieved. The relatively lower grafting efficiency in our case should be ascribed to the larger DP of *alkynyl*-PNIPAM₂₄.

Glass transition temperature (T_g) is one of the basic physical parameters of synthetic polymers. Both molecular weights (particularly in the low MW range) and chain topology can considerably affect T_g values.^{75–79} Typical DSC thermograms of poly(PMMA-*alt*-PNIPAM) alternating copolymer brush as well as *alkynyl*-PNIPAM₂₄ and poly(PMMA-*alt*-VBA) precursors were shown in Figure 4. *Alkynyl*-PNIPAM₂₄ and poly(PMMA-*alt*-

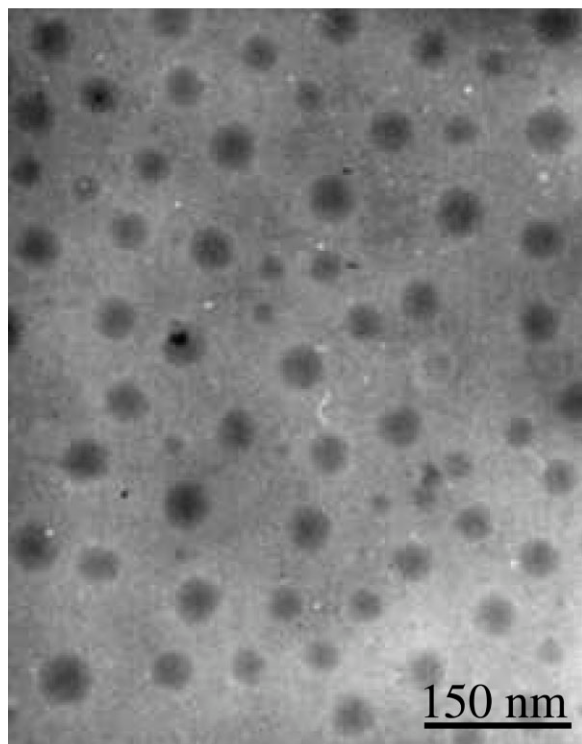


Figure 5. Typical TEM image obtained by drying the micellar solution of poly(PMMA-*alt*-PNIPAM) alternating copolymer brush at a concentration of 0.1 g/L and 25 °C.

VBA) exhibited T_g values of 142.8 ± 1.0 and 117.6 ± 0.8 °C, respectively. On the other hand, poly(PMMA-*alt*-PNIPAM) alternating copolymer brush exhibited two distinct glass transitions, with T_g values being 140.3 ± 0.8 and 129.5 ± 1.3 °C, respectively. Because of the covalent and alternating attachment of two types of grafts, the presence of two T_g 's for poly(PMMA-*alt*-PNIPAM) suggested that microphase separation occurred in the bulk state, resulting from the intrinsic immiscibility between PNIPAM and PMMA grafts.

Aggregation Behavior of Poly(PMMA-*alt*-PNIPAM) Alternating Copolymer Brush

Previously, Ishizu et al.^{12,14} synthesized poly(PEO-*alt*-PPO) and poly(PEO-*alt*-PS) amphiphilic alternating copolymer brushes. They could self-assemble into spherical or rod-like aggregates in aqueous solution, depending on the relative lengths of two types of grafts, as well as the DP of backbones. On the other hand, only rod-shaped aggregates were observed in aqueous solution for poly(PEO-*alt*-PS) alternating copolymer brush with the backbone DP in the range of 200–1500.

In this study, poly(PMMA-*alt*-PNIPAM) alternating copolymer brush possesses hydrophobic PMMA and thermoresponsive PNIPAM grafts, and it can also be considered as amphiphilic molecular brush. Using a cosolvent approach, stable aggregates of poly(PMMA-*alt*-PNIPAM) in aqueous solution can be obtained. On the basis of chemical intuition, the formed aggregates should consist of PMMA cores and thermoresponsive PNIPAM coronas.

Transmission electron microscopy (TEM) was performed to examine the actual morphology of aggregates self-assembled from poly(PMMA-*alt*-PNIPAM) brush with a backbone DP of 180 (Fig. 5). We can tell that the aggregates formed in aqueous solution are spherical and relatively narrow-distributed, with diameters ranging from 30 to 40 nm. Figure 6 shows temperature-dependent changes of average hydrodynamic radius, $\langle R_h \rangle$, obtained for micellar nanoparticles self-assembled from poly(PMMA-*alt*-PNIPAM) in aqueous solution during the heating process. $\langle R_h \rangle$ remains constant at ~ 25 nm below 38 °C. The inset in Figure 6 shows typical hydrodynamic radius distribution, $f(R_h)$, of micelles at 25 °C, yielding a polydispersity index, μ_2/Γ^2 , of 0.11. Micellar size determined by dynamic LLS is in general agreement with that determined by TEM (Fig. 5). It has been well-established that TEM determines micelle dimensions in the dry state, whereas dynamic LLS reports the intensity-average dimensions of micelles in solution and it contains the

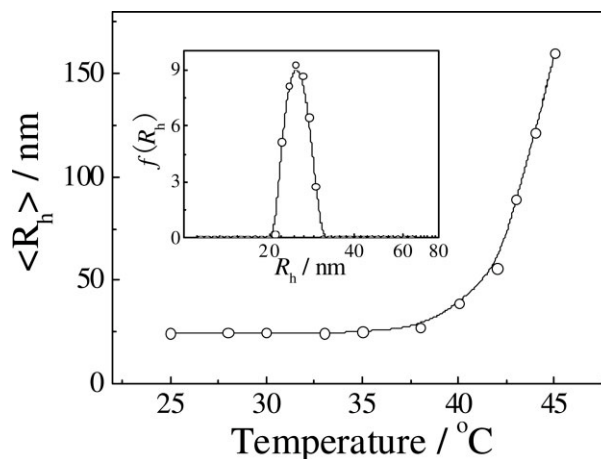


Figure 6. Temperature-dependence of average hydrodynamic radius, $\langle R_h \rangle$, obtained for the aqueous micellar solution of poly(PMMA-*alt*-PNIPAM) alternating copolymer brush at a concentration of 0.1 g/L. The inset shows typical hydrodynamic radius distribution, $f(R_h)$, at 25 °C.

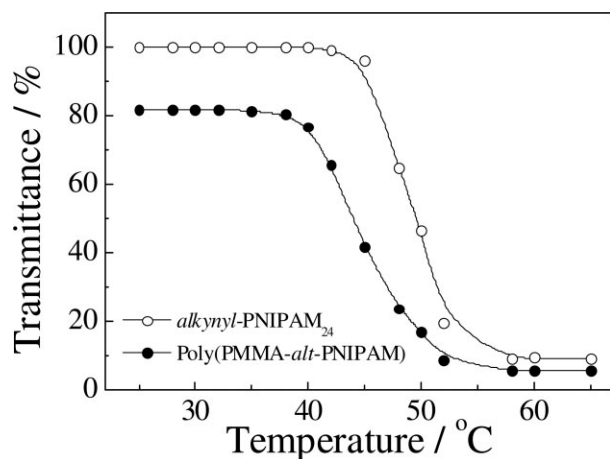


Figure 7. Temperature dependence of optical transmittance at a wavelength of 700 nm obtained for 1.0 g/L aqueous solutions of *alkynyl*-PNIPAM₂₄ and poly(PMMA-*alt*-PNIPAM) alternating copolymer brush.

contribution of well-solvated coronas. Above 38 °C, we can apparently observe the further aggregation of micellar nanoparticles because of the presence of thermoresponsive PNIPAM coronas, accompanied with the increase of $\langle R_h \rangle$ from 25 nm at 25 °C to ~ 160 nm at 45 °C. It should be noted that the thermoinduced aggregation of micellar nanoparticles self-assembled from poly(PMMA-*alt*-PNIPAM) is fully reversible. Upon cooling to 25 °C, dynamic LLS reveals that $\langle R_h \rangle$ can restore to the original value of ~ 25 nm.

Figure 7 showed the temperature-dependent optical transmittance at 700 nm obtained for 1.0 g/L micellar solution of poly(PMMA-*alt*-PNIPAM). For comparison, temperature-dependent turbidity curve of *alkynyl*-PNIPAM₂₄ was also shown. The critical phase transition temperature, T_c , was defined as the temperature corresponding to a 1% decrease of optical transmittance. Recently, Stöver and coworkers^{80,81} successfully synthesized a series of narrow-disperse PNIPAM homopolymers with varying MWs and end groups by ATRP, and reported that phase transition temperatures can vary in the broad range of 32–70 °C depending on MWs and the hydrophobicity/hydrophobicity of terminal groups. In this case, the obtained relatively high LCST value of *alkynyl*-PNIPAM₂₄ (42 °C) can thus be ascribed to the short chain length.

On the other hand, poly(PMMA-*alt*-PNIPAM) alternating copolymer brush exhibited a T_c value of ~ 37 °C. The relatively lower transition temperature compared to *alkynyl*-PNIPAM₂₄ (42 °C) could be explained as follows. Firstly, the presence of hydrophobic PMMA cores will considerably

shift the phase transition temperature of PNIPAM coronas covalently attached at the surface of micelle cores. Secondly, within micellar coronas, PNIPAM sequences were densely grafted; this will reduce the number of hydrogen-bonding interaction pairs or weaken hydrogen-bonding interactions between PNIPAM repeating units and water molecules, and this will lead to a much lower transition temperature.^{82,83}

For micelles self-assembled from poly(PMMA-*alt*-PNIPAM) alternating copolymer brush, static LLS revealed a weight-average molar mass, M_w , of 5.15×10^7 g/mol and the average aggregation numbers per micelle, N_{agg} , was estimated to be 140. Accordingly, average micelle density was calculated to be 0.18 g/cm³. On the other hand, the average radius of micellar cores can be estimated to be ~ 17.5 nm (Fig. 5). If we assume that all PNIPAM sequences were located in the micellar coronas, we can calculate that the grafting density of PNIPAM chains at the surface of micelle core is 0.30 nm² per chain. Compared to the dimension of free PNIPAM chains with a DP of 24, this high grafting density indicated that PNIPAM chains are crowded and forced to stretch away from the surface of micelle core.

Micro-DSC is further employed to investigate the thermal phase transitions of *alkynyl*-PNIPAM₂₄ and poly(PMMA-*alt*-PNIPAM) alternating copolymer brush in aqueous solution at a concentration of 1.0 g/L, and the results are shown in Figure 8. The endothermic peak of aqueous micellar solution of poly(PMMA-*alt*-PNIPAM) is much

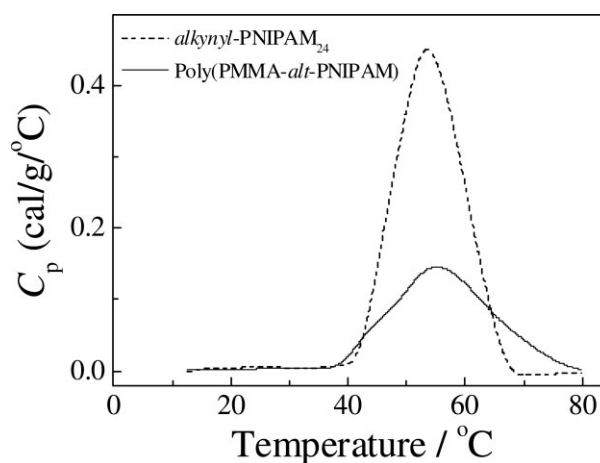


Figure 8. Temperature dependence of the specific heat capacity (C_p) obtained for 1.0 g/L aqueous solutions of *alkynyl*-PNIPAM₂₄ and poly(PMMA-*alt*-PNIPAM) alternating copolymer brush during the heating process. The heating rate was 1.0 °C/min.

broader than that of *alkynyl*-PNIPAM₂₄. Micro-DSC endothermic peaks shown in Figure 8 allow the estimation of ΔH values of 3.1 kJ/mol for *alkynyl*-PNIPAM₂₄ and 1.5 kJ/mol for poly(PMMA-*alt*-PNIPAM), respectively. Both values were expressed as per mole of NIPAM repeating units.^{62,71,83–85} It is worthy of noting that the ΔH value is closely associated with the energy required for the breakup of about one hydrogen-bonded pair between one NIPAM repeating unit and water molecules on phase transition. Considering that hydrogen-bonding interactions possess high directionality and that the high grafting density of PNIPAM sequences in poly(PMMA-*alt*-PNIPAM) micelles can exert stringent restrictions on hydrogen-bonding interactions, the lower ΔH value obtained for poly(PMMA-*alt*-PNIPAM) micelles compared to that of *alkynyl*-PNIPAM can be ascribed to the reduced number of hydrogen-bonding interaction pairs and/or weakened hydrogen-bonding interactions. In an alternate explanation, *alkynyl*-PNIPAM chains adopt random coil conformations in aqueous solution, and they will expose more accessible surface areas to water molecules than PNIPAM sequences in poly(PMMA-*alt*-PNIPAM) micelles.

CONCLUSIONS

We report on the synthesis of well-defined amphiphilic copolymer brush possessing alternating poly(methyl methacrylate) and poly(*N*-isopropylacrylamide) grafts, poly(PMMA-*alt*-PNIPAM), via a combination of ATRP and click chemistry. DSC measurements revealed two glass transition temperatures for poly(PMMA-*alt*-PNIPAM), indicating microphase separation between PMMA and PNIPAM segments. In aqueous solution, poly(PMMA-*alt*-PNIPAM) alternating copolymer brushes self-assemble into stable aggregates consisting of hydrophobic PMMA cores and densely grafted thermoresponsive coronas. Compared to that of linear PNIPAM with similar DP, PNIPAM coronas in poly(PMMA-*alt*-PNIPAM) micelles possess lower phase transition temperatures and enthalpic changes (ΔH), as revealed by temperature-dependent turbidimetry and micro-DSC, respectively.

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