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Convenient Synthesis of P*t*BA-*g*-PMA Well-Defined Graft Copolymer with Tunable Grafting Density

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ABSTRACT: A series of well-defined graft copolymers, consisting of poly(*tert*-butyl acrylate) backbone and poly(methyl acrylate) side chains, were synthesized by the combination of reversible addition−fragmentation chain transfer (RAFT) polymerization and atom transfer radical polymerization (ATRP). A new acrylate monomer containing ATRP initiation group, *tert*-butyl 2-((2-bromopropanoyloxy)methyl)acrylate, was first prepared, which can be homopolymerized or copolymerized with *tert*-butyl acrylate by RAFT in a controlled way to obtain well-defined homopolymers and copolymers with narrow molecular weight distributions ($M_w/M_n < 1.18$). The reactivity ratios were determined by Fineman−Ross and Kelen−Tudos methods, respectively. The density of ATRP initiating groups can be tuned by the feed ratio of the comonomers. These polymers directly initiated ATRP of methyl acrylate to synthesize well-defined poly(*tert*-butyl acrylate)-*g*-poly(methyl acrylate) graft copolymers ($M_w/M_n < 1.28$) with controllable grafting densities via the grafting-from strategy without any polymeric functional group transformation. Finally, the poly(*tert*-butyl acrylate) backbone was selectively hydrolyzed in acidic environment without affecting the poly(methyl acrylate) side chains to give poly(acrylic acid)-*g*-poly(methyl acrylate) amphiphilic graft copolymers.

Introduction

Recently, there has been more interest on preparing complex multicomponent block copolymers, graft and graft-block copolymers, starlike polymers with a variable number of arms, and many other complex configurations with the rapid development of new living radical polymerization (LRP) methods because only a few monomers are suitable for the preparation of copolymers by ionic polymerization. Living radical polymerization technique made the preparation of well-defined copolymers much more convenient under mild conditions compared to those of ionic polymerization. Polymers synthesized by LRP exhibit living characteristics such as a linear increase in molecular weight versus the conversion of the monomer, narrow molecular weight distributions and retention of active functional chain ends. The most commonly used LRPs include nitroxide-mediated polymerization (NMP),[1,2] atom transfer radical polymerization (ATRP),[3−6] and reversible addition−fragmentation chain transfer polymerization (RAFT).[7] In particular, ATRP and RAFT have been used with a wide range of monomer types including (meth)acrylates.[8]

The synthesis of well-defined graft copolymers is much more difficult than that of block copolymers due to the complicated and confined structure. Generally, three different strategies, including grafting-through, grafting-from, and grafting-onto have been used by polymer chemists to synthesize graft copolymer.[9] The grafting-through strategy is to obtain graft copolymer via the polymerization of macromonomers, the resulting graft copolymer via conventional radical polymerization of macromonomers possessed a broad chain-length distribution.[10] In addition, living polymerization of macromonomers yielded well-defined graft copolymer with low molecular weight.[11] The grafting-onto approach is to attach side chains onto the backbone by a coupling reaction and the coupling efficiency is usually insufficient.[12] The grafting-from method appeared lately, which utilizes the pendant initiation groups on the backbone to initiate the polymerization of another monomer to form side chains.[13] The development of "convenient" living radical polymerization made it become the most popular approach of preparing versatile comb copolymers with well-defined architectures.[14] Especially, side chains can be formed in a well-defined way with controlled molecular weights and molecular weight distributions via ATRP initiated by the pendant initiating groups on the backbone. However, the backbone is generally needed to be chemically modified in order to introduce the active pendant initiation groups and the number of grafting sites is difficult to be regulated because of the complexity of macromolecular reaction. For example, 2-hydroxyethyl acrylate (HEA)[15−20] and 2-hydroxyethyl methacrylate (HEMA)[21−28] have been extensively employed to synthesize well-defined graft copolymers with 100% grafting density, that is, polymer brush, whereas protected hydroxyls of PHEMA backbone need to be deprotected and transformed into Br-containing ATRP initiation groups before initiating a second monomer to form side chains. The combination of NMP and ATRP have been reported to synthesize graft copolymers without polymeric functional group transformation;

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however, the grafting densities of those copolymers were all lower than 10% and the suitable monomers of side chains obtained by NMP are very limited.[29−31] Thus, preparing well-defined graft copolymers with controlled grafting densities without polymeric functional group transformation may be a significant advance in polymer chemistry.

A feasible solution is to prepare a new functional monomer containing an initiation site, which can be copolymerized with another suitable monomer by living radical polymerization to give a well-defined backbone containing a certain amount of initiating groups. Thus, the density of grafting sites can be well tuned by the feed ratio of a comonomer and this kind of backbone can directly initiate the polymerization of a second monomer to afford well-defined graft copolymers without polymeric functional group transformation. When considering the possible living radical polymerization methods of preparing well-defined graft copolymers, NMP was first excluded due to the very limited suitable monomers while ATRP and RAFT can be effective with a very wide range of monomers. ATRP of functional monomers containing ATRP initiation group has been reported to give hyperbranched polymer, not linear polymer;[32,33] on the other hand, none has reported ATRP and RAFT polymerization of functional monomers containing RAFT chain transfer group such as S−C═S since that S−C═S group maybe induce the transfer of propagating radical during the polymerization. Thus, a proper way may be to introduce ATRP initiation group into the functional monomer and polymerize this functional monomer via RAFT followed by ATRP.

In this work, we report the direct synthesis of poly(*tert*-butyl acrylate)-*g*-poly(methyl acrylate) (P*t*BA-*g*-PMA) well-defined graft copolymers with controllable grafting densities by successive RAFT and ATRP (Scheme 1). A new acrylate monomer containing ATRP initiation group, *tert*-butyl 2-((2-bromo-propanoyloxy)- methyl)acrylate (*t*BBPMA), was homopolymerized and copolymerized with *tert*-butyl acrylate by RAFT to form well-defined P*t*BA-based macroinitiator with controllable density of ATRP initiation group tuned by the feed ratio of the comonomers. This macroinitiator directly initiated ATRP of methyl acrylate to obtain P*t*BA-*g*-PMA well-defined graft copolymers without polymeric functional group transformation. Finally, poly(acrylic acid)-*g*-poly(methyl acrylate) (PAA-*g*-PMA) amphiphilic graft copolymers were obtained by selective acidic hydrolysis of P*t*BA backbone.

Experimental Section

Materials. Methyl acrylate (MA, Aldrich, 99%) was washed with 5% aqueous NaOH solution to remove the inhibitor, then washed with water, dried over $CaCl_2$, and distilled twice under reduced pressure prior to use. *tert*-Butyl acrylate (*t*BA, Aldrich, 98%) was washed with 5% aqueous NaOH solution to remove the inhibitor, then washed with water, dried over $CaCl_2$, and distilled twice from CaH_2 under reduced pressure prior to use. 2,2′-Azobis(isobutyronitrile) (AIBN, Aldrich, 98%) was recrystallized from anhydrous ethanol. Copper(I) bromide (CuBr, Aldrich, 98%) was purified by stirring overnight over CH_3CO_2H at room temperature, followed by washing the solid with ethanol, diethyl ether, and acetone prior to drying at 40 °C in vacuo for one day. *N*-Phenyl-1-naphthylamine (PNA, Alfa Aesar, 97%) was purified by recrystallization in ethanol three times. Triethylamine (TEA, Aldrich, 99.5%) was dried over KOH and distilled from CaH_2 under N_2 prior to use. Tetrahydrofuran (THF, Aldrich, 99%), dichloromethane (Aldrich, 99.5%), and toluene (Aldrich, 99%) were dried over CaH_2 and distilled from sodium and benzophenone under N_2 prior to use. Cumyl dithiobenzoate (CDB) was synthesized according to previous literature.[34] Formalin (Aldrich, 38 wt %), 4-di-(methylamino)pyridine (DMAP, Aldrich, 99%), trifluoroacetic acid (TFA, Aldrich, 99%), *N*,*N*′-dicyclohexylcarbodiimide (DCC, Aldrich, 99%), 2-bromopropionic acid (Aldrich, 99%), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%) and 1,4-diazabicyclo[2.2.2]octane (DABCO, Aldrich, 98%) were used as received.

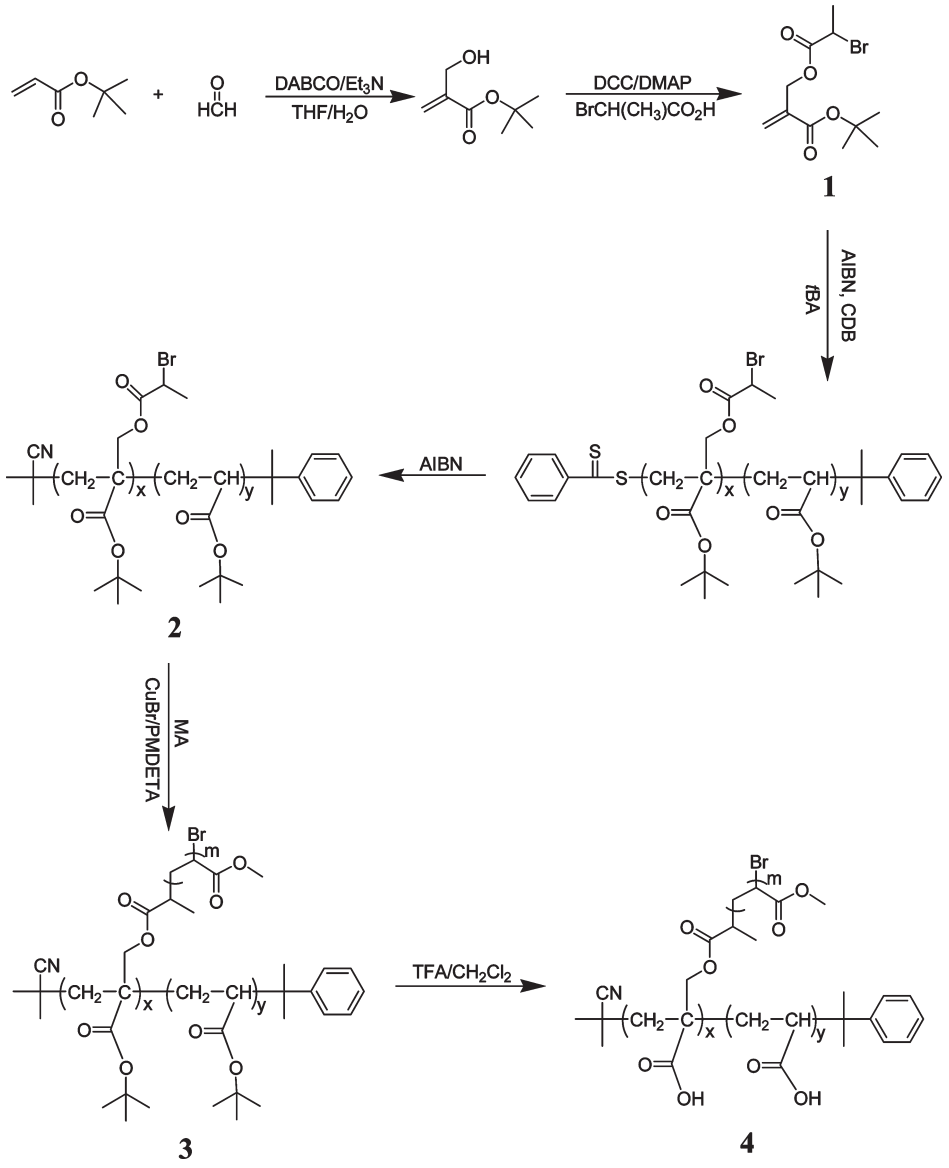
Measurements. FT-IR spectra were recorded on a Nicolet AVATAR-360 FT-IR spectrophotometer with a resolution of 4 cm^{-1}. All ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) analyses were performed on a Bruker Avance 500 spectrometer in $CDCl_3$ and DMSO-d_6; Tetramethylsilicone (^1H NMR) and $CDCl_3$ (^{13}C NMR) were used as internal standards. Elemental analysis was carried out on a Carlo-Erba1106 system. Bromine content was determined by the titration with $Hg(NO_3)_2$. Electrospray ionization mass spectrometry (ESI-MS) was measured by an Agilent LC/MSD SL system. Conversion of methyl acrylate was determined by ^1H NMR. Relative molecular weights and molecular weight distributions were measured by conventional gel permeation chromatography (GPC) system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (HR3 (500−30 000), HR4 (5000−600 000), and HR5 (50 000−4 000 000), 7.8 × 300 mm, particle size: 5 μm). GPC measurements were carried out at 35 °C using THF as eluent (flow rate: 1.0 mL/min). The system was calibrated with linear polystyrene standards. UV−vis spectra were recorded in a quartz cuvette (1 cm × 1 cm) by a Varian Cary 300 spectrophotometer. Steady-state fluorescent spectra were measured at 20 °C on a Hitachi F-4500 Fluorescence spectrophotometer with the bandwidth of 5 nm for excitation and emission, the emission intensity at 418 nm was recorded to determine the critical micelle concentration (cmc), where the excitation wavelength (λ_{ex}) was 340 nm.

Synthesis of *tert*-Butyl (2-Hydroxymethyl)acrylate. *t*BA (48 mL, 0.33 mol), formalin (39.5 g, 0.5 mol), DABCO (3.7 g, 0.033 mol), triethylamine (4.5 mL, 0.033 mol), THF (50 mL), and water (32 mL) were added to a 500 mL three-neck flask. The solution was stirred at room temperature for 3 h followed by stirring at 55 °C for 1 day. The aqueous phase was extracted by ether and all organic layers were merged and washed by brine followed by drying over $MgSO_4$. The filtrate was concentrated and distilled under reduced pressure (60 Pa/80 °C) to give 40.1 g of colorless liquid with a yield of 77%. ^1H NMR: δ (ppm): 1.38 (9H, C(CH_3)$_3$), 2.55 (1H, CH_2OH), 4.29 (2H, CH_2OH), 5.72 and 6.18 (1H, CH_2═C).

Synthesis of *tert*-Butyl 2-((2-Bromopropanoyloxy)methyl)-acrylate 1. Dry dichloromethane (300 mL), *tert*-butyl (2-hydroxymethyl)acrylate (31.6 g, 0.2 mol), 2-bromopropionic acid (30.6 g, 0.2 mol), and DMAP (0.244 g, 0.002 mol) were added to a 500 mL three-neck flask. The solution was cooled to 0 °C before adding DCC (42.0 g, 0.2 mol). The system was stirred at 0 °C for 1 h and was raised to room temperature with stirring overnight followed by the filtration. A colorless liquid, *tert*-butyl 2-((2-bromopropanoyloxy)methyl)acrylate **1** (55.3 g, 94.4%), was obtained by silica column chromatography (eluent: ethyl acetate/hexane (v:v) = 1:9). ESI-MS (*m*/*z*) found $(M-56)^+$: 237. Anal. Calcd. for $C_{11}H_{17}O_4Br$: C, 45.05%; H, 5.80%; Br, 27.30%. Found: C, 45.37%; H, 5.58%; Br, 27.20%. FT-IR ν (cm^{-1}): 2979 (ν_{C-H}), 2934 (ν_{C-H}), 1748 ($\nu_{C=O}$), 1720 ($\nu_{C=O}$), 1643 ($\nu_{C=C}$), 1448, 1394, 1369, 1146, 1063, 848, 816, 761, 515. ^1H NMR δ (ppm): 1.38 (9H, C(CH_3)$_3$), 1.71 (3H, CH_3CH), 4.31 (1H, CH_3CH), 4.72 (2H, CO_2CH_2), 5.71 and 6.17 (1H, CH_2═C). ^{13}C NMR δ (ppm): 21.5 (CH_3CH), 27.9 (C(CH_3)$_3$), 39.6 (CH_3CH), 63.6 (CO_2CH_2), 81.3 (C(CH_3)$_3$), 126.5 (CH_2═C), 136.1 (CH_2═C), 163.9 (CO_2C-(CH_3)$_3$), 169.4 (CO_2CH_2).

RAFT Copolymerization of *t*BBPMA 1 and *tert*-Butyl Acrylate. In a typical procedure, AIBN (16.4 mg, 0.1 mmol) and CDB (81.6 mg, 0.3 mmol) were first added to a 25 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N_2. Next, *t*BBPMA **1** (0.879 g, 3 mmol), *t*BA (1.152 g, 9 mmol) and dry toluene

Scheme 1. Synthesis of Poly(*tert*-butyl acrylate)-*g*-Poly(methyl acrylate) Well-Defined Graft Copolymer (DABCO, 1,4-diazabicyclo[2.2.2]octane; THF, Tetrahydrofuran; DCC, *N*,*N*′-Dicyclohexylcarbodiimide; DMAP, 4-Di(methylamino)pyridine; AIBN, 2,2′-Azobis(isobutyronitrile); CDB, Cumyldithiobenzoate; *t*BA: *tert*-Butyl acrylate; MA, Methyl Acrylate; PMDETA, *N*,*N*,*N*′,*N*′,*N*″-Pentamethyldiethylene-triamine; TFA, Trifluoroacetic Acid)



(0.6 mL) were added via a gastight syringe. The flask was degassed by three cycles of freezing−pumping−thawing followed by immersing the flask into an oil bath set at 70 °C. The polymerization was terminated by immersing the flask into liquid N_2 after 24 h. THF was added to dilute the solution and the solution was precipitated into a mixture of water and methanol (v:v = 3:7). The crude product was purified by repeated dissolution and precipitation followed by drying in vacuo overnight to give 1.50 g of pink powder.

To remove the dithiobenzoate moiety, AIBN (1.70 g, 10.4 mmol) and 1.50 g of pink powder were first added to a 100 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N_2. Next, dry toluene (80 mL) was added via a gastight syringe. The flask was immersed into an oil bath set at 80 °C and the reaction was quenched by liquid N_2 after 8 h. The solution turned to colorless and was precipitated into a mixture of water and methanol (v:v = 3:7) after concentration. After repeated purification of dissolution and precipitation, 0.95 g of white powder, poly(*tert*-butyl 2-((2-bromopropanoyloxy)-methyl)acrylate)-*co*-poly(*tert*-butyl acrylate) (P*t*BBPMA-*co*-P*t*BA) **2e** macroinitiator, was obtained by drying in vacuo overnight. GPC: M_n = 5300, M_w/M_n = 1.17. FT-IR ν (cm^{-1}): 2978 (ν_{C-H}), 2932 (ν_{C-H}), 1736 ($\nu_{C=O}$), 1476, 1448, 1394, 1368, 1253, 1143, 1074, 998, 970, 842, 753. ^{1}H NMR δ (ppm): 1.43 (9H, C(CH_3)$_3$), 1.85 (2H, CH_2CCO_2, 2H, CH_2CHCO_2 and 3H, CH_3CHBr), 2.17 (1H, CH_2CHCO_2), 4.20 (1H, CH_3CHBr), 4.48 (2H, CO_2CH_2). Element analysis: Br% = 11.93%.

Determination of Monomer Reactivity Ratios. In a typical procedure, AIBN (8.2 mg, 0.05 mmol) and CDB (40.8 mg, 0.15 mmol) were first added to a 10 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N_2. Next, *t*BBPMA **1** (1.32 g, 4.5 mmol), *t*BA (0.576 g, 4.5 mmol) and dry toluene (0.3 mL) were added via a gastight syringe. The flask was degassed by three cycles of freezing−pumping−thawing followed by immersing the flask into an oil bath set at 70 °C. The polymerization was terminated by immersing the flask into liquid N_2 after 20 min and the total conversion of both monomers was kept below 10% which was confirmed by ^{1}H NMR. THF was added to dilute the solution and the solution was precipitated into a mixture of water and methanol (v:v = 3:7). The crude product was purified

by repeated dissolution and precipitation followed by drying in vacuo overnight to give a pink viscous liquid. The composition of the copolymer was measured by ^{1}H NMR.

ATRP Graft Copolymerization of Methyl Acrylate. In a typical procedure, P*t*BBPMA-*co*-P*t*BA **2c** (M_n = 7700, M_w/M_n = 1.12, Br% = 22.92%, 70 mg, 0.2 mmol ATRP initiating group), and CuBr (28.8 mg, 0.2 mmol) were first added to a 25 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N_2. Next, MA (7.2 mL, 80 mmol) and PMDETA (78 μL, 0.4 mmol) were added via a gastight syringe. The flask was degassed by three cycles of freezing−pumping−thawing followed by immersing the flask into an oil bath set at 80 °C. The polymerization was terminated by immersing the flask into liquid N_2 after 4 h. The reaction mixture was diluted by THF and passed through an alumina column to remove the residual copper catalyst. The solution was concentrated and precipitated into hexane. After repeated purification by dissolving in THF and precipitating in hexane, 1.02 g (13.2%) of colorless viscous liquid, P*t*BA-*g*-PMA **3c**, was obtained after drying in vacuo overnight. GPC: M_n = 59 800, M_w/M_n = 1.09. FT-IR ν (cm^{-1}): 2954 (ν_{C-H}), 2852 (ν_{C-H}), 1735 ($\nu_{C=O}$), 1440, 1368, 1250, 1202, 1165, 1058, 975, 828, 763. ^{1}H NMR δ (ppm): 1.43 (9H, C(C*H*$_3$)$_3$), 1.69, 1.91 (2H, C*H*$_2$CCO$_2$ and 2H, C*H*$_2$CHCO$_2$), 2.31 (1H, CH$_2$C*H*CO$_2$), 3.67 (3H, CO$_2$C*H*$_3$). ^{13}C NMR δ (ppm): 25.3 (*C*H$_3$CH), 27.8 (C(*C*H$_3$)$_3$), 35.2 (*C*H$_2$CCO$_2$, *C*H$_2$CHCO$_2$, and CH$_3$*C*H), 40.9 (CH$_2$*C*CO$_2$ and CH$_2$*C*HCO$_2$), 51.5 (CO$_2$-*C*H$_3$), 67.7 (CO$_2$*C*H$_2$), 80.2 (*C*(CH$_3$)$_3$), 174.6 (*C*=O).

ATRP kinetics was studied using P*t*BBPMA-*co*-P*t*BA **2e** macroinitiator (M_n = 5300, M_w/M_n = 1.17) and the conversions of MA were determined by ^{1}H NMR.[35] The signals of −OC*H*$_3$ group of MA monomer and poly(methyl acrylate) were both located at 3.67 ppm. Thus, the integration area of the peak at 3.67 ppm (A_{OCH3}) was constant during the polymerization and this peak was used as internal standard. The signals of −C*H*=C*H*$_2$ group of MA monomer appeared at 5.79, 6.06, and 6.32 ppm in ^{1}H NMR spectrum. The total integration area of 3 peaks of −C*H*=C*H*$_2$ group of MA monomer before ($A_{CH=CH2}$) and after ($A'_{CH=CH2}$) the polymerization were measured by ^{1}H NMR. The conversion of MA (Conv) was calculated according to the following equation

$$\text{Conv} = [(A_{CH=CH_2} - A'_{CH=CH_2})/A_{OCH_3}] \times 100\% \quad (1)$$

Selective Acidic Hydrolysis of P*t*BA-*g*-PMA. In a typical procedure, P*t*BA-*g*-PMA **3c** (M_n = 59 800, M_w/M_n = 1.09, 800 mg, 0.27 mmol *tert*-butyl group), CH_2Cl_2 (50 mL), and TFA (0.2 mL, 2.7 mmol) were added to a 100 mL three-neck flask. The solution was stirred at 0 °C for 1 h followed by stirring at room temperature for another 12 h. The solution was concentrated and precipitated into cold hexane. After filtration, 613 mg (76.6%) of colorless viscous liquid, PAA-*g*-PMA **4c**, was obtained after drying in vacuo overnight. For GPC measurement, PAA backbone was transformed into poly(methyl acrylate) backbone by reacting with CH_2N_2 according to previous literature.[36] GPC: M_n = 59 600, M_w/M_n = 1.10. FT-IR ν (cm^{-1}): 3320 (ν_{OH}), 2954 (ν_{C-H}), 1740 ($\nu_{C=O}$), 1440, 1365, 1249, 1204, 1166, 974, 827. ^{1}H NMR (DMSO-d_6) δ (ppm): 1.62, 1.76 (2H, C*H*$_2$CCO$_2$ and 2H, C*H*$_2$CHCO$_2$), 2.18 (1H, CH$_2$C*H*CO$_2$), 3.58 (3H, CO$_2$C*H*$_3$), 12.3 (1H, COO*H*). ^{13}C NMR δ (ppm): 25.3 (*C*H$_3$CH), 34.5 (*C*H$_2$CCO$_2$, *C*H$_2$CHCO$_2$, and CH$_3$*C*H), 41.1 (CH$_2$*C*CO$_2$ and CH$_2$*C*HCO$_2$), 51.6 (CO$_2$*C*H$_3$), 67.7 (CO$_2$*C*H$_2$), 174.8 (*C*=O).

Determination of Critical Micelle Concentration. PNA was used as fluorescence probe to measure the cmc of PAA-*g*-PMA amphiphilic graft copolymer. Acetone solution of PNA (2 mM) was added to a large amount of water until the concentration of PNA reached 0.0006 mM. Different amounts of THF solutions of PAA-*g*-PMA (1, 0.1, or 0.01 mg/mL) were added to water containing PNA ([PNA] = 0.0006 mM).

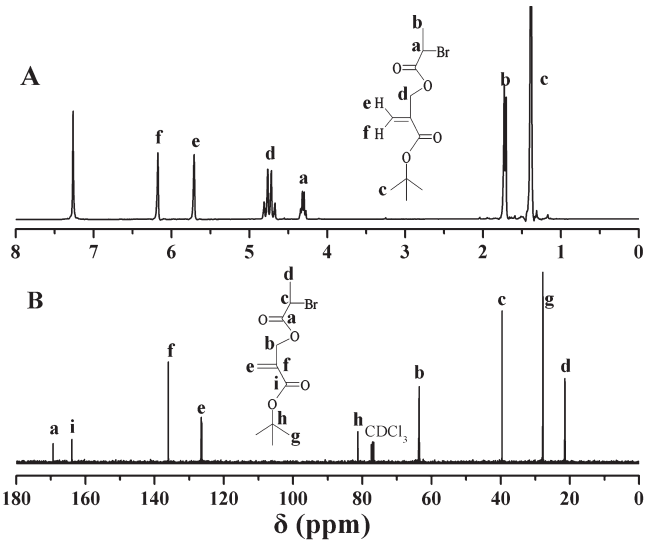


Figure 1. ^{1}H NMR (A) and ^{13}C NMR (B) spectra of 2-((2-bromopropanoyloxy)-methyl)acrylate **1**.

Results and Discussion

Synthesis of *t*BBPMA Containing ATRP Initiation Group. Generally, the hydroxyl group is easy to be converted to ATRP initiation group via common esterification reactions.[9] In the current work, hydroxymethyl was first introduced into *t*BA to give the key intermediate of *tert*-butyl (2-hydroxymethyl)-acrylate via Baylis−Hillman reaction using DABCO and TEA as basic cocatalysts and H_2O, a kind of protonic solvent, was employed to promote the reaction through either the stabilization of enolate or the activation of aldehyde.[37,38] Next, *tert*-butyl (2-hydroxymethyl)acrylate was esterified by 2-bromopropionic acid with DMAP as catalyst to provide *t*BBPMA **1** monomer containing ATRP initiation group.

The chemical structure of *t*BBPMA **1** was examined by FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopies. Typical signals at 1748, 1720, and 1643 cm^{-1} in the FT-IR spectrum demonstrated the existence of carbonyl and carbon−carbon double bonds. The resonance signals of the double bond were located at 5.71 and 6.17 ppm in the ^{1}H NMR spectrum as shown in Figure 1A. The peaks at 4.31 and 4.72 ppm belonged to 1 proton of C*H*Br and 2 protons of CO$_2$-CH$_2$, respectively, which illustrated the introduction of ATRP initiation group. In addition, the characteristic peaks at 126.5, 136.1, 163.9, and 169.4 ppm in the ^{13}C NMR spectrum (Figure 1B) confirmed the presence of double bond and carbonyl. All these points evidenced the successful synthesis of the ATRP-initiation-group-containing monomer **1**.

Preparation of ATRP Macroinitiator. RAFT polymerization appears to be the most versatile process among different living radical polymerization techniques in terms of reaction conditions, variety of monomers for which polymerization can be controlled, tolerance of monomer functionalities and it can also be conveniently employed for the preparation of a wide variety of copolymers. RAFT polymerizations of acrylates have been widely studied and they usually lead to well-defined polymers.[39,40] In particular, CDB has been verified to be an effective chain transfer agent (CTA) for RAFT of acrylate. In the current example, *t*BBPMA **1** was homopolymerized or copolymerized with *t*BA via RAFT to prepare the ATRP macroinitiator in toluene at 70 °C using AIBN as an initiator and CDB as the CTA. The conversion of the

Table 1. Preparation of Macroinitiator 2 by Reversible Addition−Fragmentation Chain Transfer (RAFT) Polymerization in Toluene at 70 °C

sample	[**1**]:[*t*BA]:[CDB]:[AIBN][a]	M_n[b] (g/mol)	M_w/M_n[b]	Br%[c]	*x*:*y*[d]
2a	120:0:3:1	6600	1.10		21.9:0
2b	180:0:3:1	8400	1.10		28.0:0
2c	90:30:3:1	7700	1.12	22.92%	22.1:8.2
2d	60:60:3:1	6600	1.11	20.25%	16.7:11.9
2e	30:90:3:1	5300	1.17	11.93%	7.9:21.9

[a] AIBN, 2,2'-azobis(isobutyronitrile); CDB, cumyl dithiobenzoate; *t*BA, *tert*-butyl acrylate. [b] M_n, number-average molecular weight; M_w/M_n, molecular weight distribution, both were measured by gel permeation chromatography at 35 °C in tetrahydrofuran. [c] Determined by the titration with $Hg(NO_3)_2$. [d] x, the number of the repeating units with an ATRP initiating group obtained by Br% as shown in Scheme 1; y, the number of the repeating units without an ATRP initiating group as shown in Scheme 1.

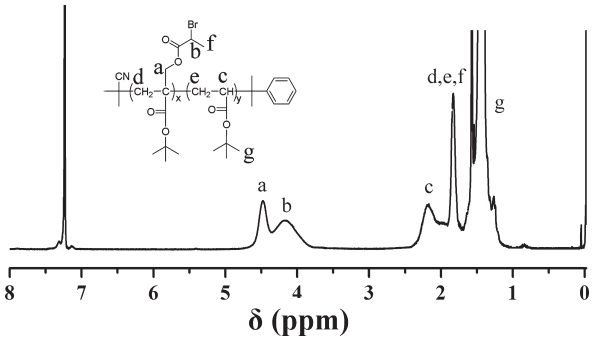


Figure 2. ^{1}H NMR spectrum of poly(*tert*-butyl 2-((2-bromopropanoyloxy)methyl)-acrylate)-*co*-poly(*tert*-butyl acrylate) **2** macroinitiator prepared by reversible addition-fragmentation chain transfer polymerization in toluene at 70 °C.

monomers was not too high to avoid any possible crosslinking. The results are summarized in Table 1.

Although the proportion of dithiobenzoate moiety was quite small, it may affect next ATRP graft polymerization and its pink color (Supporting Information, Figure S1A) may make it difficult to observe the phenomenon of polymerization. Thus, the dithiobenzoate end group was removed by AIBN[41] and a white powder (Supporting Information, Figure S1B) was obtained after the reaction, which illustrated the absence of dithiobenzoate residue. The complete removal of the dithiobenzoate end group was also confirmed by the disappearance of the characteristic peak of the dithiobenzoate end group (510 nm) in UV/vis spectrum after the treatment with AIBN[41] in comparison with that before the treatment.

FT-IR and ^{1}H NMR spectra confirmed the successful polymerization of *t*BBPMA **1**. The typical signal of the double bond at 1643 cm^{-1} disappeared in the FT-IR spectrum after RAFT polymerization and the ^{1}H NMR spectrum after polymerization (Figure 2) also showed the disappearance of resonance signals of double bond. The peaks of polyacrylate backbone appeared at 1.85 and 2.17 ppm. The resonance signal of 1 proton of CH_3CHBr ATRP initiating group still appeared at 4.20 ppm and the bromine content after RAFT homopolymerization was almost same with that of the monomer. In particular, the integration area ratio of peak "b" (CH_3CHBr) to peak "a" (CO_2CH_2) was just 1/2, which demonstrated that the bromine atom was not abstracted in the current case. All the evidence verified that CH_3CHBr ATRP initiating group was not affected during RAFT polymerization. Every GPC curve after RAFT polymerization of *t*BBPMA **1** (Figure 3) showed only a

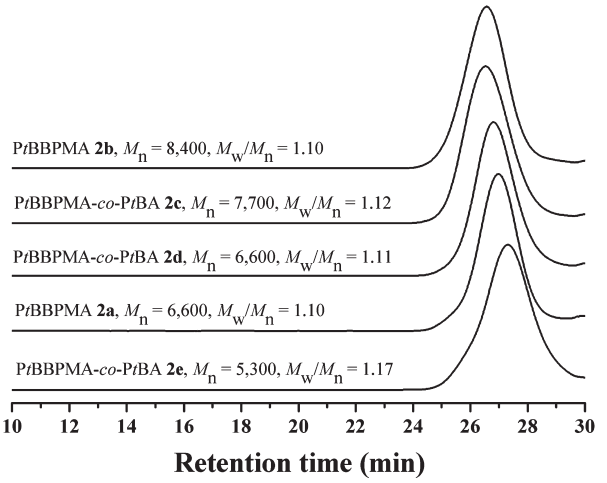


Figure 3. Gel permeation chromatography traces (measured in tetrahydrofuran at 35 °C) of poly(*tert*-butyl 2-((2-bromo-propanoyloxy)methyl)acrylate) (P*t*BBPMA) and poly(*tert*-butyl 2-((2-bromo-propanoyloxy)methyl)acrylate)-*co*-poly(*tert*-butyl acrylate) (P*t*BBPMA-*co*-P*t*BA) **2** macroinitiator prepared by reversible addition-fragmentation chain transfer polymerization in toluene at 70 °C.

unimodal and symmetrical peak with narrow molecular weight distribution. All the above results confirmed the formation of well-defined P*t*BA-based ATRP macroinitiators.

From the molecular weights of P*t*BBPMA **2** homopolymers (M_n = 6600 for **2a** and 8400 for **2b**), we can easily estimate that every P*t*BBPMA **2a** and **2b** chain possesses 21.9 and 28.0 ATRP initiation groups, respectively. The approximate number of ATRP initiation group in P*t*BBPMA-*co*-P*t*BA **2** copolymer can be calculated from the data of molecular weight and Br% according to the following equation set, in which "*x*" and "*y*" are the number of repeating units with and without an ATRP initiation group as shown in Scheme 1, respectively; 187 is the molecular weight of the end group; 293 and 128 are the molecular weight of the repeating units with and without an ATRP initiation group, respectively.

$$80x/M_n = \mathrm{Br}\% \quad (2)$$

$$293x+128y+187 = M_n \quad (3)$$

Thus, it can be concluded that the density of ATRP initiation group could be tuned by the feed ratio of comonomer and that the ATRP initiation group could be incorporated into every repeating unit by RAFT homopolymerization of *t*BBPMA **1**.

Determination of Monomer Reactivity Ratios. The reactivity ratios for RAFT copolymerizations[42] of *t*BBPMA and *t*BA were determined by linear least-squares regression analysis according to Fineman−Ross (FR)[43] and Kelen−Tudos (KT)[44] equations via the data listed in Table 2. In all cases, the total conversions of both monomers were kept below 10%. The compositions of the copolymers were measured by ^{1}H NMR.

The FR equation is given as below

$$G = r_1 H - r_2 \quad (\mathrm{FR})$$

$$G = F(f-1)/f \text{ and } H = F^2/f$$

where r_1 and r_2 correspond to the monomer reactivity ratio of *t*BBPMA and *t*BA, respectively. The parameters *G* and *H*

Table 2. FR and KT Parameters of *t*BBPMA-*t*BA Copolymerization System[a]

$[M_1]:[M_2]$	F	f	G	H	H	ξ
2: 8	0.2500	0.4381	−0.3206	0.1426	−0.3771	0.168
3: 7	0.4286	0.4117	−0.1708	0.2561	−0.1775	0.2661
4: 6	0.6667	1.0627	0.0393	0.4182	0.03495	0.3719
5: 5	1.0000	1.5776	0.358	0.6419	0.2655	0.4761
6: 4	1.5000	2.1292	0.7515	1.1221	0.411	0.6137
7: 3	2.3330	2.8698	1.5203	1.8971	0.584	0.7287
8: 2	4.0000	4.5754	3.1257	3.4969	0.7437	0.832

[a] Polymerization conditions, ([*t*BBPMA] + [*t*BA]):[CDB]:[AIBN] = 180:3:1; solvent, toluene; $[M_1]$ and $[M_2]$ represent the concentrations of *t*BBPMA and *t*BA, respectively.

are defined as follows: $F = M_1/M_2$ and $f = m_1/m_2$, where M_1 and M_2 are the monomer molar fractions in the feeding; m_1 and m_2 are the copolymer molar compositions.

The reactivity ratio can also be obtained with KT method, which is based on the following equation

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \quad \text{(KT)}$$

$$\eta = G/(\alpha + H) \text{ and } \xi = H/(\alpha + H)$$

where η and ξ are the functions of the parameters G and H, and α is a constant equal to $(H_{max}H_{min})^{1/2}$, H_{max} and H_{min} being the lowest and highest H values, respectively. α was calculated to be 0.7062 for P*t*BBPMA-*co*-P*t*BA system.

The linear extrapolation plots concerning the previous reported methods are depicted in Figure 4. Both plots afforded the similar values of the reactivity ratios. The reactivity ratios of *t*BBPMA (r_1) and *t*BA (r_2) are 1.0114 and 0.3946, respectively, inferred with FR technique, and 0.7428 and 0.4286, respectively, obtained by KT method. The higher r_1 value of *t*BBPMA confirmed the higher reactivity of *t*BBPMA compared to that of *t*BA. The copolymer sequence was statistical in structure with more *t*BBPMA units and the product of the copolymerization was not the block copolymer because the ratios are not both above 1.0.

Synthesis of P*t*BA-*g*-PMA Graft Copolymer. A grafting-from strategy was employed to synthesize P*t*BA-*g*-PMA graft copolymer via bulk ATRP of MA initiated by P*t*BA-based macroinitiator using CuBr/PMDETA as catalytic system and the results are listed in Table 3. All the molecular weights of the obtained graft copolymers were much higher than those of macroinitiator **2**, which indicated ATRP of MA was performed. A high feed ratio of MA to the ATRP initiating group (300:1 and 400:1) and a low conversion of MA were employed in the present study to suppress the intermolecular coupling, which is similar to previous reports.[9,35,45−47] The graft copolymers (**3c**, **3d**, **3e**, **3f**, and **3g**) synthesized from P*t*BBPMA-*co*-P*t*BA **2** macroinitiators with low percentages of ATRP initiating group (< 73%) showed unimodal and symmetrical GPC curves (Figure 5) with narrow molecular weight distributions ($M_w/M_n \leq 1.27$), which are characteristic of ATRP[3] and also indicated that intermolecular coupling reactions could be neglected.[22] However, a minor shoulder appeared in both GPC curves of P*t*BA-*g*-PMA **3a** and **3b** synthesized from P*t*BBPMA **2** macroinitiators with high percentages of ATRP initiating group (100%), which is indicative of the coupling. This result implies that a higher feed ratio of MA to the ATRP initiating group (500:1 or 600:1) is necessary for P*t*BBPMA **2** macroinitiator to suppress the intermolecular coupling in the future study.

The signals of the corresponding protons of P*t*BA backbone and PMA side chains were found in the ^{1}H NMR spectrum as shown in Figure 6A. A new peak appeared at 3.67 ppm (peak a), which was attributed to the 3 protons of the CO_2CH_3 group of the PMA side chain. Typical strong signal of 1 carbon of CO_2CH_3 of PMA side chains was observed at 51.5 ppm in the ^{13}C NMR spectrum (Figure 7A). All these results supported of the structure of P*t*BA-*g*-PMA **3** graft copolymer.

Generally, the evaluation of the initiation efficiency for the graft polymerization would be calculated by ^{1}H NMR.[48] However, the signal of CH_2CHBr end group of PMA side chain at 4.31 ppm overlapped with that of the macroinitiator and it is difficult to determine the initiation efficiency in the current case. As an alternative method, MMA was used in place of MA for graft copolymerization with the same feed

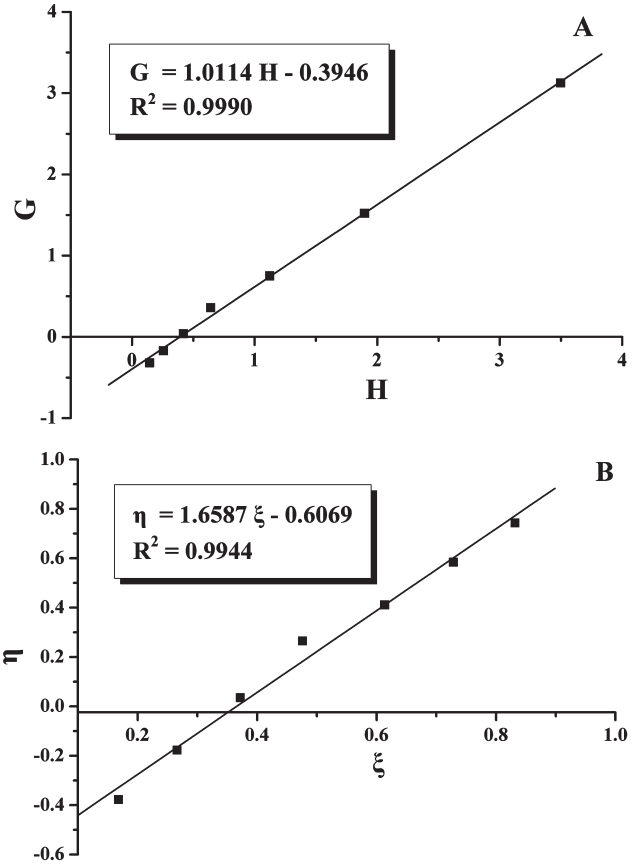


Figure 4. Fineman−Ross (A) and Kelen−Tudos (B) plots for determining the monomer reactivity ratios in the reversible addition−fragmentation chain transfer polymerization of *tert*-butyl 2-((2-bromopropanoyloxy)methyl)acrylate) and *tert*-butyl acrylate in toluene at 70 °C.

Table 3. Synthesis of Poly(*tert*-butyl acrylate)-*g*-Poly(methyl acrylate) 3 Graft Copolymer by Atom Transfer Radical Polymerization (ATRP) in Bulk at 80 °C

sample	initiator	[MA]:[Br][a]	time (h)	M_n[b] (g/mol)	M_w/M_n[b]	Conv[c](%)
3a	**2a**	400:1	4.0	87100	1.13	
3b	**2b**	400:1	4.0	99000	1.24	
3c	**2c**	400:1	4.0	59800	1.09	
3d	**2d**	400:1	4.0	29100	1.20	
3e	**2e**	300:1	1/3	9200	1.24	5.34
3f	**2e**	300:1	2/3	10700	1.27	10.33
3g	**2e**	300:1	4/3	12000	1.26	17.66

[a] MA, methyl acrylate; Br, bromine-containing ATRP initiating group. [b] M_n, number-average molecular weight; M_w/M_n, molecular weight distribution, both were measured by gel permeation chromatography at 35 °C in tetrahydrofuran. [c] Conversion of methyl acrylate measured by ^{1}H NMR.

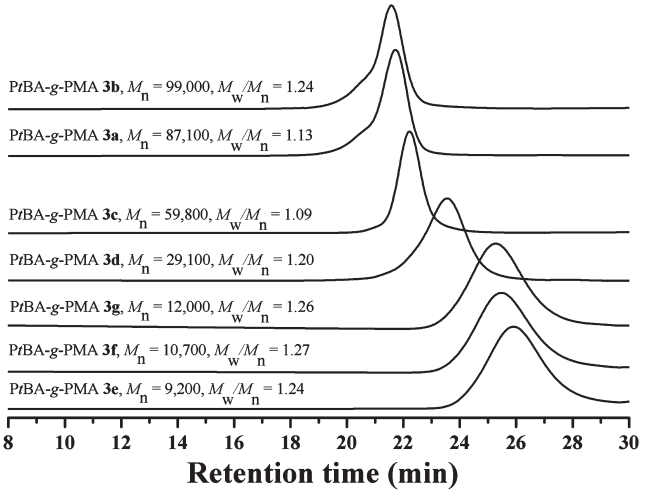


Figure 5. Gel permeation chromatography traces (measured in tetrahydrofuran at 35 °C) of poly(*tert*-butyl acrylate)-*g*-poly(methyl acrylate) (P*t*BA-*g*-PMA) **3** graft copolymer prepared by atom transfer radical polymerization in bulk at 80 °C.

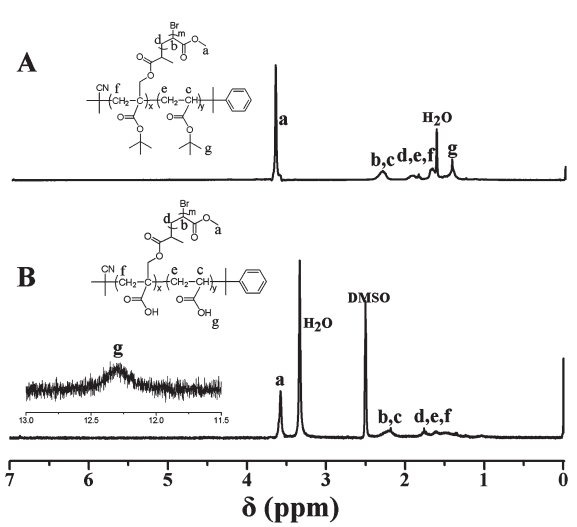


Figure 6. ^{1}H NMR spectra of poly(*tert*-butyl acrylate)-*g*-poly(methyl acrylate) **3** (A) prepared by atom transfer radical polymerization in bulk at 80 °C and poly(acrylic acid)-*g*-poly(methyl acrylate) **4** (B) selectively hydrolyzed from poly(*tert*-butyl acrylate)-*g*-poly(methyl acrylate) **3**.

ratio and polymerization condition. ^{1}H NMR spectrum after the graft copolymerization of MMA showed the disappearance of the peak of CH_2CHBr at 4.31 ppm, this indicating the initiation efficiency of CH_2CHBr ATRP initiation groups was 100%. Thus, we can deduce rationally that the initiation efficiency of CH_2CHBr ATRP initiation for the graft copolymerization of MA is also 100%.

The semilogarithmic plot of $Ln([M]_0/[M])$ versus time, as depicted in Figure 8, shows the conversion of MA increased with a linear dependence. The first order polymerization kinetics demonstrated a constant number of propagating species during the polymerization, which is a typical characteristic of ATRP.[3] Therefore, it was concluded that the polymerizations of backbone and side chains were both controllable within the low conversion realm.

Selective Hydrolysis of P*t*BA Backbone. The hydrophobic P*t*BA backbone was easily hydrolyzed to a hydrophilic PAA backbone by trifluoroacetic acid in CH_2Cl_2.[49−51] The structure of the hydrolyzed product was characterized by ^{1}H NMR, ^{13}C NMR, and FT-IR spectroscopies. We could

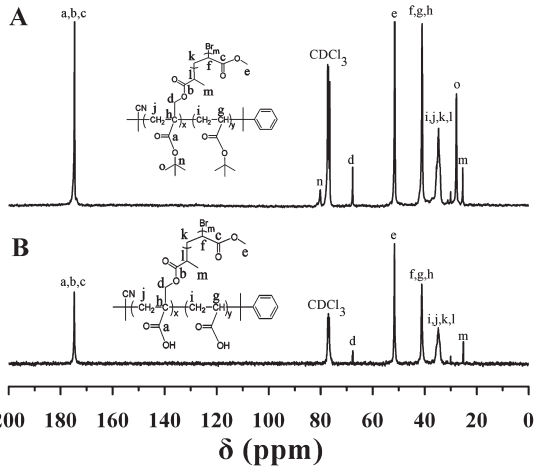


Figure 7. ^{13}C NMR spectra of poly(*tert*-butyl acrylate)-*g*-poly(methyl acrylate) **3** (A) prepared by atom transfer radical polymerization in bulk at 80 °C and poly(acrylic acid)-*g*-poly(methyl acrylate) **4** (B) selectively hydrolyzed from poly(*tert*-butyl acrylate)-*g*-poly(methyl acrylate) **3**.

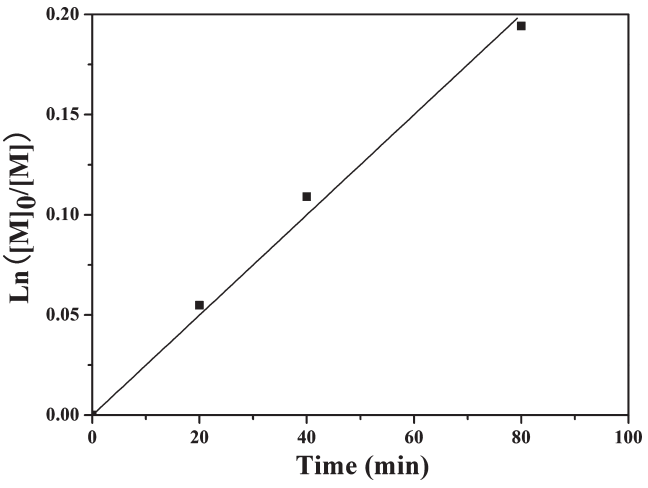


Figure 8. Kinetic plot for bulk atom transfer radical polymerization of methyl acrylate at 80 °C initiated by poly(*tert*-butyl 2-((2-bromopropanoyloxy)methyl)-acrylate)-*co*-poly(*tert*-butyl acrylate) **2e**, [methyl acrylate]:[Br group]:[CuBr]:[*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine] = 300:1:1:2.

not find any trace of the peak of 9 protons of *tert*-butyl group at 1.43 ppm in the ^{1}H NMR spectrum (peak "g" in Figure 6A) after the hydrolysis as shown in Figure 6B and a new signal was found to locate at 12.3 ppm, which was attributed to the proton of −COO*H* group. The characteristic signals of the carbons of *tert*-butyl group at 27.8 and 80.2 ppm in the ^{13}C NMR spectrum (peak "o" and "n" in Figure 7A) also completely disappeared after the hydrolysis as shown in Figure 7B, which demonstrated the successful hydrolysis of P*t*BA backbone. A new broad peak was found to appear at 3320 cm^{-1} in FT-IR spectrum after the hydrolysis (Figure 9B) in contrast with that before the hydrolysis (Figure 9A), which showed the presence of −COOH groups and the formation of PAA backbone. In addition, typical signals of PMA segments were found to remain in both ^{1}H NMR and ^{13}C NMR spectra, this indicated that PMA side chains were not influenced during the hydrolysis. All these evidence showed that P*t*BA-*g*-PMA **3** graft copolymer was selectively hydrolyzed to PAA-*g*-PMA **4** graft copolymer.

Self-Assembly of PAA-*g*-PMA Amphiphilic Graft Copolymer. Fluorescence technique was used to examine the cmc value

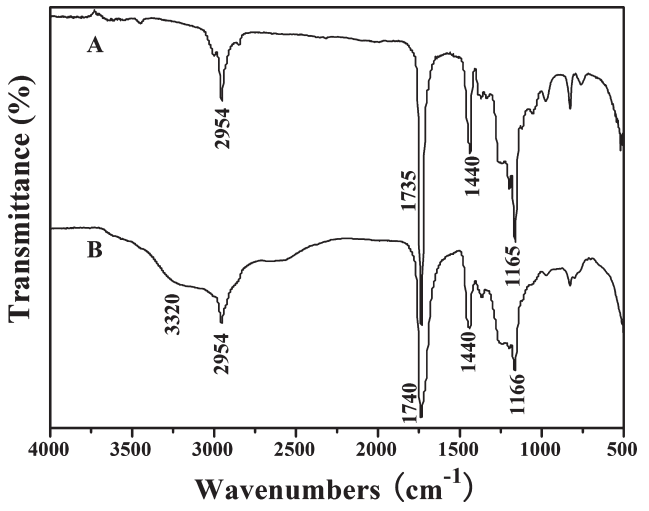


Figure 9. FT-IR spectra of poly(*tert*-butyl acrylate)-*g*-poly(methyl acrylate) **3** (A) prepared by atom transfer radical polymerization in bulk at 80 °C and poly(acrylic acid)-*g*-poly(methyl acrylate) **4** (B) selectively hydrolyzed from poly(*tert*-butyl acrylate)-*g*-poly(methyl acrylate) **3**.

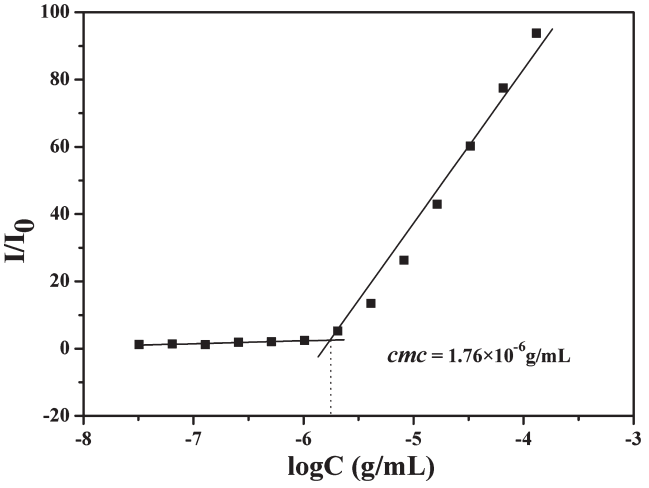


Figure 10. Dependence of fluorescence intensity ratio of *N*-phenyl-1-naphthylamine emission band at 418 nm on the concentration of poly(acrylic acid)-*g*-poly(methyl acrylate) **4b**, excitation wavelength: 340 nm.

Table 4. Critical Micelle Concentration of Poly(acrylic acid)-*g*-Poly(methyl acrylate) (PAA-*g*-PMA) 4 Amphiphilic Graft Copolymer Selectively Hydrolyzed from Poly(*tert*-butyl acrylate)-*g*-Poly(methyl acrylate) (P*t*BA-*g*-PMA) 3[a]

P*t*BA-*g*-PMA	PAA-*g*-PMA	cmc (g/mL)
3a	**4a**	1.86×10^{-6}
3b	**4b**	1.76×10^{-6}
3c	**4c**	2.57×10^{-6}
3d	**4d**	3.33×10^{-6}

[a] Determined by fluorescence spectroscopy using *N*-phenyl-1-naphthylamine as probe, excitation wavelength: 340 nm.

of PAA-*g*-PMA **4** amphiphilic graft copolymer in aqueous media with PNA as probe. PNA can display higher fluorescence activity in nonpolar surroundings and its fluorescence can be very easily quenched by polar solvents such as water; moreover, it is a more suitable fluorescent probe than pyrene in terms of reproducibility.[52] The relationship of the fluorescence intensity ratio (I/I_0) of PNA as a function of the concentration of **4b** at 20 °C is shown in Figure 10. It was found that I/I_0 increased sharply when the concentration exceeded a certain value, which demonstrated PNA probe was incorporated into the hydrophobic region of micelles. Thus, the intersection of two straight lines with a value of 1.76×10^{-6} g/mL was determined to be cmc of **4b**. The cmc values of PAA-*g*-PMA **4** are listed in Table 4, which were comparable with those of polymeric amphiphiles.[53,54] Furthermore, these values decreased when the molecular weights (namely the contents of hydrophobic PMA side chains) increased.

Conclusion

In summary, we have presented the convenient synthesis of P*t*BA-*g*-PMA well-defined graft copolymer with narrow molecular weight distribution ($M_w/M_n < 1.30$) via sequential RAFT and ATRP. Polymeric functional group transformation was avoided in this process since that ATRP initiation group was directly incorporated into acrylate monomer and its density can be regulated by the feed ratio of comonomer. The syntheses of the backbone and side chains are both controllable within the low conversion realm. The P*t*BA-based backbone was selectively hydrolyzed to afford PAA-*g*-PMA amphiphilic graft copolymers and their cmc values in aqueous media were determined by fluorescence spectroscopy using PNA as probe and the values decreased with the increasing of molecular weights. This is a significant progress for synthesis of well-defined graft copolymers because side chains can be easily extended to other polymers. In particular, double hydrophilic graft copolymers can be easily obtained via selective hydrolysis of the backbone when side chains are hydrophilic polymers.

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Supporting Information Available: Color images of the macroinitiator before (A) and after (B) the removal of the dithiobenzoate end group. This material is available free of charge via the Internet at http://pubs.acs.org.

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