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Synthesis of Block, Statistical, and Gradient Copolymers from Octadecyl (Meth)acrylates Using Atom Transfer Radical Polymerization

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ABSTRACT: The synthesis of well-defined homopolymers and random, block, and gradient copolymers from octadecyl acrylate (OA) and octadecyl methacrylate (OMA) using atom transfer radical polymerization (ATRP) is reported. Random copolymers were synthesized by the one-pot copolymerization of either *tert*-butyl acrylate/octadecyl acrylate ($M_{\mathrm{n,p(tBA}\text{-}r\text{-}\mathrm{OA)}} = 13\,680$; $M_w/M_n = 1.13$) or *tert*-butyl methacrylate/octadecyl methacrylate ($M_{\mathrm{n,p(tBMA}\text{-}r\text{-}\mathrm{OMA)}} = 24\,250$; $M_w/M_n = 1.14$) monomer pairs. Additionally, gradient copolymers were prepared by the simultaneous copolymerization of either *tert*-butyl acrylate/octadecyl methacrylate ($M_{\mathrm{n,p(tBA}\text{-}co\text{-}\mathrm{OMA)}} = 21\,790$; $M_w/M_n = 1.25$) or *tert*-butyl methacrylate/octadecyl acrylate ($M_{\mathrm{n,p(tBMA}\text{-}co\text{-}\mathrm{OA)}} = 21\,900$; $M_w/M_n = 1.20$) monomer pairs. AB and ABA triblock copolymers containing octadecyl groups were also prepared with controlled molar mass and composition. The sequence of blocking was varied starting from either poly(*tert*-butyl (meth)acrylate) or poly(octadecyl (meth)acrylate) macroinitiators. The halogen-exchange technique allowed preparation of various well-defined polyacrylate−polymethacrylate block copolymers. Furthermore, uniform phase-separated structures were formed in ultrathin films cast from AB diblock copolymers of ptBMA-*b*-pOMA ($M_n = 52\,000$; $M_w/M_n = 1.12$) and ptBA-*b*-pOMA ($M_n = 28\,750$; $M_w/M_n = 1.20$) as determined from AFM. ABA triblock copolymers of pOMA-*b*-ptBA-*b*-pOMA ($M_n = 75\,900$; $M_w/M_n = 1.14$) and poly(octadecyl methacrylate)-*block*-poly(*n*-butyl acrylate)-*block*-poly(octadecyl methacrylate) ($M_n = 74\,400$; $M_w/M_n = 1.16$) were also analyzed using AFM.

Introduction

Homopolymers and copolymers of poly(octadecyl acrylate) (pOA) and poly(octadecyl methacrylate) (pOMA) were extensively studied due to their interesting bulk and solution properties.[1−10] The presence and cooperative organization of long side chain groups enable the crystallization of these polymers, despite atacticity in the main chain.[1,2] These comblike polymers cocrystallize with hydrocarbon chains in crude and lubricating oils, resulting in a reduction of crystallite size in the mixture.[11,12] Consequently, poly(octadecyl)-based materials have generated interest as pour-point depressants, rheological modifiers, and other additives in petroleum-based products.[13] Block copolymers containing polyoctadecyl segments also were reported as stabilizers in carbon black dispersions.[14] Copolymers of octadecyl acrylate and acrylic acid have found applications as smart gels with chemomechanical and shape memory properties.[15,16]

A major challenge in this research is the preparation of well-defined (co)polymers possessing poly(octadecyl) segments. The synthesis of these materials was widely conducted via conventional radical polymerization.[3,7,12] However, this approach does not enable control over structural features in the (co)polymer, such as molecular weight, composition, and functionality.

Previously, anionic polymerization of OMA was conducted, yielding polymers with low polydispersity ($M_w/M_n > 1.2$) when low molar masses were targeted ($M_n <$ 10 000 g/mol).[8] High polydispersities ($M_w/M_n = 1.8$) were observed when higher molar masses of pOMA were attempted. Anionic polymerization was also employed in the synthesis of poly(styrene)-*b*-poly(octadecyl methacrylate) (pS-*b*-pOMA).[14] However, the polydispersity in the final block copolymer was found to be significantly higher than the living pS macroinitiator ($M_w/M_{\mathrm{n,pS}} <$ 1.2; $M_w/M_{\mathrm{n,pS}\text{-}b\text{-}\mathrm{pOMA}} \leq 1.75$). The primary obstacle in the anionic processes was the higher temperatures (−10 to 0 °C) required to solubilize OMA in organic solvents.

Recently, controlled/living radical polymerization was extensively used to prepare well-defined (co)polymers.[17−20] In particular, atom transfer radical polymerization (ATRP)[21−31] appeared as a robust process in the controlled polymerization of styrenes and (meth)acrylates. ATRP was deemed a good candidate for the controlled polymerization of both OMA and OA as the higher temperatures required for radical processes eliminate solubility issues encountered in anionic polymerization. Similar success in the ATRP of other long alkyl acrylates, namely dodecyl acrylate, strongly implied that the presence of long side chain groups did not affect the polymerization process but required some adjustments of the reaction conditions.[32] An additional feature of the ATRP is the ability to copolymerize monomer pairs, enabling the synthesis of block, statistical, and gradient copolymers.[33,34] Of particular interest was the incorporation of highly incompatible segments by copolymerization of polar and nonpolar monomers.

Herein, we report the synthesis of well-defined homopolymers and block, statistical, and gradient copolymers containing either pOMA or pOA using ATRP. In this study, octadecyl (meth)acrylates and *tert*-butyl (meth)acrylates were copolymerized or chain extended from macroinitiators in a variety of combinations to afford materials with both nonpolar and polar segments. The deprotection of the *tert*-butyl group can yield even more polar (meth)acrylic acid moieties.

Experimental Section

Materials and Characterization. *n*-Octadecyl acrylate(OA) (Polysciences Inc., 99%) and *n*-octadecyl methacrylate (OMA) (Polysciences Inc., 99%) were purified by dissolution

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in hexane and extraction four times with 5% aqueous NaOH. After drying the organic phase over magnesium sulfate, the solution was passed through neutral alumina and solvent was removed under reduced pressure. *tert*-Butyl acrylate (tBA) (Aldrich, 98%) and *tert*-butyl methacrylate (tBMA) (Aldrich, 98%) were dried over calcium hydride and then distilled under reduced pressure. Methyl 2-bromopropionate (Acros, 99%) and ethyl 2-bromoisobutyrate (Acros, 98%) were distilled before use. Copper(I) bromide (Cu(I)Br) (Acros, 98%) and copper(I) chloride (Cu(I)Cl) (Acros, 99%) were purified by washing with glacial acetic acid, followed by absolute ethanol and acetone, and then dried under vacuum. 4,4′-Di(5-nonyl)-2,2′-bipyridine (dNbpy) was prepared as described elsewhere.[35] *p*-Dimethoxybenzene (Acros, 99+%), copper(II) bromide (Cu(II)Br$_2$) (Aldrich, 99%), copper(II) chloride (Cu(II)Cl$_2$) (Aldrich, 99+%), dimethyl 2,6-dibromoheptanedioate (DMDBH), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA),[36] and xylenes (Fisher Scientific, 99%) were all used as received.

Monomer conversion of tBA and tBMA was determined using a Shimadzu GC 14-A gas chromatograph equipped with a FID detector using a J&W Scientific 30 m DB WAX Megabore column. Injector and detector temperatures were kept constant at 250 °C with a heating rate of 40 °C/min. Monomer conversion of OA and OMA and (co)polymer composition were determined by ^{1}H NMR in CDCl$_3$ on a Bruker 300 MHz instrument. (Co)polymer molecular weights were estimated using a SEC system equipped with a Waters WISP 712 autosampler, Polymer Standards Service columns (guard, 10^2 Å, 10^3 Å, 10^5 Å), and a Waters 410 RI detector in THF (1 mL/min) at 35 °C. All determinations of molar mass were performed relative to polystyrene standards (Polymer Standards Services). Toluene was used as an internal standard for both systems. ^{1}H NMR measurements were performed in CDCl$_3$ (using TMS as an internal standard) on a Bruker 300 MHz instrument.

Synthesis of Monofunctional pOA Macroinitiator. Cu(I)Br (28.7 mg; 0.2 mmol), dNbpy (163.5 mg; 0.4 mmol), and Cu(II)Br$_2$ (2.2 mg; 0.01 mmol) were placed in a 25 mL dried Schlenk flask containing a magnetic stir bar. The flask was sealed with a rubber septum, evacuated (1−5 mmHg), backfilled with nitrogen three times, and left under nitrogen. OA (6.49 g; 20 mmol) was dissolved into 8 mL of xylenes, and the resulting solution was bubbled with nitrogen for 20 min. The solution of nOA in xylenes was then added to the solids in the Schlenk flask, and the resulting mixture was stirred for 10 min at room temperature (rt) until homogeneous. Methyl 2-bromopropionate (22.3 μL; 0.2 mmol) was added to the mixture, an initial kinetic sample was removed, and the Schlenk flask was placed in a 90 °C oil bath for 30 h. Aliquots were removed at timed intervals. The mixture was then dissolved in 15 mL of THF and precipitated into 300 mL of a MeOH/H$_2$O (80/20 volume ratio) solution.

Synthesis of Monofunctional ptBA Macroinitiator. DNbpy (204 mg, 0.5 mmol) was added to a 25 mL Schlenk flask; the flask was fitted with a rubber septum and evacuated (1−5 mmHg) followed by backfilling with nitrogen (three cycles). Deoxygenated tBA (3.2 g, 0.025 mol) and *o*-xylene (3.65 mL, 50 vol %) were then added, and the reaction mixture was degassed by three freeze−pump−thaw cycles. After stirring for 1 h at room temperature, CuBr (35.9 mg, 0.25 mmol) was added, and the flask was placed in a thermostated oil bath at 90 °C. After 3 min, methyl 2-bromopropionate (27.9 μL; 0.25 mmol) was injected, and an initial kinetic sample was taken. Aliquots were removed at timed intervals during the polymerization to analyze conversion by GC using *o*-xylene as the internal standard and analyze molecular weight by SEC. After 36 h, the polymerization was stopped at 57% conversion by cooling to room temperature and opening the flask to air. The mixture was dissolved in 15 mL of THF, passed through neutral alumina column, and precipitated into 300 mL of a MeOH/H$_2$O (4:1 volume ratio) solution.

Synthesis of Monofunctional pOMA Macroinitiator. Cu(I)Cl (19.8 mg; 0.2 mmol), dNbpy (163.5 mg; 0.4 mmol), and Cu(II)Cl$_2$ (1.3 mg; 0.01 mmol) were placed in a 25 mL dried Schlenk flask that was evacuated (1−5 mmHg) and backfilled with nitrogen (three cycles). OMA (6.77 g; 20 mmol) was dissolved into 8 mL of xylene, and the resulting solution was bubbled with nitrogen for 30 min. The solution of OMA in xylene was then added to the solids in the Schlenk flask, and the resulting mixture was stirred for 10 min until homogeneous. Ethyl 2-bromoisobutyrate (29.3 μL; 0.2 mmol) was added to the mixture, an initial kinetic sample was removed, and the Schlenk flask was placed in a 90 °C oil bath for 6 h. Aliquots were removed after 120, 270, and 360 min (6 h). The mixture was then dissolved in 15 mL of THF and precipitated into 300 mL of MeOH. The polymer obtained (white powder) was washed with a large quantity of acetone (400 mL) to remove unreacted monomer.

Synthesis of Monofunctional ptBMA Macroinitiator. CuBr$_2$ (4.5 mg, 0.02 mmol) and dNbpy (327 mg, 0.8 mmol) were added to a 25 mL Schlenk flask; the flask was then fitted with a rubber septum and evacuated (1−5 mmHg) and backfilled with nitrogen (three cycles). Deoxygenated tBMA (5.69 g, 0.04 mol) and *o*-xylene (6.5 mL, 50 vol %) were then added, and the reaction mixture was degassed by three freeze−pump−thaw cycles. After stirring for 1 h at room temperature, CuBr (57.4 mg, 0.4 mmol) was added, and the flask was placed in a thermostated oil bath at 60 °C. After 3 min, ethyl 2-bromoisobutyrate (58.7 μL; 0.4 mmol) was injected, and an initial kinetic sample was taken. During the polymerization, samples were removed to analyze conversion by GC using *o*-xylene as the internal standard and analyze molecular weight by SEC. After 2 h, the polymerization was stopped at 58% conversion by cooling to room temperature and opening the flask to air. The mixture was then dissolved in 20 mL of THF, passed through neutral alumina column, and precipitated into 300 mL of a MeOH/H$_2$O (4:1 volume ratio) solution. The obtained polymer was then filtered off through a Buchner funnel and fully dried under vacuum.

Synthesis of Difunctional pnBA Macroinitiator. Deoxygenated *n*-BA (12.8 g, 0.1 mol), PMDETA (41.8 μL, 0.2 mmol), and anisole (3.0 mL, 20 vol %) were added to a 25 mL Schlenk flask, and the reaction mixture was degassed by three freeze−pump−thaw cycles. After stirring for 1 h at room temperature, CuBr (28.7 mg, 0.2 mmol) was added, and the flask was placed in a thermostated oil bath at 70 °C. After 3 min, DMDBH (43.5 μL; 0.2 mmol) was injected via a microliter syringe, and an initial kinetic sample was taken. During the polymerization, samples were removed to analyze conversion by GC using anisole as the internal standard and analyze molecular weight by SEC. After 18 h, the polymerization was stopped at 31% conversion by cooling to room temperature and opening the flask to air. The mixture was then dissolved in 50 mL of THF and passed through a neutral alumina column. The solvent and the residual monomer were then removed by vacuum distillation (1−5 mmHg) at room temperature.

Synthesis of Difunctional ptBA Macroinitiator. Deoxygenated tBA (6.4 g, 0.05 mol), PMDETA (20.9 μL, 0.1 mmol), and anisole (1.5 mL, 20 vol %) were added to a 25 mL Schlenk flask, and the reaction mixture was degassed by three freeze−pump−thaw cycles. After stirring for 1 h at room temperature, CuBr (14.3 mg, 0.1 mmol) was added, and the flask was placed in a thermostated oil bath at 65 °C. After 3 min, DMDBH (21.7 μL; 0.1 mmol) was injected, and an initial kinetic sample was taken. During the polymerization, samples were removed to analyze conversion by GC using anisole as the internal standard and analyze molecular weight by SEC. After 44 h, the polymerization was stopped at 32% conversion by cooling to room temperature and opening the flask to air. The mixture was then dissolved in 25 mL of THF, passed through neutral alumina column, and precipitated into 300 mL of a MeOH/H$_2$O (4:1 volume ratio) solution.

Synthesis of pOA-*b*-ptBA Block Copolymer. Cu(I)Br (14.3 mg; 0.1 mmol), dNbpy (81.7 mg; 0.2 mmol), Cu(II)Br$_2$ (1.1 mg; 0.005 mmol), and *p*-methoxybenzene (32 mg) were placed in a 10 mL dried Schlenk flask that was evacuated (1−5 mmHg) and backfilled with nitrogen three times. tBA was bubbled with nitrogen for 45 min, and 0.73 mL (5 mmol) of this monomer was added to the solids in the Schlenk flask. The pOA macroinitiator (0.91 g; 0.05 mmol) was dissolved into

1.5 mL of xylene, deoxygenated by a bubbling of nitrogen for 15 min, and added to the previous mixture. The resulting mixture was stirred for 10 min until homogeneous, an initial kinetic sample was removed, and the flask was placed in a 100 °C oil bath for 20 h. Aliquots were removed after 1, 2, 8, and 20 h. The mixture was then dissolved in 5 mL of THF and precipitated into 200 mL of MeOH.

Synthesis of ptBA-*b*-pOA Block Copolymer. Cu(I)Br (28.7 mg; 0.2 mmol), dNbpy (163.5 mg; 0.4 mmol), and Cu(II)-Br_2 (2.2 mg; 0.01 mmol) were placed in a 25 mL dried Schlenk flask that was evacuated (1−5 mmHg) and backfilled with nitrogen (three cycles). The ptBA macroinitiator (0.95 g; 0.1 mmol) and OA (3.246 g; 10 mmol) were dissolved into 4 mL of xylene, bubbled with nitrogen for 20 min, and added to the solids in the Schlenk flask. The resulting mixture was stirred for 10 min until homogeneous, an initial kinetic sample was removed, and the flask was placed in a 100 °C oil bath for 20 h. Aliquots were removed after 2, 6, 10, and 20 h. The mixture was then dissolved in 15 mL of THF and precipitated into 300 mL of MeOH.

Synthesis of pOMA-*b*-ptBMA Block Copolymer. Cu(I)-Cl (5 mg; 0.05 mmol), dNbpy (40.9 mg; 0.1 mmol), Cu(II)Cl_2 (0.67 mg; 0.005 mmol), and *p*-methoxybenzene (5 wt %/M; 35.5 mg) were placed in a 10 mL dried Schlenk flask that was evacuated (1−5 mmHg) and backfilled with nitrogen (three cycles). tBMA was bubbled with nitrogen for 45 min, and 0.81 mL (5 mmol) of this monomer was added to the solids in the Schlenk flask. The pOMA macroinitiator (1.48 g; 0.05 mmol) was dissolved into 2.5 mL of xylene, bubbled with nitrogen for 15 min, and added to the previous mixture. The resulting mixture was stirred for 10 min until homogeneous, an initial kinetic sample was removed, and the flask was placed in a 100 °C oil bath for 48 h. Aliquots were removed after 1, 2, 8, 20, 30, and 48 h. The mixture was then dissolved in 5 mL of THF and precipitated into 200 mL of MeOH.

Synthesis of ptBMA-*b*-pOMA Block Copolymer. Cu(I)-Cl (19.8 mg; 0.2 mmol), dNbpy (163.5 mg; 0.4 mmol), and Cu(II)Cl_2 (2.7 mg; 0.02 mmol) were placed in a 25 mL dried Schlenk flask that was evacuated (1−5 mmHg) and backfilled with nitrogen (three cycles). The ptBMA macroinitiator (1.04 g; 0.1 mmol) and OMA (3.385 g; 10 mmol) were dissolved into 4 mL of xylene, bubbled with nitrogen for 20 min, and added to the solids in the Schlenk flask. The resulting mixture was stirred for 10 min until homogeneous, an initial kinetic sample was removed, and the flask was placed in a 100 °C oil bath for 8 h. Aliquots were removed after 2, 4, 6, and 8 h. The mixture was then dissolved in 15 mL of THF and precipitated into 300 mL of MeOH.

Synthesis of p(OA-*r*-tBA) Random Copolymer. Cu(I)-Br (57.4 mg; 0.4 mmol), dNbpy (327 mg; 0.8 mmol), Cu(II)Br_2 (4.4 mg; 0.02 mmol), and *p*-methoxybenzene (128 mg) were placed in a 25 mL dried Schlenk flask that was evacuated (1−5 mmHg) and backfilled with nitrogen (three cycles). tBA (2.93 mL; 20 mmol) and OA (6.49 g; 20 mmol) were dissolved into 4 mL of xylene, and the resulting solution was bubbled with nitrogen for 20 min. The solution of tBA and OA in xylene was then added to the solids in the Schlenk flask, and the resulting mixture was stirred for 10 min until homogeneous. Methyl 2-bromopropionate (44.6 μL; 0.4 mmol) was added to the mixture, an initial kinetic sample was removed, and the Schlenk flask was placed in a 100 °C oil bath for 10 h. Aliquots were removed after 2, 6, and 10 h. The mixture was then dissolved in 15 mL of THF and precipitated into 300 mL of MeOH.

Synthesis of p(OMA-*r*-tBMA) Random Copolymer. Cu(I)Cl (39.6 mg; 0.4 mmol), dNbpy (327 mg; 0.8 mmol), Cu(II)-Cl_2 (5.4 mg; 0.04 mmol), and *p*-methoxybenzene (5 wt %/tBMA; 142 mg) were placed in a 25 mL dried Schlenk flask that was evacuated (1−5 mmHg) and backfilled with nitrogen (three cycles). tBMA (3.25 mL; 20 mmol) and OMA (6.77 g; 20 mmol) were dissolved into 8 mL of xylene, and the resulting solution was bubbled with nitrogen for 20 min. The solution of BMA and OMA in xylene was then added to the solids in the Schlenk flask, and the resulting mixture was stirred for 10 min until homogeneous. Ethyl 2-bromoisobutyrate (58.7 μL; 0.4 mmol) was added to the mixture, an initial kinetic sample was removed, and the Schlenk flask was placed in a 100 °C oil bath for 5 h. Aliquots were removed after 2, 4, and 5 h. The mixture was then dissolved in 15 mL of THF and precipitated into 300 mL of MeOH.

Synthesis of p(OA-*grad*-tBMA). Cu(I)Br (57.4 mg; 0.4 mmol), dNbpy (327 mg; 0.8 mmol), Cu(II)Br_2 (4.4 mg; 0.02 mmol), and *p*-methoxybenzene (142 mg) were placed in a 25 mL dried Schlenk flask that was evacuated (1−5 mmHg) and backfilled with nitrogen (three cycles). tBMA (3.25 mL; 20 mmol) and OA (6.49 g; 20 mmol) were dissolved into 4 mL of xylene, and the resulting solution was bubbled with nitrogen for 15 min. The solution of BMA and OA in xylene was then added to the solids in the Schlenk flask, and the resulting mixture was stirred for 10 min until homogeneous. Ethyl 2-bromoisobutyrate (58.7 μL; 0.4 mmol) was added to the mixture, an initial kinetic sample was removed, and the Schlenk flask was placed in a 100 °C oil bath for 20 h. Aliquots were removed after 30 min, 1, 2, 3, 4, 6, 8, 10, and 20 h. The mixture was then dissolved in 15 mL of THF and precipitated into 300 mL of MeOH.

Synthesis of p(OMA-*grad*-tBA). Cu(I)Br (57.4 mg; 0.4 mmol), dNbpy (327 mg; 0.8 mmol), Cu(II)Br_2 (4.4 mg; 0.02 mmol), and *p*-methoxybenzene (128 mg) were placed in a 25 mL dried Schlenk flask that was evacuated (1−5 mmHg) and backfilled with nitrogen (three cycles). tBA (2.93 mL; 20 mmol) and OMA (6.77 g; 20 mmol) were dissolved into 8 mL of xylene, and the resulting solution was bubbled with nitrogen for 30 min. The solution of BA and OMA in xylene was then added to the solids in the Schlenk flask, and the resulting mixture was stirred for 15 min until homogeneous. Ethyl 2-bromoisobutyrate (58.7 μL; 0.4 mmol) was added to the mixture, an initial kinetic sample was removed, and the Schlenk flask was placed in a 100 °C oil bath for 20 h. Aliquots were removed after 15 min, 30 min, 1, 2, 3, 4, 6, 8, 10, and 20 h. The mixture was then dissolved in 15 mL of THF and precipitated into 300 mL of MeOH.

Results and Discussion

Homopolymerization of Octadecyl and *tert*-Butyl (Meth)acrylates. Conditions similar to those used in the ATRP of dodecyl acrylate (DA) were applied to the polymerization of octadecyl (meth)acrylates (Scheme S-1, Supporting Information).[32,37] The hydrophobic nature of long alkyl (meth)acrylates required the use of a nonpolar solvent media (*o*-xylene) and a substituted bipyridine ligand (4,4′-di(5-nonyl)-2,2′-bipyridine, dNbpy) to attain homogeneity of the reaction mixture. Of particular importance was the addition of Cu(II) complexes at the beginning of the ATRP reaction, which suppressed the formation of high molar mass polymer. The addition of deactivator at the beginning of the reaction may be necessary due to the low values of termination rate constants in polymerization of these monomers and weak spontaneous persistent radical effect.[38,39] The heterogeneous catalytic system lead to poor control over ATRP of OMA.[40,41]

In the homopolymerization of OA by ATRP, a catalyst system of copper(I) bromide (Cu(I)Br), copper(II) bromide (Cu(II)Br_2), and dNbpy in solution of *o*-xylene (entry 1, Table 1) was used with methyl 2-bromopropionate (MBP) as an initiator. The ATRP of OA was stopped after 30 h, and monomer conversion was determined to be 45% (^{1}H NMR). Similar conditions were also employed in the ATRP of OMA (entry 2, Table 1), except that a copper(I) chloride/copper(II) chloride catalyst was used to improve control of the polymerization by the halogen-exchange technique.[42] Additionally, ethyl 2-bromoisobutyrate (EBiB) was used as an initiator for OMA. As expected, OMA polymerization proceeded at a significantly faster rate than for OA,

Table 1. Experimental Conditions for the Synthesis of Homopolymers from *tert*-Butyl and Octadecyl (Meth)acrylates Using ATRP

entry	monomer (M)	initiator (I)	conditions [M]:[I]:[Cu(I)]:[Cu(II)]:[dNbpy] temp (°C) reaction time (h) ratio of monomer/*o*-xylene	conversion (%)	$M_{n,SEC}$	M_w/M_n
1[a]	OA	MBP	100:1:1:0.05:2.10, 90 °C, 30 h 1:1 by vol monomer/*o*-xylene	45	11 680	1.20
2[b]	OMA	EBiB	100:1:1:0.05:2.10, 90 °C, 6 h 1:1 by vol monomer/*o*-xylene	87	26 400	1.14
3[a]	tBMA	EBiB	100:1:1:0.05: 2, 60 °C, 2 h 1:1 by vol monomer/*o*-xylene	57.9	9 250	1.17
4[a]	tBA	MBP	100:1:1:0:2, 90 °C, 36 h 1:1 by vol. monomer/*o*-xylene	57.3	8 300	1.14
5[a]	nBA	DMDBH	500:1:1:0:1, 70 °C, 18 h 5:1 by vol monomer/anisole	31	34 980	1.16
6[c]	tBA	DMDBH	500:1:1:0:1, 65 °C, 44 h 1:1 by vol monomer/anisole	32	42 380	1.12

[a] $Cu(I)Br/Cu(II)Br_2$/dNbpy used in the polymerization. [b] $Cu(I)Cl/Cu(II)Cl_2$/dNbpy used in the polymerization. [c] Cu(I)Br/PMDETA used in the polymerization.

Table 2. Experimental Conditions for the Synthesis of Polyacrylate or Polymethacrylate AB Diblock and ABA Triblock Copolymers Using *tert*-Butyl or Octadecyl Containing Macroinitiators and Monomers

entry	monomer (M)	macro-initiator (I)	conditions [M]:[I]:[Cu(I)]:[Cu(II)]:[dNbpy] temp (°C) reaction time (h) ratio of monomer/*o*-xylene	conversion (%)	$M_{n,SEC}$ (g/mol)	M_w/M_n
7[a]	tBA	pOA[c]	100:1:2:0.1:4.20, 100 °C, 20 h 1:2 by vol monomer/*o*-xylene	69	14 710	1.26
8[a]	tBMA	pOMA[c]	100:1:1:0.1:2.20, 100 °C, 48 h 1:1 by vol monomer/*o*-xylene	61	32 400	1.14
9[a]	OA	ptBA[c]	100:1:2:0.1:4.20, 100 °C, 20 h 1:1 by vol monomer/*o*-xylene	42	17 580	1.23
10[a]	OMA	ptBMA[c]	100:1:1:0.1:2.2, 85 °C, 16.5 h 1:4 by vol monomer/*o*-xylene	86	52 000	1.20
11[a]	OMA	ptBA[c]	100:1:1:0.1:2.2, 90 °C, 32 h 1:3 by vol monomer/*o*-xylene	47	28 750	1.20
12[d]	OMA	pnBA[d]	300:1:1:0.05:2.1, 90 °C, 31.5 h 1:2 by vol monomer/*o*-xylene	45	74 400	1.16
13[d]	OMA	ptBA[d]	440:1:1:0.1:2.2, 90 °C, 27.5 h 1:1.5 by vol monomer/*o*-xylene	37	75 900	1.14

[a] $Cu(I)Br/Cu(II)Br_2$/dNbpy used in the polymerization. [b] $Cu(I)Cl/Cu(II)Cl_2$/dNbpy used in the polymerization. [c] Monofunctional macro-inititator. [d] Difunctional macroinitiator.

reaching a monomer conversion of 87% (^{1}H NMR) after 6 h. In both cases, homopolymers of low polydispersity were obtained ($M_{n,pOA} = 11\,680$, $M_w/M_n = 1.20$; $M_{n,pOMA} = 26\,400$, $M_w/M_n = 1.14$). The ATRP of *tert*-butyl methacrylate (BMA) (entry 3, Table 1) and *tert*-butyl acrylate (tBA) (entry 4, Table 1) was also conducted using the similar conditions as for OMA and OA, respectively, to prepare monofunctional macroinitiators as precursors for block copolymers. In both cases, well-defined polymers were prepared ($M_{n,ptBMA} = 9250$, $M_w/M_n = 1.17$; $M_{n,ptBA} = 8300$, $M_w/M_n = 1.14$). Difunctional macroinitiators from pnBA (entry 5, Table 1) and ptBA (entry 6, Table 1) were also synthesized using a dimethyl 2,6-dibromoheptanedioate (DMDBH) difunctional initiator and a Cu(I)Br/*N,N,N′,N″,N‴*-pentamethyldiethylenetriamine (PMDETA) catalytic system. SEC analysis indicated good control for ATRP using both difunctional macroinitiators ($M_{n,pnBA} = 34\,980$, $M_w/M_n = 1.16$; $M_{n,ptBA} = 42\,380$, $M_w/M_n = 1.12$).

Synthesis of AB Diblock Copolymers. AB diblock copolymers were prepared by chain extension of pOMA, pOA, ptBMA, or ptBA macroinitiators with the appropriate octadecyl or *tert*-butyl containing (meth)acrylate monomers. The chain extension from a pOA macroinitiator ($M_n = 11\,680$, $M_w/M_n = 1.20$; entry 1, Table 1) using tBA was successful using the appropriate conditions (entry 7, Table 2) and proceeded to a monomer conversion of 67%. SEC revealed a shift in molar mass ($M_n = 14\,760$; $M_w/M_n = 1.26$), indicating that the presence of the long octadecyl group did not affect accessibility of the halogen chain end to the copper catalyst (Scheme S-2, Figure S-1, Supporting Information). Using a similar approach, a pOMA macroinitiator ($M_{n,SEC} = 26\,400$; $M_w/M_n = 1.14$, entry 2, Table 1) was chain extended in the presence of tBMA, reaching a monomer conversion of 61% in 48 h. SEC confirmed the formation of a higher molar mass product ($M_{n,SEC,pOMA\text{-}b\text{-}ptBMA} = 32\,370$; $M_w/M_n = 1.14$, entry 8, Table 2).

The preparation of AB diblock copolymers was also conducted by changing the sequence of blocking, by chain extending ptBA and ptBMA macroinitiators with OA and OMA, respectively. ATRP of OA from the ptBA macroinitiator ($M_n = 7820$; $M_w/M_n = 1.11$; entry 4, Table 1) reached a monomer conversion of 61%, and SEC indicated a shift toward higher molecular weight ($M_{n,SEC,ptBA\text{-}b\text{-}pOA} = 17\,580$, $M_w/M_n = 1.23$; entry 9, Table 2). The chain extension from a ptBMA macroinitiator ($M_n = 9250$; $M_w/M_n = 1.17$) using OMA was carried in a dilute *o*-xylene solution at 85 °C, catalyzed using a $Cu(I)Br(dNbpy)_2$ complex in conjunction with 5 mol % (relative to Cu(I)Br) of a $CuBr_2/(dNbpy)_2$ complex (entry 10, Table 2). SEC of macroinitiator and product after chain extension revealed the successful preparation of the ptBMA-*b*-pOMA copolymer, by a shift to higher molar mass relative to the macroinitiator (Scheme S-2,

Table 3. Experimental Conditions for the Synthesis of Statistical and Gradient Copolymers by the Copolymerization of Methacrylate/Acrylate Monomer Pairs

entry	monomer (M_1/M_2) and molar feed ratio	initiator (I)	conditions [M]:[I]:[Cu(I)]:[Cu(II)]:[dNbpy] temp (°C) reaction time (h) ratio of monomer/*o*-xylene	conversion (M_1 %) (M_2 %)	$M_{n,SEC}$	M_w/M_n
14[a]	OA/BA 1:1 by mole	EBiB	100:1:1:0.05:2.1, 100 °C, 10 h 2:1 by vol monomer/*o*-xylene	62 (BA) 68 (OA)	13 680	1.13
15[b]	OMA/BMA 1:1 by mole	EBiB	100:1:1:0.1:2.2, 100 °C, 5 h 1:1 by vol monomer/*o*-xylene	87 (OMA) 91 (BMA)	24 250	1.14
16[a]	OA/BMA 1:1 by mole	EBiB	100:1:1:0.05:2.1, 100 °C, 20 h 2:1 by vol monomer/*o*-xylene	81 (OA) 95 (BMA)	21 900	1.20
17[a]	BA/OMA 1:1 by mole	EBiB	100:1:1:0.05:2.1, 100 °C, 8 h 1:1 by vol monomer/*o*-xylene	89 (BA) 95 (OMA)	21 790	1.25

[a] Cu(I)Br/Cu(II)Br_2/dNbpy used in the polymerization. [b] Cu(I)Cl/Cu(II)Cl_2/dNbpy used in the polymerization.

Figure S-2, Supporting Information). This result further confirmed that the presence of the long octadecyl group did not affect accessibility of the halogen chain end to the copper catalyst.

AB diblock copolymers containing both polyacrylate and polymethacrylate segments were also prepared. In this approach, a ptBA macroinitiator (M_n = 8300; M_w/M_n = 1.14) was synthesized and then chain extended with OMA using ATRP (entry 11, Table 2). The halogen-exchange technique was employed in chain extension of OMA from Br-terminated ptBA macroinitiator using a CuCl/CuCl_2/dNbpy catalyst system; the technique is necessary when methacrylate monomers are employed in ATRP from polyacrylate initiators.[42-44] The formation of ptBA-*b*-pOMA block copolymer (M_n = 28 750; M_w/M_n = 1.20) was confirmed from by SEC, where the traces of block copolymer shifted toward higher molar mass without residual ptBA macroinitiator (Scheme S-2, Figure S-3, Supporting Information).

Synthesis of ABA Triblock Copolymers. ABA triblock copolymers composed of pOMA-*b*-pnBA-*b*-pOMA and pOMA-*b*-ptBA-*b*-pOMA triblock copolymers were designed and prepared by chain extensions from difunctional pnBA (M_n = 34 980, M_w/M_n = 1.16; entry 5, Table 1) and ptBA macroinitiators (M_n = 42 380, M_w/M_n = 1.12; entry 6, Table 2). The former materials may be potentially used as thermoplastic elastomers because of the microphase separation and additional crystallization of pOMA segments. The "halogen-exchange" technique was used as previously discussed, and successful extension of difunctional macroinitiators was observed in SEC traces (Scheme S-3, Figure S-4, Supporting Information). In pOMA-*b*-pnBA-*b*-pOMA triblock copolymer synthesis, the OMA monomer conversion reached 45% after 31.5 h at 90 °C, and the final triblock copolymer possessed low polydispersity (M_n = 74 360, M_w/M_n = 1.16) (entry 12, Table 2). A pOMA-*b*-ptBA-*b*-pOMA triblock copolymer (M_n = 75 870, M_w/M_n = 1.14; entry 13, Table 2, Figure 1) and a copolymer possessing a glassy polyacrylate middle segment were prepared by chain extension of ptBA using OMA. An OMA conversion of 37% was obtained after 27.5 h. In the polymerization of OMA from both pnBA and ptBA macroinitiators, high initiation efficiencies were observed.

Random Copolymers of Polyacrylates and Polymethacrylates. Statistical polyacrylate copolymers were prepared by the copolymerization of BA and OA, while BMA and OMA were also copolymerized to afford the corresponding polymethacrylate copolymers (Scheme S-4, Supporting Information). For the preparation of random copolymers, BA/OA and BMA/OMA monomers were chosen, as the reactivity ratios of the respective pairs were assumed to be comparable.

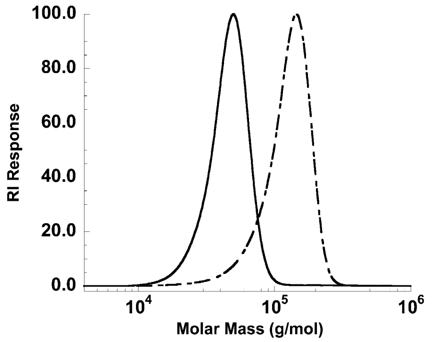


Figure 1. SEC of ptBA difunctional macroinitiator (solid trace, $M_{n,SEC}$ = 42 380; M_w/M_n = 1.12) and pOMA-*b*-ptBA-*b*-pOMA block copolymer after chain extension reaction (dashed trace, $M_{n,SEC}$ = 75 900; M_w/M_n = 1.14). Conditions for chain extension of OMA from ptBA noted in entry 13, Table 2.

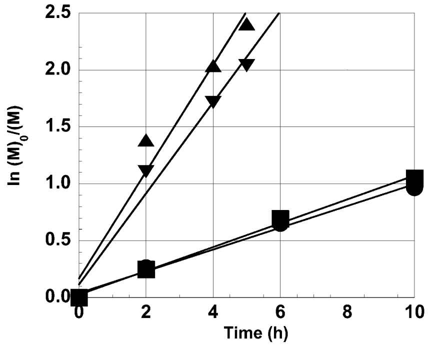


Figure 2. First-order plot of monomer consumption vs time for the copolymerization of the following monomer pairs: tBA (squares)/OA (circles) and tBMA (triangles)/OMA (inverted triangles). Conditions for the copolymerization of tBA and OA noted in entry 14, Table 3 and copolymerization of tBMA and OMA noted in entry 15, Table 3.

In the one-pot copolymerization, a 1:1 molar ratio of BA and OA were used in the feed and a MBP initiator was used along with a Cu(I)Br/Cu(II)Br_2/dNbpy catalyst system at 100 °C (entry 14, Table 3). As shown in the semilogarithmic plot of monomer consumption vs time, polymerization of BA and OA proceeded at similar rates to moderate conversion after 10 h (p_{BA} = 0.68, p_{OA} = 0.62; Figure 2). SEC of kinetic samples taken at different times in the polymerization revealed a progressive increase of molar mass with conversion, yielding well-defined copolymers of low polydispersity ($M_{n,SEC}$ = 14 420, M_w/M_n = 1.13; Figure 3).

Copolymerization of BMA and OMA was also conducted at a 1:1 molar ratio, yielding well-defined

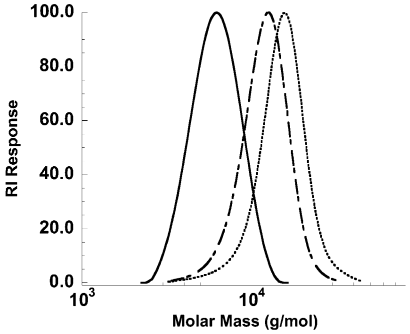
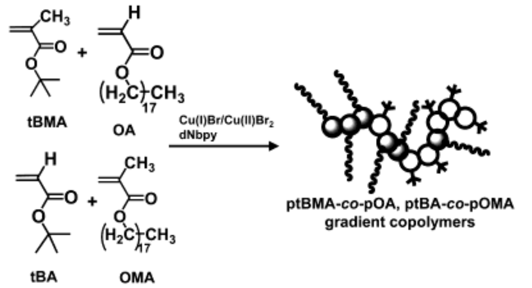


Figure 3. SEC of kinetic samples from the copolymerization of tBA and OA. Copolymer products at the following monomer conversions: $OA_{conversion} = 23\%$, $tBA_{conversion} = 22\%$ (solid trace), $OA_{conversion} = 48\%$, $tBA_{conversion} = 50\%$ (dashed trace), $OA_{conversion} = 62\%$, $tBA_{conversion} = 65\%$ (dotted trace, $M_n = 13\,680$; $M_w/M_n = 1.13$). Conditions for the copolymerization are noted in entry 14, Table 3.

Scheme 1. Synthesis of Gradient Copolymers by the ATRP of tBA/OMA or tBMA/OA Monomers Pairs Using ATRP[a]



[a] Because of higher reactivity ratios of methacrylate vs acrylate monomers, OMA and tBMA are consumed at a faster rate in their respective copolymerizations. The resulting copolymer contains a gradual tapering of composition along the copolymer backbone, resembling a block copolymer.

statistical copolymers. In this reaction, EBiB was used as the initiator, while a Cu(I)Cl/Cu(II)Cl$_2$/dNbpy catalyst was added to mediate the copolymerization at 100 °C (entry 15, Table 3). Consumption of BMA and OMA occurred with similar rates to high conversion in 5 h ($p_{BMA} = 0.91$, $p_{OMA} = 0.87$), as shown in the semilogarithmic plot (Figure 2). SEC of the kinetic samples taken at various conversions also confirmed that molar mass progressively increased, forming well-defined copolymers ($M_{n,SEC} = 24\,250$, $M_w/M_n = 1.14$; entry 15, Table 3).

Gradient Copolymers from Methacrylate/Acrylate Monomer Pairs. The synthesis of gradient copolymers containing *tert*-butyl and octadecyl side chains groups was conducted by the ATRP of methacrylate and acrylate monomers (Scheme 1). Previously, the ATRP copolymerization of methacrylates and acrylates was demonstrated to yield spontaneous gradient copolymers possessing a continuous tapering of composition along the copolymer chain.[44] In the same manner, gradient copolymers were targeted by the ATRP of the following monomer pairs: tBMA/OA or tBA/OMA.

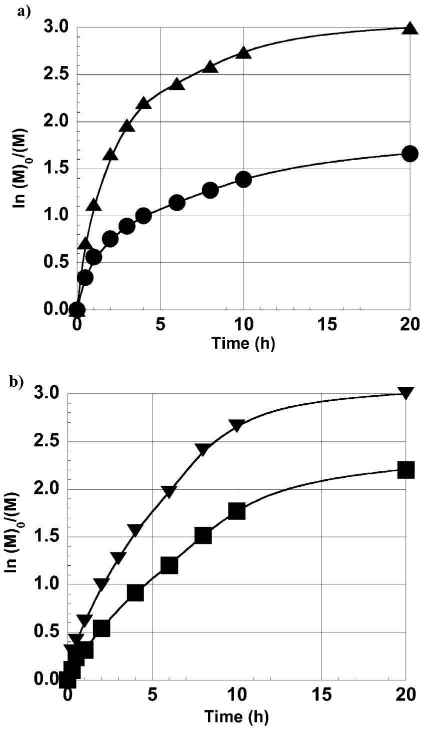


Figure 4. First-order plot of monomer consumption vs time for the copolymerization of the following monomer pairs: (a) tBMA (triangles)/OA (circles) and (b) tBA (squares)/OMA (inverted triangles). Conditions for the copolymerization of tBMA and OA noted in entry 16, Table 3 and copolymerization of tBA and OMA noted in entry 17, Table 3.

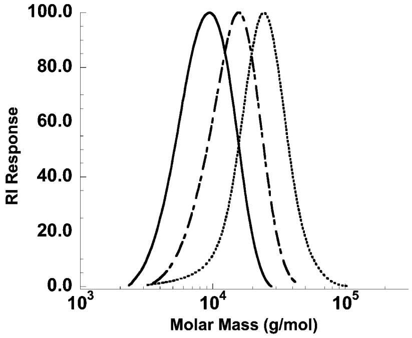
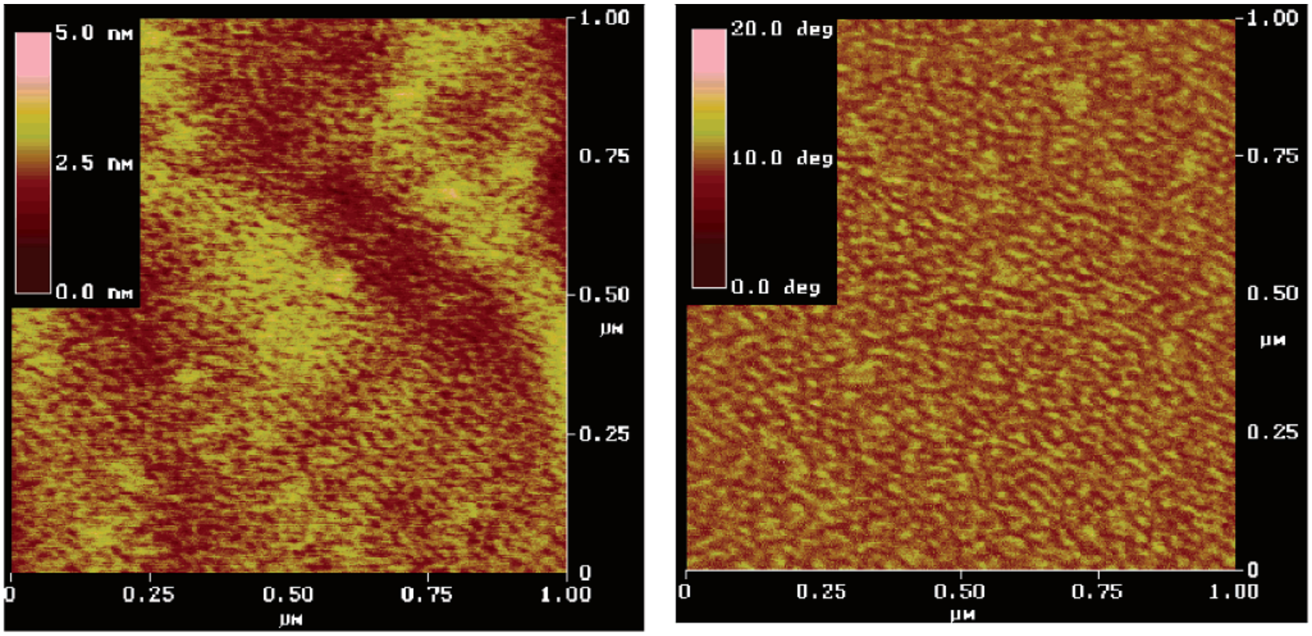


Figure 5. SEC of kinetic samples from the copolymerization of tBA and OMA. Copolymer products at the following monomer conversions: $OMA_{conversion} = 2\%$, $tBA_{conversion} = 10\%$ (solid trace), $OMA_{conversion} = 46\%$, $tBA_{conversion} = 27\%$ (dashed trace), $OMA_{conversion} = 95\%$, $tBA_{conversion} = 89\%$ (dotted trace, $M_n = 21\,900$; $M_w/M_n = 1.20$). Conditions for the copolymerization are noted in entry 16, Table 3.

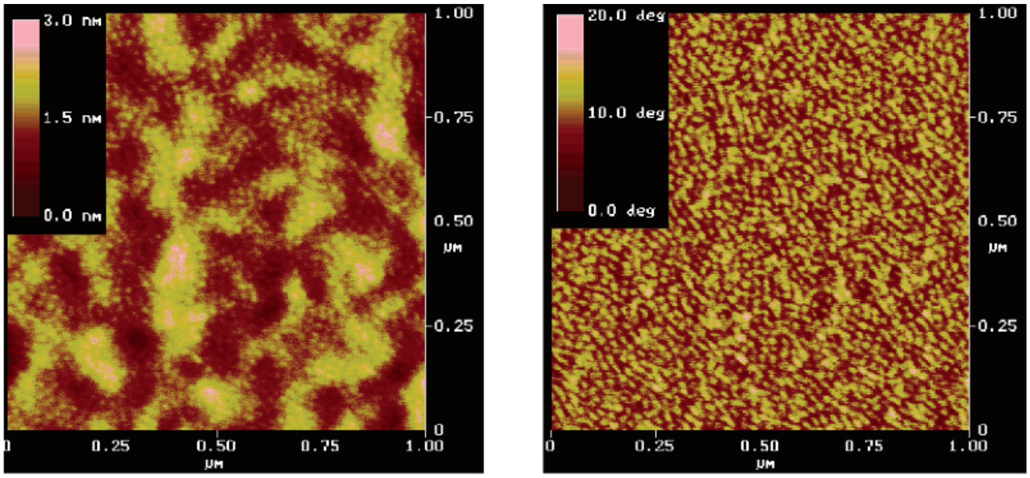
The ATRP of tBMA and OA was conducted using similar conditions as for the synthesis of random copolymers, where a 1:1 molar feed of monomers was copolymerized using a Cu(I)Br/Cu(II)Br$_2$/dNbpy catalyst in the presence of a EBiB initiator at 100 °C (entry 16, Table 3). Copolymerization kinetics revealed BMA was consumed at a faster rate than OA and after 20 h the reaction reached high conversion of tBMA (95%) and OA (81%) (Figure 4a), yielding a gradient copolymer ($M_{n,SEC} = 21\,900$, $M_w/M_n = 1.21$).

The ATRP of tBA and OMA was also conducted using the same conditions as for the synthesis of the tBMA/OA gradient copolymer (entry 17, Table 3). As for the previous system, the copolymerization kinetics also revealed that the methacrylate comonomer (OMA) reacted at a faster rate than the acrylate comonomer (tBA), also reaching high conversions ($p_{OMA} = 0.95$, $p_{BA} = 0.89$; Figure 4b). SEC of kinetic samples measured at various compositions demonstrated that molar mass distribution increased with conversion, resulting in a well-defined copolymer of precise composition and low polydispersity ($M_{n,SEC} = 19\,700$, $M_w/M_n = 1.25$; Figure 5).



a) **b)**

Figure 6. Tapping mode AFM height (a) and phase (b) images of ptBMA-*b*-pOMA (entry 10, Table 2).



a) **b)**

Figure 7. Tapping mode AFM height (a) and phase (b) images of ptBA-*b*-pOMA (entry 11, Table 2).

Morphology of Ultrathin Films. Tapping mode atomic force microscopy (AFM) studies provided evidence for nanoscale phase separation in studied materials. AFM observations were carried out on ultrathin films which were prepared by spin-coating on freshly cleaved mica from 1 to 20 mg/mL solutions of copolymers in chloroform followed by annealing at 150 °C and slow cooling to room temperature.

Surfaces of AB diblock copolymers of ptBMA-*b*-pOMA (entry 10, Table 2) and of ptBA-*b*-pOMA (entry 11, Table 2) containing a larger weight fraction of pOMA revealed the presence of uniformly spaced ~20 nm round domains dispersed in a continuous matrix (Figures 6 and 7). In the case of ptBMA-*b*-pOMA the features corresponding to the dispersed phase appeared as depressions in height images, whereas in the case of ptBA-*b*-pOMA the height contrast was inverted.

In contrast, the surface of an ABA triblock copolymer composed of pOMA-*b*-ptBA-*b*-pOMA (entry 13, Table 2) revealed the presence of highly regular, meandering features, reminiscent of lamellar morphologies reported elsewhere (Figure 8).

It is clear that the visualization of different phases in presented images was facilitated by the differences in their mechanical compliance and/or mechanical lossiness. However, unlike in the case of widely described in the literature systems with strong contrast between mechanical properties of phases (e.g., rigid domains dispersed in rubbery matrices), the origin of contrast in materials being the subject of this study could not be inferred immediately from their composition. Thus, the AFM images are used here solely to indicate the presence of nanoscale phase separation. The detailed mechanism of contrast and identification of phases are the subject of a

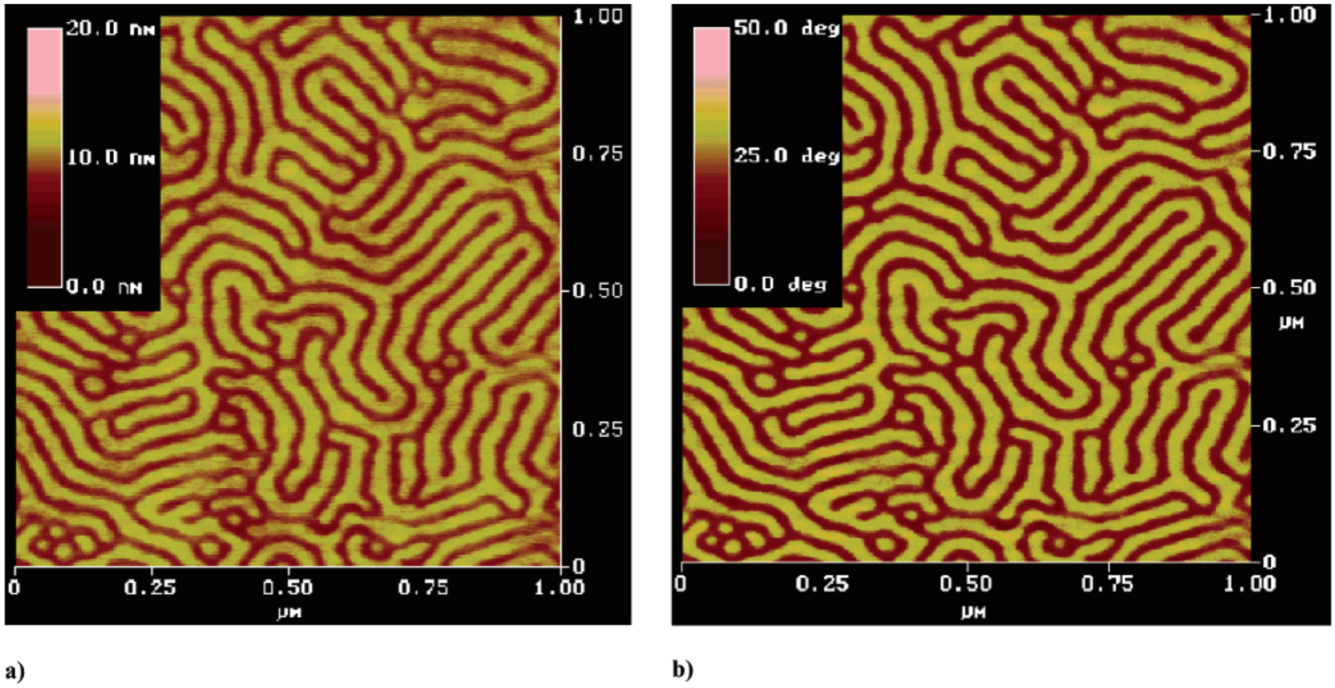


Figure 8. Tapping mode AFM height (a) and phase (b) images of pOMA-*b*-ptBA-*b*-pOMA (entry 13, Table 2).

separate study, the results of which will be reported elsewhere.

Conclusion

Well-defined homopolymers and random, block, and gradient copolymers from *tert*-butyl (meth)acrylate and octadecyl (meth)acrylate monomers were prepared using ATRP. Random copolymers were synthesized by the one-pot copolymerization of either *tert*-butyl acrylate/octadecyl acrylate or *tert*-butyl methacrylate/octadecyl methacrylate monomer pairs. Additionally, gradient copolymers were prepared by the direct copolymerization of either *tert*-butyl acrylate/octadecyl methacrylate or *tert*-butyl methacrylate/octadecyl acrylate monomers pairs. Using this approach, AB and ABA triblock copolymers containing octadecyl groups were also prepared with control of molar mass and composition. The sequence of blocking was varied using either poly(*tert*-butyl (meth)acrylate) or poly(octadecyl (meth)acrylate) macroinitiators, and the halogen-exchange technique allowed preparation of well-defined polyacrylate−polymethacrylate block copolymers. Furthermore, uniform phase-separated structures were formed in ultrathin films cast from AB diblock or ABA triblock copolymers, as determined from AFM.

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Supporting Information Available: Synthetic schemes and SEC chromatograms for the synthesis of octadecyl-containing homopolymers and block copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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