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Preparation of Segmented Copolymers in the Presence of an Immobilized/Soluble Hybrid ATRP Catalyst System

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ABSTRACT: A hybrid catalyst system (CuBr/PS8-dMbpy)/(CuBr$_2$/Me$_6$TREN) for atom transfer radical polymerization (ATRP) was successfully used for preparation of polymers with complex polymeric architectures including star, graft, and bottle-brush copolymers. No significant differences between hybrid and CuBr/dNbpy homogeneous catalyst system were observed in the synthesis of 3-arm star poly(methyl acrylate) and poly(methyl methacrylate) graft copolymer with poly(lactic acid)/poly(dimethylsiloxane) mixed side chains. However, when PIB graft copolymers with styrene and methyl methacrylate were attempted by a "grafting-from" technique, a radical coupling resulted in a gel, due to a high local concentration of radicals with the hybrid catalyst system. This poor control was partially ascribed to poor solubility of the macroinitiator in the reaction medium, since the synthesis of molecular brushes was successful and the hybrid catalyst system afforded a well-defined poly(2-(2-bromopropionyloxy)ethyl methacrylate)-*graft*-poly(*n*-butyl acrylate) (pBPEM-*graft*-pnBA) from pBPEM as a macroinitiator. The polymerization in the presence of the hybrid catalyst system led to a faster reaction than that using a homogeneous catalyst system, while retaining a well-controlled reaction and affording polymers with narrow molecular weight distribution.

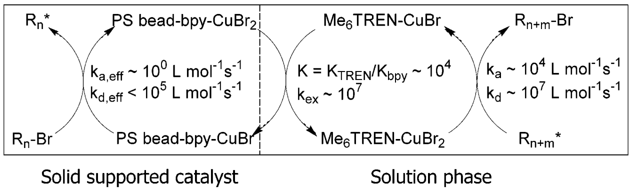
Introduction

Polymeric materials play a crucial role in many areas of nanoscale science and processes. Because of the scale involved, when targeting nanoscale polymeric structures, the precision of control over molecular weight, polydispersity, chain end functionality, and architectures becomes fundamental factors in determining the performance of the materials. Therefore, preparation of tailor-made polymeric architectures such as star, block, graft, and brush copolymers is increasingly important for specific applications. At the same time, the new processes for the preparation of the well-defined polymers should be more environmentally friendly. This paper aims to test applicability of the new hybrid catalyst for atom transfer radical polymerization (ATRP) in the synthesis of well-defined segmented copolymers.

Controlled/living radical polymerization (CRP) techniques offer one of the best opportunities to achieve this level of architectural and functional control.[1−3] Among the techniques, ATRP[4−7] has been extensively investigated since it can be applied to a wide variety of monomers and provides well-defined polymers.[6,8−11] However, the ATRP technique requires the presence of "large" amounts of transition-metal catalyst in polymerization system, which may cause process and environmental issues. Alternative approaches include catalyst immobilization, biphasic systems, or catalyst removal.[12−19] In addition, an immobilized/soluble hybrid ATRP system has been developed to overcome this limitation (Scheme 1).[20,21]

The catalyst system is composed of a CuBr/4,4′-dimethyl-2,2′-bipyridine (dMbpy) complex immobilized on a polystyrene bead (PS) working in conjunction with a small amount of low molecular weight soluble catalyst CuBr/tris(2-(dimethylamino)ethyl)amine (Me$_6$TREN) to accelerate the deactivation process of growing radicals. The hybrid catalyst system provides well-defined polymers with a significantly lower concentration of residual metal (<20 ppm) in the formed products. Since the hybrid catalyst system employs a transition-metal complex tethered to a bulky carrier, it was of interest to determine whether it is possible to retain the same level of control in the preparation of more complex polymeric architectures, including star, graft, and bottle-brush copolymers, as in homogeneous ATRP systems.

Scheme 1. Concept of Immobilized/Soluble Hybrid ATRP Catalyst System



R$_n$-Br = dormant polymer chains ; R$_n$*= active polymer chains ; k$_a$ = rate constant of activation ; k$_d$ = rate constant of deactivation ; K = k$_a$/k$_d$

Experimental Part

Chemicals. CuBr/4,4′-dimethyl-2,2′-bipyridine (dMbpy) catalysts immobilized on cross-linked polystyrene (CuBr/PS8-dMbpy, 8 μm size, 1.028 × 10^{-3} mol of Cu/g of cat.),[20] tris(2-(dimethylamino)ethyl)amine (Me$_6$TREN),[22] 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy),[23] 1,1,1-tris(4-(2-bromoisobutyryloxy)phenyl)ethane (3Br^{i}Bu),[24] poly(lactic acid) macromonomer (PLA-M, M_n = 3000 g/mol),[25] poly(dimethylsiloxane) macromonomer (PDMS-M, M_n = 3000 g/mol),[26] and 2-(trimethylsilyloxy)ethyl methacrylate (HEMA-TMS, 97.4% by GC)[27,28] were synthesized following previously reported procedures. Poly(isobutylene-*co*-*p*-methylstyrene-*co*-*p*-bromomethylstyrene) copolymer (PIB) was obtained from Exxon (EXXPRO 3035; Br content, 8 × 10^{-5} mol of Br/g of polymer; M_n = 2.0 × 10^5; M_w/M_n = 2.1). Styrene (99%, Aldrich), methyl methacry-

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late (MMA, 99%, Aldrich), methyl acrylate (MA, 99%, Aldrich), and *n*-butyl acrylate (*n*BA, 99%, Acros) were passed through a column filled with neutral alumina, dried over CaH_2, distilled under reduced pressure, and stored in a freezer under nitrogen. Tosyl chloride (TosCl) was recrystallized from hexane. Methyl 2-bromopropionate (98%, Aldrich) was distilled under vacuum prior to use. Tetrahydrofuran (THF, HPLC grade, Fisher) and toluene (certified grade, Fisher) were freshly distilled from Na/K alloy with benzophenone (99%, Aldrich) and stored under nitrogen. Benzene (99%, Aldrich) and anisole (99%, Aldrich) were distilled over potassium and calcium hydride, respectively. CuBr (99+%, Aldrich) was purified by stirring in acetic acid for 5 h followed by washing with ethanol and diethyl ether. 1-Phenylethyl bromide (PEBr, 97%, Aldrich), $CuBr_2$ (98%, Aldrich), *p*-dimethoxybenzene (DMB), and all other chemicals were used without further purification.

$CuBr_2/Me_6TREN$ Stock Solution. A stock solution of $CuBr_2/Me_6TREN$ in acetone was freshly prepared prior to use. $CuBr_2$ (5.32 mg, 2.38×10^{-5} mol) was added to a 20 mL glass vial fitted with a rubber septum. The vial was evacuated and backfilled with nitrogen three times. Me_6TREN (6.28 μL, 2.38×10^{-5} mol) and degassed acetone (10 mL) were added to the vial, and the resulting solution was placed in an ultrasonic bath for 5 min to completely dissolve the complex. A light green clear solution (Cu(II): 2.38×10^{-3} mol/L) was obtained and was used as a stock solution to add the appropriate amount of the soluble deactivator to the system.

Preparation of Poly(methyl acrylate) 3-Arm Star Polymer. CuBr/PS8-dMbpy (51.4 mg, 5.26×10^{-5} mol of Cu), 1,1,1-tris(4-(2-bromoisobutyryloxy)phenyl)ethane (3Br^{i}Bu, 39.8 mg, 5.26×10^{-5} mol), and *p*-dimethoxybenzene (DMB, 0.15 g) were added to a 25 mL Schlenk flask equipped with a stirring bar under nitrogen. Methyl acrylate (MA, 1.42 mL, 1.58×10^{-5} mol) was added to this flask, after degassing by bubbling with nitrogen for 30 min, followed by the addition of 0.22 mL of the $Me_6TREN-CuBr_2$ stock solution (5.26×10^{-7} mol of Cu). The mixture was then heated to 70 °C under stirring for 3 h. During the polymerization, kinetic samples were taken from the flask via a syringe at timed intervals. The samples were immediately diluted with THF followed by filtration through a Gelman Acrodisc 0.2 μm PTFE filter prior to analyses by gas chromatography (GC) and gel permeation chromatography (GPC). After the polymerization was complete, the reaction mixture was cooled to room temperature and diluted with THF followed by filtration through a PTFE filter, and the polymer was precipitated by addition to methanol. The resulting polymer was filtered off and dried under vacuum at 60 °C.

Preparation of pMMA Graft Copolymer with Poly(lactic acid)/Poly(dimethylsiloxane) Mixed Side Chains Using the Grafting-Through Technique. Poly(lactic acid) macromonomer (PLA-M, 1 g, 3.3×10^{-4} mol, $M_n = 3000$ g/mol), poly(dimethylsiloxane) macromonomer (PDMS-M, 1 g, 3.3×10^{-4} mol, $M_n = 3000$ g/mol), *p*-xylene (1 mL), and diphenyl ether (1 mL) were added to a dry Schlenk flask. The mixture was thoroughly purged by nitrogen and heated until the PLA-M macromonomer dissolved. For the homogeneous ATRP catalyst system, a solution of CuCl/dNbpy (1.3×10^{-4} mol of CuCl, 2.6×10^{-4} mol of dNbpy) in methyl methacrylate (1.5 g, 1.5×10^{-2} mol) was added into the Schlenk flask. For the hybrid ATRP catalyst system, a dispersion of CuBr/PS8-dMbpy (1.3×10^{-4} mol of Cu) in methyl methacrylate (1.5 g, 1.5×10^{-2} mol) was added into the Schlenk flask. In the case of the hybrid catalyst system, a solution of $CuBr_2/Me_6TREN$ (1.3×10^{-6} mol of Cu) in acetone was introduced via a degassed syringe. Finally, for both systems, a solution of ethyl 2-bromoisobutyrate (EBI) (13 mg, 6.6×10^{-5} mol) in MMA (0.5 g, 5.0×10^{-3} mol) was added. The mixture was heated to and thermostated at 90 °C. Samples were taken through a degassed syringe at timed intervals.

Preparation of Poly(isobutylene-*co*-*p*-methylstyrene-*co*-*p*-bromomethylstyrene) (PIB)-*graft*-pMMA and PIB-*graft*-polystyrene through Grafting-From Technique. A typical polymerization procedure is as follows. PIB (0.139 g, 1.11×10^{-5} mol of Br) was dissolved in chlorobenzene (6.78 mL) in a 25 mL Schlenk flask, and the polymer solution was degassed through three cycles of freeze−pump−thaw. Separately, CuBr/PS8-dMbpy (15.4 mg, 1.58×10^{-5} mol of Cu) was placed in 25 mL Schlenk flask under a nitrogen atmosphere, and 0.86 mL of styrene (7.51×10^{-3} mol) was added followed by anisole (0.1 mL), and then the mixture was degassed by bubbling with nitrogen for 30 min. The $CuBr_2/Me_6TREN$ stock solution (0.20 mL, 4.76×10^{-7} mol of Cu) was then added. The catalyst and monomer suspension was transferred to the PIB/chlorobenzene solution via syringe. The resulting mixture was warmed to 110 °C and stirred for 76 h. During the polymerization, kinetic samples were taken from the flask via a syringe at timed intervals. The samples were immediately diluted with THF followed by filtration through a Gelman Acrodisc 0.2 μm PTFE filter prior to analysis.

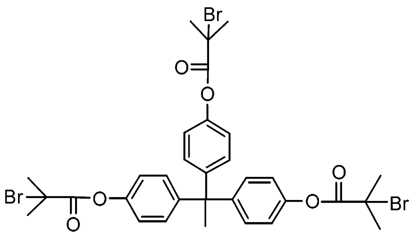
Polymerization of 2-(Trimethylsilyloxy)ethyl Methacrylate (HEMA-TMS).[27] In a 5 mL round-bottom flask, tosyl chloride (9.5 mg, 5.0×10^{-5} mol), HEMA-TMS (1.0 mL, 4.63×10^{-3} mol), and anisole (0.54 mL, 10 vol %) were combined, and the solution was purged by bubbling with nitrogen for 10 min at 0 °C. dNbpy (30.6 mg, 7.5×10^{-5} mol) and the rest of the monomer (4.4 mL, 2.04×10^{-2} mol) were combined in a 25 mL Schlenk flask. The flask was degassed by placing under vacuum followed by nitrogen backfilling (three times). CuBr (5.4 mg, 3.75×10^{-5} mol) was then added. After stirring for 10 min at room temperature, the Schlenk flask was placed in a thermostated oil bath at 90 °C. After 3 min the tosyl chloride/HEMA-TMS/anisole mixture was transferred to the Schlenk flask via a syringe. The reaction mixture was stirred for 5.5 h, and then polymerization was terminated by exposure to air, and dilution with CH_2Cl_2, prior to being filtered through a neutral alumina column to remove the catalyst. The solvent was removed, and the polymer was dried under vacuum ($M_n = 8.1 \times 10^4$; $M_w/M_n = 1.19$, $DP_n = 400$).

Transformation of Poly(2-(trimethylsilyloxy)ethyl methacrylate) (pHEMA-TMS) to Poly(2-(2-bromopropionyloxy)ethyl methacrylate) (pBPEM).[29] PHEMA-TMS (5 g, 2.5×10^{-2} mol of HEMS-TMS, $M_n = 8.1 \times 10^4$; $M_w/M_n = 1.19$) was dissolved in 65 mL of dry THF under nitrogen. Potassium fluoride (1.45 g, 2.5×10^{-2} mol) was added to the solution followed by slow addition of tetrabutylammonium fluoride (0.25 mL, 1 M THF; 2.5×10^{-4} mol). 2-Bromopropionyl bromide (3.9 mL, 3.75×10^{-2} mol) was added to the mixture slowly over 15 min. The reaction mixture was stirred at room temperature for 4 h and exposed to air, the polymer precipitated by addition to methanol/ice solution (50/50 v/v),and the solid was dissolved in 100 mL of $CHCl_3$ and filtered through an activated basic alumina column. The polymer was further purified by dissolving in $CHCl_3$ and precipitation by addition to hexanes (three times) and dried under vacuum at 25 °C for 24 h, yielding PBPEM: $M_n = 8.2 \times 10^4$, $M_w/M_n = 1.16$, $DP_n = 400$).

Synthesis of Poly(2-(2-bromopropionyloxy)ethyl methacrylate)-*graft*-poly(*n*-butyl acrylate) Bottle-Brush Polymers (pBPEM-*graft*-p*n*BA). 0.2 g of CuBr/PS8-dMbpy was weighed into a 25 mL Schlenk flask. pBPEM (0.11 g, 4.18×10^{-4} mol of initiating groups), *n*BA (23.4 mL, 0.164 mol) and methyl ethyl ketone (0.94 mL) were combined in a second Schlenk flask and degassed by subjecting the mixture to three freeze−pump−thaw cycles prior to being transferred to the flask containing CuBr/PS8-dMbpy catalyst. Finally, $CuBr_2/Me_6TREN$ stock solution in acetone (0.69 or 3.45 mL corresponding to 1 or 5 mol % of Cu in immobilized catalyst) was added to the reaction mixture, and the Schlenk flask was placed in an oil bath at 70 °C. Throughout the polymerization, kinetic samples were taken from the flask via a syringe at timed intervals. After a certain polymerization time, the mixture was exposed to air and diluted with CH_2Cl_2. The immobilized catalyst was removed from the mixture by filtration through a Gelman Acrodisc 0.2 μm PTFE filter. Solvent and unreacted monomer were removed by distilling off, and the resulting polymer was dried under vacuum.

Synthesis of pBPEM-*graft*-p*n*BA Bottle-Brush Polymers Using a Homogeneous CuBr/dNbpy Catalyst System. A sample of pBPEM-*graft*-p*n*BA bottle-brush polymer was also synthesized following previously described procedures

Scheme 2. Structure of 1,1,1-Tris(4-(2-bromoisobutyryloxy)phenyl)ethane ($3Br^iBu$)



using a homogeneous catalyst system.[29] PBPEM (0.1 g, 3.8×10^{-4} mol of initiator groups), dNbpy (0.15 g, 3.8×10^{-4} mol), $CuBr_2$ stock solution (0.35 g, 5% of Cu(I)), *n*-BA (21.7 mL, 0.152 mol), and MEK (0.9 mL, 4 vol %) were added to a 100 mL Schlenk flask, and the mixture was degassed by three freeze—pump—thaw cycles. After stirring for 1 h at room temperature, CuBr (27.0 mg, 1.9×10^{-4} mol) was added, and the flask was placed in an oil bath at 70 °C. Kinetic samples were taken at timed intervals. The reaction was terminated by exposing the catalyst to air. The mixture was diluted with CH_2Cl_2 and filtered through a neutral alumina column to remove copper catalyst. The solvent and unreacted monomer were removed by distilling off, and the resulting polymer was dried under vacuum to a constant weight.

Hydrolysis of pBPEM-*graft*-p*n*BA Bottle-Brush Copolymers.[29] Hydrolysis of samples taken during the preparation pBPEM-*graft*-p*n*BA bottle-brush polymers was conducted in order to release the p*n*BA side chains for separate characterization. 0.02 g of polymer from each kinetic sample was dissolved in 1 mL of THF in a 20 mL vial. 1-Butanol (5 mL) and concentrated sulfuric acid (2 drops) were added, and the mixture was heated to 97 °C for 7 days. The solvent was removed under vacuum, and the remaining polymer was dissolved in chloroform. After extraction with a small amount of water, the organic phase was isolated and the solvent was distilled off. The remaining polymer was analyzed by GPC.

Characterization. The conversion of monomers was determined by detecting the decrease of the monomer peak area relative to the standard peak area using a Shimadzu GC 14-A gas chromatograph equipped with a FID detector using J&W Scientific 30m DB WAX Megabore column. DMB or anisole was used as an internal standard. Injector and detector temperature were kept constant at 250 °C. Analysis was run isothermally at 40 °C for 5 min followed by an increase of temperature to 120 °C at the heating rate of 40 °C/min and holding at 120 °C for 3 min. The molecular weight and molecular weight distribution of polymers were determined by GPC equipped with a Waters 515 liquid chromatograph pump and a Waters 2410 differential refractometer using PSS columns (Polymer Standards Services, styrogel 10^5, 10^3, and 10^2 Å). GPC was performed using THF or toluene as eluent at the flow rate of 1 mL/min. Linear poly(methyl methacrylate) ($960-1.577 \times 10^6$ g/mol) or polystyrene ($376-2.0 \times 10^6$ g/mol) standards were used for calibration. Theoretical molecular weights were calculated by the following equation:

$$M_{n,th} = ([\text{monomer}]_0/[\text{initiator}]_0) \times \text{conversion} \times \text{MW(monomer)} \quad (1)$$

The conversion of PLA-M and PDMS-M macromonomers was calculated by GPC by comparing the macromonomer peak area to the diphenyl ether peak area.

Results and Discussion

Preparation of Poly(methyl acrylate) 3-Arm Star Polymer. 1,1,1-Tris(4-(2-bromoisobutyryloxy)phenyl)ethane ($3Br^iBu$) (Scheme 2) was used as a trifunctional initiator[24] to synthesize a three-arm star poly(methyl acrylate) in the presence of (CuBr/PS8-dMbpy)/($CuBr_2/Me_6TREN$) hybrid catalyst system. 1 mol % of soluble deactivator ($CuBr_2/Me_6TREN$) was used along with the immobilized catalyst (CuBr/PS8-dMbpy).

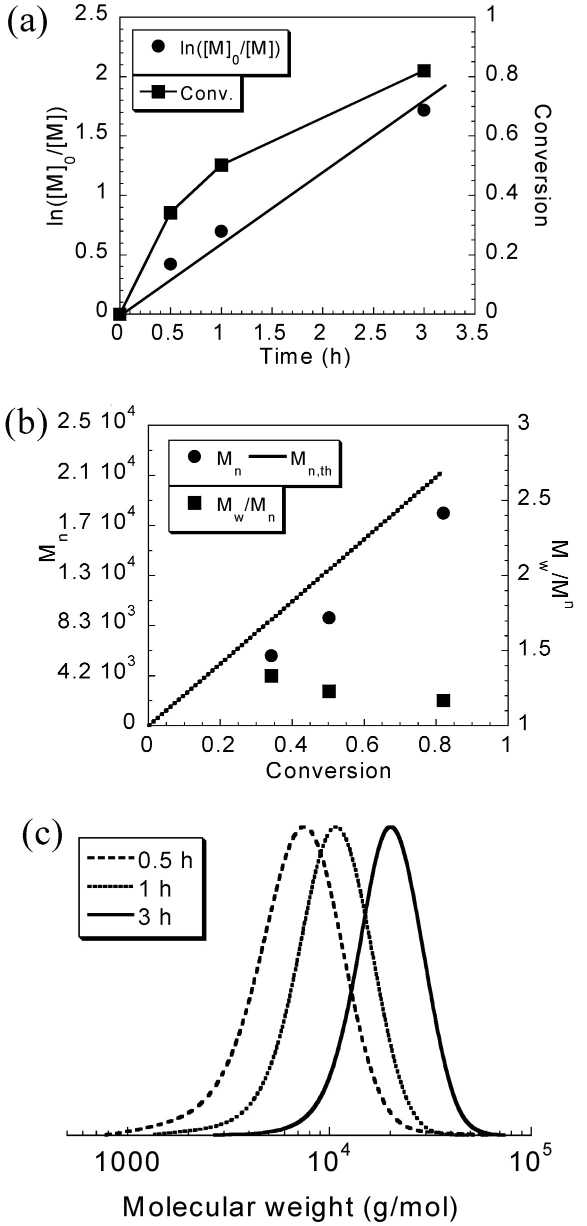


Figure 1. Kinetic plot (a), evolution of M_n and M_w/M_n with conversion (b), and GPC traces (c) for the ATRP of methyl acrylate initiated by 1,1,1-tris(4-(2-bromoisobutyryloxy)phenyl)ethane ($3Br^iBu$) using a hybrid catalyst system. Polymerization conditions: $[MA]_0:[3Br^iBu]_0:[CuBr/PS8\text{-}dMbpy]_0:[CuBr_2/Me_6TREN]_0 = 300:1:1:0.01$, $[MA]_0 = 8.79$ mol/L, MA/*p*-dimethoxybenzene/acetone = 1/0.11/0.15 v/v/v; temperature = 70 °C.

At 70 °C, methyl acrylate was polymerized successfully using the hybrid catalyst and the trifunctional initiator, $3Br^iBu$. Monomer conversion reached 82.0% after 3 h. The semilogarithmic kinetic plot (Figure 1a) exhibits essentially linear correlation with conversion while the GPC traces shown in Figure 1c display narrow and monomodal peaks that shift to higher molecular weight region with conversion. Molecular weight distribution (M_w/M_n) values were 1.35 or less and decreased during the polymerization as shown in Figure 1b.

However, the experimental molecular weights were lower than the theoretical values predicted from the eq

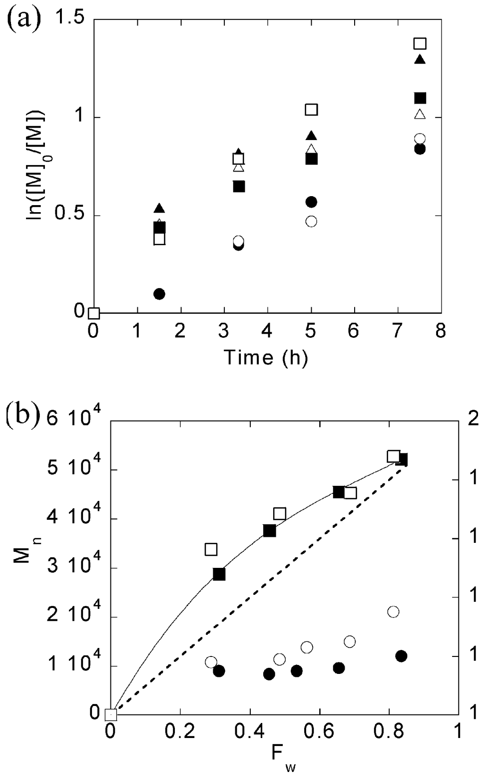


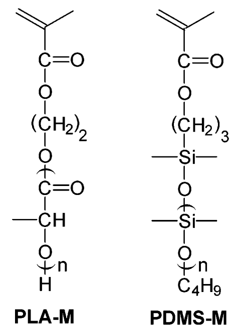
Figure 2. Plots of ln([M]$_0$/[M]) vs time (a) for the copolymerization of MMA (■, □), PLA-M (▲, △), and PDMS-M (●, ○) at 90 °C; number-average molecular weight M_n (■, □) and polydispersity index M_w/M_n (●, ○) vs polymer yield F_w (b) for the copolymerization of MMA, PLA-M, and PDMS-M at 90 °C in the presence of homogeneous catalyst (filled symbols) or hybrid catalyst (empty symbols). $F_w = (\text{conv}_{\text{MMA}}w_{\text{MMA}} + \text{conv}_{\text{PLA-M}}w_{\text{PLA-M}} + \text{conv}_{\text{PDMS-M}}w_{\text{PDMS-M}})/(w_{\text{MMA}} + w_{\text{PLA-M}} + w_{\text{PDMS-M}})$ where conv is the monomer conversion and w the initial weight of monomer. Theoretical $M_n = F_w([\text{MMA}]_0\,M_{\text{MMA}} + [\text{PLA-M}]_0\,M_{\text{PLA-M}} + [\text{PDMS-M}]_0\,M_{\text{PDMS-M}})/([\text{EBI}]_0)$, where M is the molecular weight of each monomer. Polymerization conditions: for hybrid catalyst system, [MMA]$_0$:[PLA-M]:[PDMS-M]:[EBiB]$_0$:[CuBr/PS8-dMbpy]$_0$:[CuBr$_2$/Me$_6$TREN]$_0$ = 260:5:5:1:2:0.02, for homogeneous ATRP system, [MMA]$_0$:[PLA-M]:[PDMS-M]:[EBiB]$_0$:[CuCl]$_0$:[dNbpy]$_0$ = 260:5:5:1:2:4, [MMA]$_0$ = 4.85 mol/L, MMA/p-xylene/diphenyl ether = 1/0.47/0.47 v/v/v; temperature = 90 °C.

1. This deviation stems from the difference between the hydrodynamic volume of star and linear polymers.[24,30] GPC traces exhibited no low molecular weight tails, indicative of negligible chain transfer reactions (Figure 1b,c). The linear semilogarithmic kinetic plot and low M_w/M_n along with a linear increase of molecular weight confirmed that a well-controlled polymerization reaction had been conducted in the presence of a hybrid catalyst system.

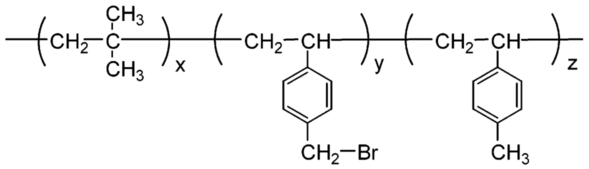
Preparation of Poly(methyl methacrylate) Graft Copolymer with Poly(lactic acid)/Poly(dimethylsiloxane) Side Chains by the Grafting-Through Technique. Figure 2a summarizes the first-order kinetic plots for MMA, poly(lactic acid) macromonomer (PLA-M) (Scheme 3), and poly(dimethylsiloxane) macromonomer (PDMS-M) (Scheme 3) copolymerization.

In the presence of the hybrid system, the consumption of MMA was faster than that in the presence of the homogeneous catalyst system. This behavior is probably a consequence of a slower deactivation process with the hybrid system, which leads to a higher radical concentration ($R_p = k_p[\text{P*}][\text{M}]$, $[\text{P*}] = k_{\text{act}}[\text{Cu}^{\text{I}}][\text{P}-\text{X}]/k_{\text{deact}}[\text{Cu}^{\text{II}}]$), since the rate constant of deactivation ($k_{\text{deact}} = 1.4 \times 10^7$ M^{-1} s^{-1} for 1-phenylethyl radical in acetonitrile at 75 °C)[31] and the concentration of the complex CuBr$_2$/Me$_6$TREN (1% vs CuBr/PS8-dMbpy) are lower than the corresponding values for the homogeneous ATRP with dNbpy ligands ($k_{\text{deact}} = 2.5 \times 10^7$ M^{-1} s^{-1}; ~5% vs Cu$^{\text{I}}$Br catalyst).[31,32] In both copolymerization reactions, because of the thermodynamic incompatibility between the inorganic PDMS and the organic polymers, PMMA and PLA, preferential incorporation of PLA-M into the backbone was observed leading to a gradient distribution of both macromonomers along the backbone. Figure 2b exhibits the evolution of molecular weight and polydispersity with polymer yield. A plot of molecular weights vs conversion cannot be applied for this system, due to large differences in molar mass of macromonomer and the comonomer. At low conversion, experimental molecular weights are higher than predicted for living systems. Nevertheless, molecular weight increases with polymer yield in both systems. Although the polydispersity is slightly higher for the polymer obtained using the hybrid catalyst system, the results indicate that the hybrid catalyst system afford good control over the reaction, comparable to the homogeneous catalyst system (CuBr/dNbpy).[25,26]

Scheme 3. Structure of Poly(lactic acid) Macromonomer and Poly(dimethylsiloxane) Macromonomer



Scheme 4. Structure of Poly(isobutene-*co*-*p*-methylstyrene-*co*-*p*-bromomethylstyrene) Macroinitiator[a]



[a] EXXPRO 3035; Br content, 8×10^{-5} mol of Br/g of polymer; approximately one Br for every 220 repeating units; approximately 16 Br per each polymer chain; $M_n = 2.0 \times 10^5$; $M_w/M_n = 2.1$.

Grafting-From Polymerization of MMA and Styrene Using Poly(isobutene-*co*-*p*-methylstyrene-*co*-*p*-bromomethylstyrene) (PIB) Macroinitiator. Commercially available poly(isobutene-*co*-*p*-methylstyrene-*co*-*p*-bromomethylstyrene) (PIB) was selected as a macroinitiator to demonstrate graft polymerization from a macroinitiator (Scheme 4).[33]

The experimental conditions were initially similar as used for graft copolymerization with the homogeneous catalyst system; [M]$_0$/[I]$_0$/[CuBr/PS8-dMbpy]$_0$ = 670/1/4.3 and methyl methacrylate/solvent ratio was 1/4 (v/v).[33] The ratio of the soluble catalyst component to the immobilized catalyst ([CuBr$_2$/Me$_6$TREN]$_0$/[CuBr/PS8-dMbpy]$_0$) in this hybrid system was 1 mol % (experiment 2 in Table 1). However, a polymer gel,

Table 1. Conditions and Results for the ATRP of Methyl Methacrylate Initiated by Poly(isobutene-*co*-*p*-methylstyrene-*co*-*p*-bromomethylstyrene) (PIB) in the Presence of (CuBr/PS8-dMbpy)/(CuBr$_2$/Me$_6$TREN) Hybrid Catalyst System[a]

expt	$[I]_0/[CuBr/PS8\text{-}dMbpy]_0$	hybrid ratio[b] (mol %)	MMA/solv (v/v)[c]	t (h)	conv (%)	M_n ($\times 10^{-5}$)	M_w ($\times 10^{-5}$)	M_w/M_n
2	1/4.3	1	1/4	0.2	*d*			
3	1/1.4	3	1/8	3.0	*d*			
4	1/1.4	10	1/8	2.5	23.6	2.55[e]	6.58[e]	2.58[e]

[a] Polymerization conditions: initiator = PIB, $[MMA]_0/[I]_0 = 670/1$, $[MMA]_0 = 1.78$ mol/L (experiment 2), $[MMA]_0 = 1.01$ mol/L (experiment 3), $[MMA]_0 = 0.95$ mol/L (experiment 4), temperature = 90 °C. [b] $[CuBr_2/Me_6TREN]_0/[CuBr/PS8\text{-}dMbpy]_0$ (mol %). [c] MMA/(chlorobenzene + anisole) (v/v). [d] Gel formation was observed. [e] After 1 h.

insoluble in organic solvents, was formed in 10 min. This was attributed to a higher local concentration of active radicals originating from the relatively poorly soluble PIB in reaction solvent (chlorobenzene) and less efficient deactivation process with the hybrid catalyst system probably leading to a cross-linked network through a termination by radical coupling. Furthermore, the local concentration of both initiator and activator can be much higher, because several initiating units are distributed along the polymer chain and activators are concentrated on the surface of a polystyrene bead. High local concentration of initiator and activator might therefore provide high local concentration of radicals which terminate, forming a polymer gel.

To decrease the radical concentration and facilitate the deactivation process, a smaller amount of immobilized catalyst along with more solvent was used ($[M]_0/[I]_0/[CuBr/PS8\text{-}dMbpy]_0$ of 670/1/1.4 and methyl methacrylate/solvent of 1/8 (v/v)). Additionally, the concentration of the soluble deactivator was increased to 3 mol % to increase the deactivation rate (experiment 3 in Table 1). The polymerization was much slower, but a polymer gel was formed again. With an even greater ratio of soluble deactivator to supported catalyst (10 mol %, experiment 4 in Table 1), a homogeneous system was obtained, and the results are summarized in Figure 3a. Under these conditions, monomer conversion reached 23.6% after 2.5 h. The linear semilogarithmic kinetic plot confirms a constant concentration of radicals, indicating significantly less termination. The molecular weight distribution traces shifted to high molecular weight region with conversion (Figure 3b), indicating a controlled polymerization. However, coupling termination reactions were not totally suppressed, even under these conditions, resulting in formation of a gel after 2.5 h of polymerization.

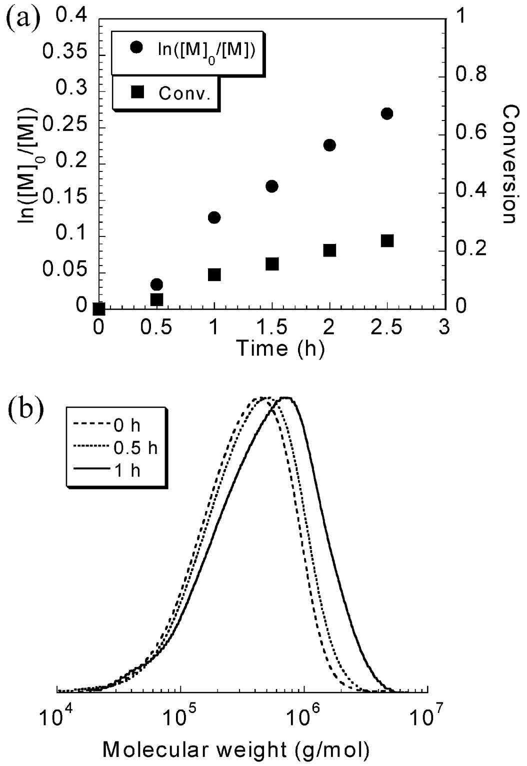


Figure 3. Kinetic plot (a) and GPC traces (b) for the ATRP of methyl methacrylate initiated by poly(isobutene-*co*-*p*-methylstyrene-*co*-*p*-bromomethylstyrene) macroinitiator using (CuBr/PS8-dMbpy)/(CuBr$_2$/Me$_6$TREN) hybrid catalyst system. Polymerization conditions: initiator = PIB, $[MMA]_0$:[Br in PIB]$_0$:[CuBr/PS8-dMbpy]:[CuBr$_2$/Me$_6$TREN] = 670:1:1.4:0.14, $[MMA]_0 = 0.95$ mol/L, MMA/(chlorobenzene) = 1/8 v/v, anisole = 0.1 mL, temperature = 90 °C.

Grafting-from polymerization was also conducted with styrene using the hybrid catalyst. The polymerization rate was slower than that seen for methyl methacrylate, but essentially similar behavior was observed.

Conducting graft polymerization from a PIB macroinitiator therefore shows a limitation of the hybrid catalyst system for the preparation of complex polymer architectures. The deactivation step with the hybrid catalyst seems to be too inefficient for a fully controlled graft polymerization from the PIB macroinitiator.

Preparation of Poly(2-(2-bromopropionyloxy)ethyl methacrylate)-*graft*-poly(*n*-butyl acrylate) (pBPEM-*graft*-pnBA) Bottle-Brush Copolymers. The grafting-from synthetic approach can be also applied to the preparation of the densely grafted, or bottle-brush, copolymers.[34] A well-defined macroinitiator, poly(2-(2-bromopropionyloxy)ethyl methacrylate) macroinitiator (pBPEM, Scheme 5), with a high concentration of ATRP-active halogens, was prepared from poly(2-(trimethylsilyloxy)ethyl methacrylate) (pHEMA-TMS), which had been synthesized using the homogeneous ATRP technique.[27] The TMS end groups were removed, and initiating groups were incorporated through the reaction with 2-bromopropionyl bromide (Scheme 5).[29] In this study, we tested the utility of the hybrid catalyst system in the synthesis of poly(*n*-butyl acrylate) bottle-brush copolymers (Scheme 6). A well-defined pBPEM macroinitiator ($M_n = 8.2 \times 10^4$, $M_w/M_n = 1.16$, DP$_n$ = 400) was prepared, and a grafting-from technique was used to synthesize a densely grafted pBPEM-*graft*-pnBA bottle-brush copolymers in the presence of (CuBr/PS8-dMbpy)/(CuBr$_2$/Me$_6$TREN) hybrid catalyst system (1 or 5 mol % of CuBr$_2$/Me$_6$TREN to CuBr/PS8-dMbpy immobilized catalyst). Polymerizations conducted with the hybrid catalyst system containing the lower amount of deactivator (CuBr$_2$/Me$_6$TREN, 1 mol % to CuBr/PS8-dMbpy immobilized catalyst) led to a faster reaction (Figure 4). The grafting-from polymerization of *n*BA with 1% of CuBr$_2$/Me$_6$TREN was stopped at 10% monomer conversion after 4 h, affording the bottle-brush copolymers, pBPEM-*graft*-p*n*BA (**I**). The rate of nBA polymerization conducted with 5 mol % of CuBr$_2$/Me$_6$-

Scheme 5. Synthesis of Multifunctional Macroinitiator PBPEM

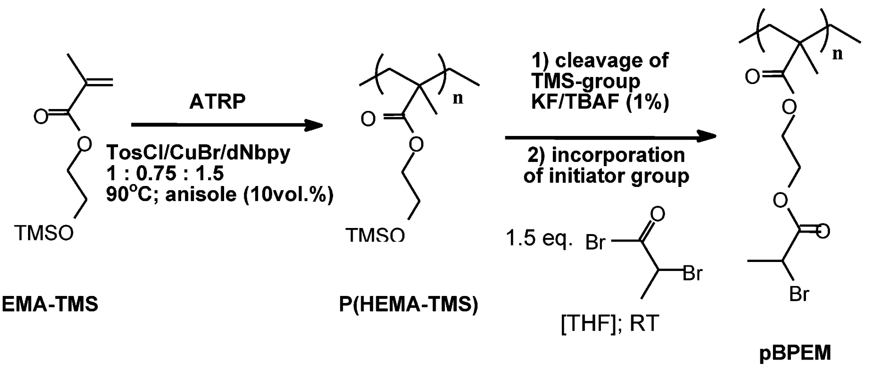
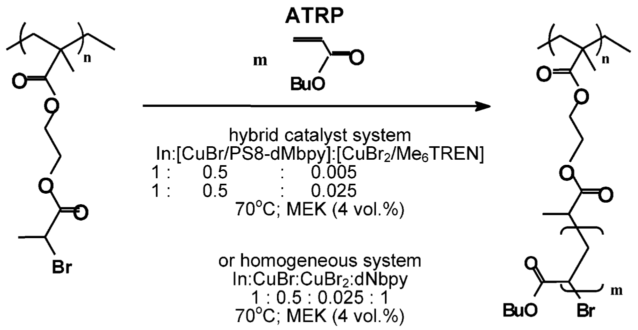


Table 2. Synthesis of Poly(2-(2-bromopropionyloxy)ethyl methacrylate)-*graft*-poly(*n*-butyl acrylate) (PBPEM-*graft*-P*n*BA, I) in the Presence of (CuBr/PS8-dMbpy)/($CuBr_2/Me_6TREN$) Hybrid Catalyst System with 1 mol % of $CuBr_2/Me_6TREN$ Deactivator[a]

time (h)	conv. (%)	$M_{n,appar}$ ($\times 10^{-3}$)	M_w/M_n	$DP_{sc(conv)}$[b]	$DP_{sc(grav)}$[c]	$DP_{sc(av)}$[d]
0	0	82	1.16	0	0	0
1		167	1.19			
2	4.00	343	1.23	15	14	15
3	8.21	666	1.29	33	35	34
4	10.12	771	1.32	40	39	40

[a] Polymerization conditions: initiator = pBPEM, $[nBA]_0/[I]_0/[CuBr/PS8\text{-}dMbpy]_0/[CuBr_2/Me_6TREN]_0 = 400/1/0.5/0.005$, $[nBA]_0 = 7.00$ mol/L, temperature = 70 °C. [b] Degree of polymerization of pnBA side chains determined by conversion (calculated from GC analysis). [c] Degree of polymerization of p*n*BA side chains determined by gravimetry (calculated from the weight of final polymer). [d] Average degree of polymerization of p*n*BA side chains of $DP_{sc(conv)}$ and $DP_{sc(grav)}$.

Scheme 6. Synthesis of Macromolecular Bottle-Brush Copolymer



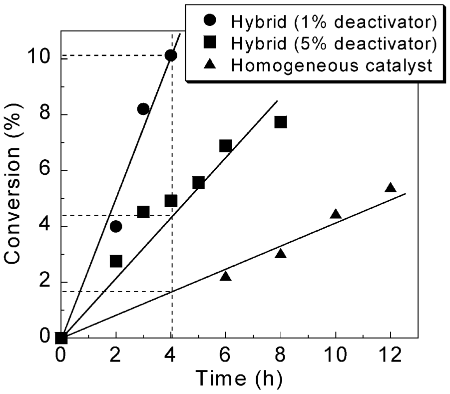


Figure 4. Kinetic plots for the ATRP of *n*-butyl acrylate for the preparation of poly(2-(2-bromopropionyloxy)ethyl methacrylate)-*graft*-poly(*n*-butyl acrylate) bottle-brush copolymers in the presence of (CuBr/PS8-dMbpy)/($CuBr_2/Me_6TREN$) hybrid and ($CuBr/CuBr_2$)/dNbpy homogeneous catalyst system. Polymerization conditions: initiator = pBPEM; for hybrid catalyst system with 5 (or 1) mol % of deactivator, $[nBA]_0:[R-Br]_0:[CuBr/PS8\text{-}dMbpy]_0:[CuBr_2/Me_6TREN]_0 = 400:1:0.5:0.025$ (or 0.005); for homogeneous catalyst system, $[nBA]_0:[I]_0:[CuBr]_0:[CuBr_2]_0:[dNbpy]_0 = 400:1:0.5:0.025:1$; $[nBA]_0 = 7.00$ mol/L; temperature = 70 °C.

TREN deactivator was approximately twice slower than that with 1 mol % deactivator (conversion after 4 h: 4.9%), and the polymerization continued for 8 h until 7.75% of monomer was grafted to the macroinitiator.

The apparent molecular weights of graft copolymers (vs linear polystyrene standards) are presented in Table 3 for pBPEM-*graft*-p*n*BA (**I**), prepared with 1 mol % deactivator, and in Table 3 for pBPEM-*graft*-p*n*BA (**II**), prepared with 5 mol % deactivator. The average degree of polymerization of p*n*BA side chains of polymers was determined by gravimetry ($DP_{sc(grav)}$) and GC ($DP_{sc(conv)}$). The polydispersity of polymers increased from M_w/M_n = 1.16 (macroinitiator) to 1.3 for pBPEM-*graft*-p*n*BA (**I**) and to 1.4 for the brush (**II**).

As shown in Figure 5, the apparent molecular weights of the bottle-brush copolymers increased linearly with conversion, indicating a controlled polymerization. The molecular weight distribution of the resulting brushes remained narrow ($M_w/M_n \sim 1.3$).

In both cases, GPC traces of pBPEM-*graft*-p*n*BA (**I**) (Figure 6a) and **II** (Figure 6b) show a shift to the higher molecular weight region with conversion, indicating good control over the graft copolymerization using the hybrid catalyst system. Although formation of a small shoulder was observed in Figure 6b, suggesting some coupling termination reactions, the successful synthesis of bottle-brush polymers was achieved without significant side reactions. The molecular weight distribution of the copolymers was usually symmetric and monomodal.

When compared to a homogeneous ATRP catalyst system, ($CuBr/CuBr_2$)/dNbpy,[29] the polymerization rate was substantially higher in the presence of the hybrid catalyst system (Figure 4) since monomer conversion in the homogeneous system had only reached 5.2% after 12 h, while the same conversion was obtained within 2 h for pBPEM-*graft*-p*n*BA, **I**, and after 4 h for pBPEM-*graft*-p*n*BA, **II**, in the presence of hybrid catalyst

Table 3. Synthesis of Poly(2-(2-bromopropionyloxy)ethyl methacrylate)-*graft*-poly(*n*-butyl acrylate) (PBPEM-*graft*-P*n*BA, II) in the Presence of ($CuBr/PS8\text{-}dMbpy$)/($CuBr_2/Me_6TREN$) Hybrid Catalyst System with 5 mol % of $CuBr_2/Me_6TREN$ Deactivator[a]

time (h)	conv (%)	$M_{n,appar}$ ($\times 10^{-3}$)	M_w/M_n	$DP_{sc(conv)}$[b]	$DP_{sc(grav)}$[c]	$DP_{sc(av)}$[d]
0	0	82	1.16	0	0	0
1		130	1.19			
2	2.76	220	1.21	11	13	12
3	4.52	319	1.37	18	16	17
4	4.92	346	1.38	20	21	20
5	5.57	409	1.39	22	25	23
6	6.88	498	1.40	28	29	28
8	7.74	572	1.39	31	34	32

[a] Polymerization conditions: initiator = pBPEM, $[nBA]_0/[I]_0/[CuBr/PS8\text{-}dMbpy]_0/[CuBr_2/Me_6TREN]_0 = 400/1/0.5/0.025$, $[nBA]_0 = 7.00$ mol/L, temperature = 70 °C. [b] Degree of polymerization of pnBA side chains determined by conversion (calculated from GC analysis). [c] Degree of polymerization of pnBA side chains determined by gravimetry (calculated from the weight of final polymer). [d] Average degree of polymerization of pnBA side chains of $DP_{sc(conv)}$ and $DP_{sc(grav)}$.

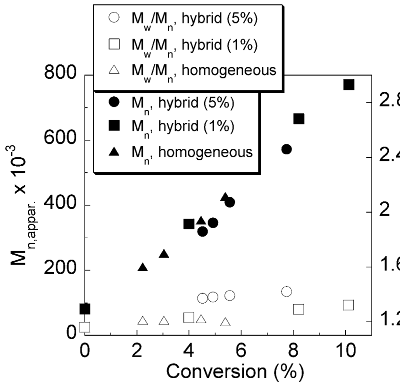


Figure 5. Evolution of M_n and M_w/M_n vs conversion in the synthesis of poly(2-(2-bromopropionyloxy)ethyl methacrylate)-*graft*-poly(*n*-butyl acrylate) bottle-brush copolymers in the presence of ($CuBr/PS8\text{-}dMbpy$)/($CuBr_2/Me_6TREN$) hybrid and ($CuBr/CuBr_2$)/dNbpy homogeneous catalyst system. Polymerization conditions: initiator = pBPEM; for hybrid catalyst system with 5 (or 1) mol % of deactivator, $[nBA]_0:[I]_0:[CuBr/PS8\text{-}dMbpy]_0:[CuBr_2/Me_6TREN]_0 = 400:1:0.5:0.025$ (or 0.005); for homogeneous catalyst system, $[nBA]_0:[I]_0:[CuBr]_0:[CuBr_2]_0:[dNbpy]_0 = 400:1:0.5:0.025:1$; $[nBA]_0 = 7.00$ mol/L; temperature = 70 °C.

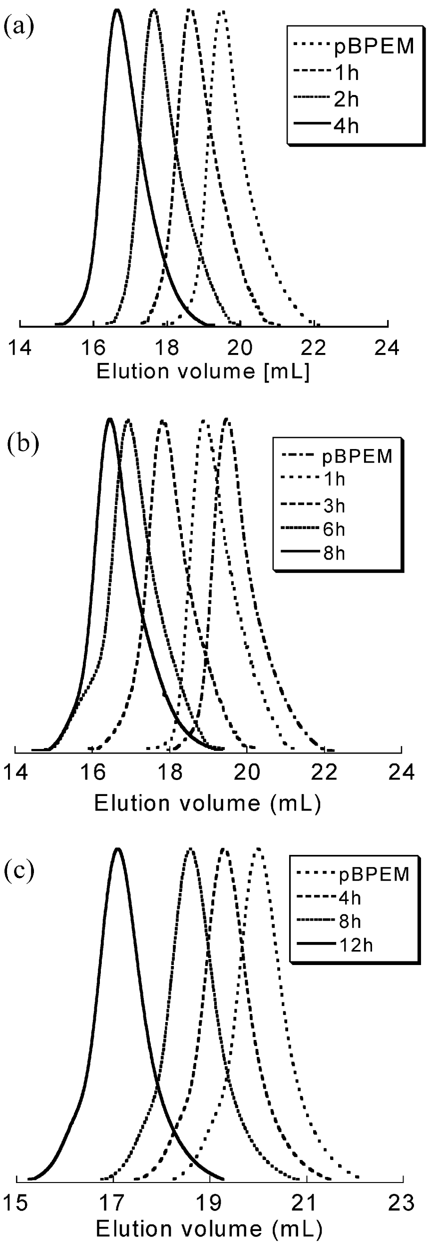


Figure 6. GPC traces in the synthesis of poly(2-(2-bromopropionyloxy)ethyl methacrylate)-*graft*-poly(*n*-butyl acrylate) bottle-brush copolymers in the presence of ($CuBr/PS8\text{-}dMbpy$)/($CuBr_2/Me_6TREN$) hybrid catalyst system with 1 mol % of $CuBr_2/Me_6TREN$ deactivator (a), 5 mol % of $CuBr_2/Me_6TREN$ deactivator (b), and in the presence of ($CuBr/CuBr_2$)/dNbpy homogeneous catalyst system (c). Polymerization conditions: initiator = pBPEM; for hybrid catalyst system with 5 (or 1) mol % of deactivator, $[nBA]_0:[I]_0:[CuBr/PS8\text{-}dMbpy]_0:[CuBr_2/Me_6TREN]_0 = 400:1:0.5:0.025$ (or 0.005); for homogeneous catalyst system, $[nBA]_0:[I]_0:[CuBr]_0:[CuBr_2]_0:[dNbpy]_0 = 400:1:0.5:0.025:1$; $[nBA]_0 = 7.00$ mol/L; temperature = 70 °C.

systems. This behavior can be attributed to a higher radical concentration as a consequence of a slower deactivation process with $CuBr_2/Me_6TREN$ for the hybrid catalyst system.[31] Different from PIB graft copolymer case, no cross-linking was observed, probably because of the low conversion employed (<10%) and good solubility of pBPEM in *n*BA/methyl ethyl ketone. In the homogeneous reaction the resulting bottle-brush copolymer (**III**) exhibited a narrower molecular weight distribution, $M_w/M_n \sim 1.2$, closer to that of the starting macroinitiator, than seen for those prepared using a hybrid catalyst system (Table 4). GPC traces pBPEM-*graft*-pnBA copolymers (**III**) are presented in Figure 6c and show symmetrical shifts with conversion.

An acid-catalyzed transesterification with 1-butanol conducted with the pBPEM-*graft*-pnBA bottle-brush copolymers **II** and **III** (Scheme 7) was employed to cleave the ester bond between the side chains and the polymer backbone, releasing the grafted side chains with DP_{sc}.

The cleaved pnBA side chains were analyzed by GPC (Table 5). The theoretical molecular weight ($M_{n,calc}$) corresponds to the calculated chain lengths of the side chains, which was determined using the following formula:[29]

$$M_{n,calc} = 128.17 \text{ g/mol} \times DP_{sc(av)}, \quad \text{where } DP_{sc(av)} = [DP_{sc(conv)} + DP_{sc(grav)}]/2$$

GPC traces in Figure 7 show that the signal of high molecular weight brushes (**II, III**), disappeared after

Table 4. Synthesis of Poly(2-(2-bromopropionyloxy)ethyl methacrylate)-*graft*-poly(*n*-butyl acrylate) (PBPEM-*graft*-P*n*BA, III) in the Presence of (CuBr/CuBr$_2$)/DNbpy Homogeneous Catalyst System[a]

time (h)	conv (%, by GC)	$M_{n,appar}$ (GPC) ($\times 10^{-3}$)	M_w/M_n (GPC)	$DP_{sc(conv)}$[b] (by GC)	$DP_{sc(grav)}$[c]	$DP_{sc(av)}$[d]
0	0	82	1.16	0	0	0
1		120	1.17			
2		158	1.17			
4		181	1.19			
6	2.23	210	1.21	9	11	10
8	3.04	252	1.21	12	14	13
10	4.46	354	1.22	18	16	17
12	5.40	427	1.20	22	19	21

[a] Polymerization conditions: initiator = pBPEM, $[nBA]_0/[I]_0/[CuBr]_0/[CuBr_2]_0/[dNbpy]_0 = 400/1/0.5/0.025/1$, $[nBA]_0 = 7.00$ mol/L, temperature = 70 °C. [b] Degree of polymerization of pnBA side chains determined by conversion (calculated from GC analysis). [c] Degree of polymerization of pnBA side chains determined by gravimetry (calculated from the weight of final polymer). [d] Average degree of polymerization of pnBA side chains of $DP_{sc(conv)}$ and $DP_{sc(grav)}$.

Scheme 7. Hydrolysis of Molecular Brushes[29]

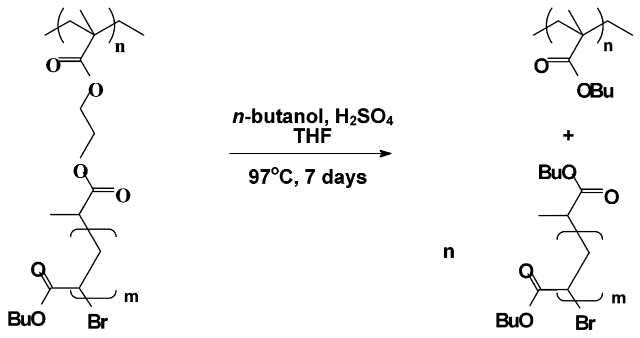


Table 5. Characterization of P*n*BA (IIA, IIIA) Side Chains Obtained after Hydrolysis of PBPEM-*graft*-P*n*BA (II, III) Bottle-Brush Copolymers with 1-Butanol

system	time (h)	$M_{n,calc}$	$M_{n,appar}$ (GPC)	M_w/M_n (GPC)
hybrid catalyst system	2	1540	1690	1.25
	3	2180	2280	1.31
	4	2560	2480	1.34
	5	2950	2740	1.36
	6	3590	3440	1.39
	8	4100	3870	1.41
homogeneous catalyst system	6	1280	1180	1.24
	8	1670	1580	1.26
	10	2180	1990	1.26
	12	2690	2580	1.27

hydrolysis, and a signal of hydrolyzed pnBA side chains (**IIA, IIIA**) with lower molecular weight and symmetrical molecular weight distribution appeared.

Figure 8 shows that molecular weights of the pnBA side chains from both hybrid and homogeneous catalyst systems are very close to the theoretical values. The polydispersities of pnBA side chains obtained from polymerization using the hybrid catalyst system were slightly higher than those from polymerization with the homogeneous catalyst system. These results suggest that the hybrid catalyst system can activate and deactivate the dormant and active species effectively, even when a complex polymeric architecture is targeted, indicating the high efficiency of the hybrid catalyst system in ATRP.

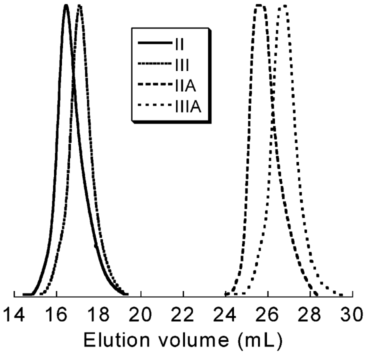


Figure 7. GPC traces of poly(2-(2-bromopropionyloxy)ethyl methacrylate)-*graft*-poly(*n*-butyl acrylate) in the presence of (CuBr/PS8-dMbpy)/(CuBr$_2$/Me$_6$TREN) hybrid catalyst system with 5 mol % of deactivator (**II**) and (CuBr/CuBr$_2$)/dNbpy homogeneous systems (**III**) and poly(*n*-butyl acrylate) obtained after the hydrolysis of corresponding bottle-brush copolymers (**IIA** and **IIIA**). Hydrolysis conditions: polymers **II** and **III**, 0.02 g; THF, 1 mL; 1-butanol, 5 mL; sulfuric acid, 2 drops; temperature = 97 °C; time = 7 days.

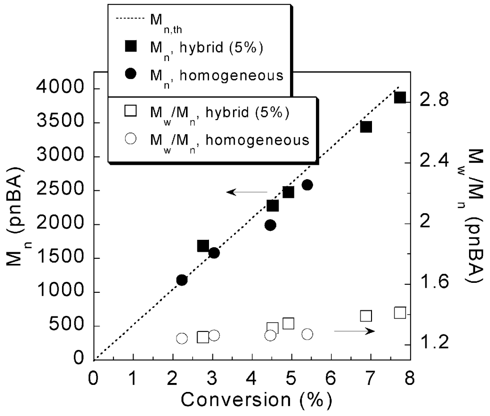


Figure 8. Evolution of M_n and M_w/M_n of poly(*n*-butyl acrylate) side chains vs conversion of *n*-butyl acrylate for the preparation of poly(2-(2-bromopropionyloxy)ethyl methacrylate)-*graft*-poly(*n*-butyl acrylate) bottle-brush copolymers, poly(*n*-butyl acrylate) side chains were isolated from the corresponding bottle-brush copolymer through hydrolysis reaction. Polymerization conditions: initiator = pBPEM; for hybrid catalyst system with 5 mol % of deactivator, $[nBA]_0:[I]_0:[CuBr/PS8\text{-}dMbpy]_0:[CuBr_2/Me_6TREN]_0 = 400:1:0.5:0.025$; for homogeneous catalyst system, $[nBA]_0:[I]_0:[CuBr]_0:[CuBr_2]_0:[dNbpy]_0 = 400:1:0.5:0.025:1$; $[nBA]_0 = 7.00$ mol/L; temperature = 70 °C. Hydrolysis conditions: polymers **II** and **III**, 0.02 g; THF, 1 mL; 1-butanol, 5 mL; sulfuric acid, 2 drops; temperature = 97 °C.

Conclusion

The preparation of complex polymeric architectures, star, graft, and bottle-brush copolymers, was successfully demonstrated in the presence of the (CuBr/PS8-dMbpy)/(CuBr$_2$/Me$_6$TREN) hybrid catalyst system. No noticeable differences between hybrid and CuBr/dNbpy homogeneous catalyst system were observed in the synthesis of 3-arm star poly(methyl acrylate) and poly(methyl methacrylate) graft copolymer with poly(lactic acid)/poly(dimethylsiloxane) mixed side chains. However, when PIB graft copolymers with styrene and methyl methacrylate were attempted by a grafting-from technique, a radical coupling resulted in a gel, due to a high local concentration of radicals with the hybrid catalyst system. This poor control was partially ascribed to poor solubility of the macroinitiator in the reaction medium, since the synthesis of molecular brushes was successful and the hybrid catalyst system afforded a well-defined poly(2-(2-bromopropionyloxy)ethyl methacrylate)-*graft*-poly(*n*-butyl acrylate) (pBPEM-*graft*-pnBA) from pBPEM as a macroinitiator. The polymerization in the presence of the hybrid catalyst system led to a faster reaction than that using a homogeneous catalyst system, while retaining a well-controlled reaction and affording polymers with a narrow molecular weight distribution.

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References and Notes

(1) Matyjaszewski, K., Ed. *Controlled Radical Polymerization*; American Chemical Society: Washington, DC, 1998; Vol. 685.
(2) Matyjaszewski, K., Ed. *Controlled/Living Radical Polymerization: Progress in ATRP, NMP, and RAFT*; American Chemical Society: Washington, DC, 2000; Vol. 768.
(3) Matyjaszewski, K., Davis, T. P., Eds. *Handbook of Radical Polymerization*; Wiley-Interscience: Hoboken, 2002.
(4) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
(5) Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901.
(6) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921.
(7) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689.
(8) Matyjaszewski, K. *Chem. Eur. J.* **1999**, *5*, 3095.
(9) Patten, T. E.; Matyjaszewski, K. *Acc. Chem. Res.* **1999**, *32*, 895.
(10) Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901.
(11) Coessens, V.; Pintauer, T.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 337.
(12) Haddleton, D. M.; Kukulj, D.; Radigue, A. P. *Chem. Commun.* **1999**, 99.
(13) Kickelbick, G.; Paik, H.-j.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 2941.
(14) Carmichael, A. J.; Haddleton, D. M.; Bon, S. A. F.; Seddon, K. R. *Chem. Commun.* **2000**, 1237.
(15) Sarbu, T.; Matyjaszewski, K. *Macromol. Chem. Phys.* **2001**, *202*, 3371.
(16) Xia, J.; Johnson, T.; Gaynor, S.; Matyjaszewski, K.; DeSimone, J. *Macromolecules* **1999**, *32*, 4802.
(17) Qiu, J.; Charleux, B.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 2083.
(18) Matyjaszewski, K.; Pintauer, T.; Gaynor, S. *Macromolecules* **2000**, *33*, 1476.
(19) Sarbu, T.; Pintauer, T.; McKenzie, B.; Matyjaszewski, K. *J. Polym. Sci., Polym. Chem.* **2002**, *40*, 3153.
(20) Hong, S. C.; Paik, H.-J.; Matyjaszewski, K. *Macromolecules* **2001**, *34*, 5099.
(21) Hong, S. C.; Matyjaszewski, K. *Macromolecules* **2002**, *35*, 5792.
(22) Queffelec, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **2000**, *33*, 8629.
(23) Matyjaszewski, K.; Patten, T. E.; Xia, J. *J. Am. Chem. Soc.* **1997**, *119*, 674.
(24) Matyjaszewski, K.; Miller, P. J.; Pyun, J.; Kickelbick, G.; Diamanti, S. *Macromolecules* **1999**, *32*, 6526.
(25) Shinoda, H.; Matyjaszewski, K. *Macromolecules* **2001**, *34*, 6243.
(26) Shinoda, H.; Miller, P. J.; Matyjaszewski, K. *Macromolecules* **2001**, *34*, 3186.
(27) Beers, K. L.; Gaynor, S. G.; Matyjaszewski, K.; Sheiko, S. S.; Moeller, M. *Macromolecules* **1998**, *31*, 9413.
(28) Beers, K. L.; Boo, S.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 5772.
(29) Boerner, H. G.; Beers, K.; Matyjaszewski, K.; Sheiko, S. S.; Moeller, M. *Macromolecules* **2001**, *34*, 4375.
(30) Xia, J.; Zhang, X.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 4482.
(31) Matyjaszewski, K.; Paik, H.-j.; Zhou, P.; Diamanti, S. J. *Macromolecules* **2001**, *34*, 5125.
(32) Beuermann, S.; Buback, M. *Prog. Polym. Sci.* **2002**, *27*, 191.
(33) Hong, S. C.; Pakula, T.; Matyjaszewski, K. *Macromol. Chem. Phys.* **2001**, *202*, 3392.
(34) Boerner, H. G.; Matyjaszewski, K. *Macromol. Symp.* **2002**, *177*, 1.

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