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Direct Synthesis of Well-Defined Poly[{2-(methacryloyloxy)ethyl}trimethylammonium chloride] Brush via Surface-Initiated Atom Transfer Radical Polymerization in Fluoroalcohol

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ABSTRACT: A well-defined cationic polymer and polymer brush were simultaneously prepared by copper-catalyzed atom transfer radical polymerization (ATRP) of 2-(methacryloxy)ethyltrimethylammonium chloride (MTAC) in 2,2,2-trifluoroethanol (TFE) at 60 °C initiated with ethyl 2-bromoisobutylate and the corresponding alkylbromide immobilized on silicon wafer. ATRP of MTAC in TFE as well as aqueous solution proceeded quickly but in a poorly controlled manner, leading to a relatively higher molecular weight distribution (MWD) than $M_w/M_n = 1.3$, where M_w and M_n are weight-average and number-average molecular weights, respectively. Addition of a small amount of isopropyl alcohol to the TFE-based reaction mixture reduced the polymerization rate and produced a poly(MTAC) with predictable molecular weight and narrower MWD than 1.19. The M_n of poly(MTAC) was controllable in the range 10^4-10^5 g mol^{-1} based on the molar ratio of monomer and initiator in the feed. The M_n of the brush on a flat silicon wafer matched that of the free poly(MTAC). The graft density of poly(MTAC) was 0.20 chains nm^{-2}. The ATRP of MTAC in TFE/1-ethyl-3-methylimidazolium chloride (EMImCl) also proceeded in a controlled manner at 60 °C, yielding polymers with narrow MWDs ($M_w/M_n = 1.12-1.13$). Analysis of the ^{13}C NMR spectra of the carbonyl region of the resulting poly(MTAC)s revealed that syndiotactic-rich configurations were produced by ATRP of MTAC in aqueous solution, TFE/isopropyl alcohol, and TFE/EMImCl. The solvent effect of TFE and ionic liquid on the tacticity of polymer was negligible.

Introduction

Swollen structure and interactions between polyelectrolyte brushes in aqueous solution are very important to understand friction and adhesion among the amino acid constituents of polypeptide. The swollen structure of polyelectrolytes in an aqueous solution has been studied by using atomic force measurement,[1] X-ray reflectivity,[2] and neutron reflectivity.[3,4] These analytical techniques require well-defined polymer brushes with precisely determined molecular weights and narrow molecular weight distributions (MWDs), and well-defined grafting densities to determine the swollen brush thickness and the chain structure at the interface between the brush and solution. For instance, polymer chains immobilized on a flat surface with high-graft density in a good solvent stretch in a direction perpendicular to the substrate surface due to high osmotic pressure arising from the excluded volume effect by densely grafted neighboring chains.[5] Therefore, a polymer brush with large MWD containing chains of various lengths in a good solvent affords a large gradient layer and roughness at the interface between the brush and solvent, which makes it difficult to estimate the swollen thickness and depth profile of the swollen brush structure based on reflectivity curves. Precise analysis of swollen polyelectrolyte brushes in an aqueous media requires well-defined polyelectrolyte brushes with uniform thickness on a flat substrate with large surface area.

Over the past decade, various types of well-defined polymer brush[6] have been prepared by surface-initiated polymerization combined with controlled/living radical polymerization, such as atom transfer radical polymerization (ATRP) and reversible addition−fragmentation chain transfer (RAFT) polymerization. However, it is still difficult to control the polymerization of vinyl monomers with polar functional groups, such as carboxylic acid,[7] sulfuric acid,[8−10] phosphoric acid,[11] ammonium salt,[12,13] sulfobetaines,[14−16] and phosphobetaines,[17−22] to produce a polyelectrolyte with predictable molecular weight larger than 10^5 g mol^{-1} and narrower MWD than $M_w/M_n < 1.2$, where M_w and M_n are weight-average molecular weight and number-average molecular weight, respectively. In most cases, the MWD of the polyelectrolyte are larger than 1.5 when the high-molecular-weight polyelectrolyte was synthesized by ATRP.

Armes et al. have achieved the direct synthesis of well-defined cationic polymers based on [2-(methacryloyloxy)ethyl]trimethylammonium chloride (MTAC) by ATRP in aqueous solution initiated with water-soluble alkyl bromides.[23] ATRP of MTAC in a water/isopropyl alcohol (iPrOH) mixture at 20 °C yielded poly(MTAC) with the M_n of 1.28×10^4 and a polydispersity index lower than 1.19, indicating that adding alcohol to the aqueous polymerization solution effectively controlled the ATRP of MTAC. The additive ratio of iPrOH to aqueous solution should be carefully controlled so as not to precipitate the resulting polymer because iPrOH is a poor solvent for poly(MTAC). Although Armes et al. did not describe a preparation of poly(MTAC) brush by surface-initiated ATRP (SI-ATRP) in water/iPrOH system, we supposed

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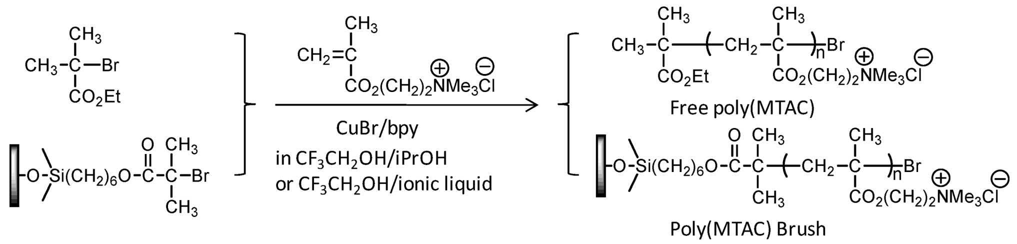
Scheme 1



that heterogeneous polymerization solution must be unfavorable for preparing uniformly grafted polymer brushes on the substrate. Water is a good solvent for poly(MTAC) but usually results in poor control in ATRP probably due to coordination with copper-based catalysts to displace halide ligands.

We focused on 2,2,2-trifluoroethanol (TFE) and ionic liquid as a solvent for ATRP of MTAC. TFE is known as a good solvent for sulfobetaine-type polymer[24] and can dissolve MTAC monomer and poly(MTAC). The ATRP of electrolyte monomers in TFE will proceed in homogeneous solution without water. Although TFE has already been used as a solvent or cosolvent for the conventional free radical polymerization of styrene,[25] vinyl acetate,[26] ring-opening metathesis polymerization of norbornene derivatives,[27] and RAFT polymerization of [2-(methacryloyloxy)ethyl]phosphorylcholine (MPC),[28] controlled polymerization has not been achieved yet. Ionic liquids are widely known as nonvolatile and recyclable solvents[29] that readily dissolve many inorganic compounds, including copper-based ATRP catalysts, and so a homogeneous reaction mixture can be obtained. Since Haddleton and his co-workers first reported ATRP of methyl methacrylate (MMA) in 1-butyl-3-methylimidazolium hexafluorophosphate,[30] various types of ionic liquid have been applied on ATRP,[31−33] reverse ATRP,[34] and activators generated by electron transfer (AGET) ATRP.[35] One of the unique effects of ionic liquid is the higher propagation rate constant of ATRP in ionic liquid than those in bulk or other organic solvents. Recently, ionic liquid was used for surface-initiated ATRP to produce a PMMA brush at a confined geometry area on the substrate by using microdroplets.[36]

We demonstrate here the surface-initiated ATRP of MTAC in TFE to prepare high-density well-defined poly(MTAC) brushes with narrow MWD and higher molecular weight than 10^5 g mol^{-1}. The effects of the solvent on the polymerization rate, MWD, and tacticity of the resulting poly(MTAC) were investigated by using TFE containing iPrOH or imidazolium type ionic liquids as the cosolvent.

Experiments

Materials. Copper(I) bromide (CuBr, Wako Pure Chemicals, 99.9%) was purified by successive washing with acetic acid and ethanol and dried under vacuum. Ethyl 2-bromoisobutyrate (EB, Tokyo Chemical Inc., 98%) was dried and distilled over CaH_2 before use. 2,2′-Bipyridyl (bpy, Wako, 99.5%), 2,2,2-trifluoroethanol (TFE, Acros, 99.9%), 1-ethyl-3-methylimidazolium chloride (EMImCl), and 1-ethyl-3-hexylimidazolium chloride (HMImCl) were used without further purification. MTAC aqueous solution (Aldrich) was concentrated by a vacuum pump to remove water and was dissolved in TFE. The MTAC/TFE solution was purified by alumina column chromatography and filtration by a membrane filter. [((2-Bromo-2-methylpropionyl)oxy)hexyl]triethoxysilane (BHE) was synthesized as described previously.[37,38] The BHE monolayer was immobilized on a silicon wafer by chemical vapor adsorption. Deionized water was purified with the NanoPure Water system (Millipore Inc.).

Polymer Brush Preparation. A typical protocol for the SI-ATRP on MTAC in TFE was as follows (Scheme 1). A few sheets of the BHE-immobilized silicon wafers (general-use size = 10 × 40 × 0.5 mm^3), 4.0 mL of MTAC/TFE solution (2.0 M), and 0.30 mL of iPrOH were charged in a well-dried glass tube with a stopcock and degassed by the freeze−thaw process three times. CuBr (0.020 mmol) and bpy (0.040 mmol) were introduced into another glass tube, which was degassed by seven cycles of vacuum pumping and flushing with argon. A free initiator EB (0.025 mmol) diluted with TFE was added to a catalyst to immediately give a homogeneous solution with characteristic red color. The copper catalyst solution was degassed by repeated freeze−thaw cycles and then injected to the monomer solution. The resulting reaction mixture was again degassed by repeated freeze−thaw cycles to remove the oxygen and stirred in an oil bath at 60 °C for 16 h under argon to simultaneously generate a poly(MTAC) brush from the substrate and free (unbound) poly(MTAC) from EB. The reaction was stopped by opening the glass vessel to air at 20 °C. The reaction mixture was poured into THF to precipitate the free polymer and unreacted MTAC. The MTAC monomer was insoluble in THF, and hence the conversion of polymerization was determined by ^1H NMR analysis of the reaction mixture in methanol-d_4 after evaporation of TFE solvent, and by comparing the peak integrals due to the monomer vinyl signals between 5.5 and 6.0 ppm to those of the ester methylene groups at 4.2 ppm, *N*-methyl groups at 3.5 ppm, and the methacrylate backbone at 0.5−1.1 or at 1.5−2.0 ppm attributed to polymer and monomer. The silicon wafers were washed with TFE using a Soxhlet apparatus for 12 h to remove the free polymer adsorbed on their surface, and were dried under reduced pressure.

Characterization. Size exclusion chromatography (SEC) of the free soluble poly(MTAC) was performed to determine the M_n, M_w, *z*-averaged mean-square radius of gyration, and MWD with a Shimadzu HPLC system connected to three polystyrene gel columns of Tosho G3000PW_{XL}-CP (pore size 20 nm, bead size 7 μm) + G5000PW_{XL}-CP (pore size 100 nm, bead size 10 μm) × 2 and equipped with a multi-angle light-scattering detector (MALS; Wyatt Technology DAWN-EOS, 30 mW GaAs linearly polarized laser, wavelength: $\lambda = 690$ nm) and reflective index detector (Shimadzu RID-10A) using an acetic acid aqueous solution (500 mM) containing sodium nitrate (200 mM) as an eluent at a rate of 0.6 mL min^{-1}. The polystyrene gel columns of G3000PW_{XL}-CP and G5000PW_{XL}-CP are claimed to separate the polymer with the molecular ranges 9×10^4 to 1×10^2 and 1×10^6 to 1×10^3 g mol^{-1}, respectively. The Rayleigh ratio at a scattering angle of 90° was based on that of pure toluene at a wavelength of 632.8 nm at 25 °C. The corrections for sensitivity of 17 detectors at angles of other than 90° and dead volume for each detector were performed using the scattering intensities of 0.30 wt % aqueous solution of poly(ethylene oxide) standard with $M_w = 2.22 \times 10^4$ g mol^{-1} and $M_w/M_n = 1.08$.

Table 1. Surface-Initiated ATRP of MTAC in TFE[a]

run	solvents (volume ratio, v/v)	temp, °C	time, h	conv,[b] %	$10^{-4}M_n$ calc[c]	$10^{-4}M_n$ obs[d]	M_w/M_n	thickness, nm[e]
1	H_2O/iPrOH (1/1.5)	25	1	47	4.68	6.41	1.58	15
2	H_2O/iPrOH (1/1.5)	25	12	72	12.9	14.1	1.43	43
3	TFE	25	1	73	4.84	3.48	1.31	3
4	H_2O/TFE (1/50)	25	1	74	4.91	2.79	1.31	4
5	H_2O/TFE (1/20)	25	3	47	3.22	3.44	1.23	5
6	H_2O/TFE (1/5)	25	3	27	1.85	3.24	1.21	3
7	H_2O/TFE (1/4)	25	20	73	4.99	3.73	1.18	3
8	H_2O/TFE (1/1.3)	25	20	50	3.42	2.29	1.14	2
9	^{i}PrOH/TFE (1/2)	30	20	58	4.70	4.05	1.21	6
10	^{i}PrOH/TFE (1/20)	30	20	53	4.29	5.50	1.23	11
11	^{i}PrOH/TFE (1/2)	60	16	66	4.37	5.37	1.12	12
12	^{i}PrOH/TFE (1/20)	60	16	80	5.26	7.19	1.12	20
13	^{i}PrOH/TFE (1/20)	60	48	99	26.4	22.0	1.19	56

[a] Atom transfer radical polymerization (ATRP) of [2-(methacryloxy)ethyl]trimethylammonium chloride (MTAC) in 2,2,2-trifluoroethanol (TFE) was carried out with CuBr (0.025 mmol), bpy (0.050 mmol), MTAC (7.2−8.3 mmol), and ethyl 2-bromoisobutylate (EB, 0.025 mmol) in an Ar atmosphere. M_n and M_w represent the number-averaged and weight-averaged molecular weights, respectively. [b] ^{1}H NMR. [c] M_n(calc) = [MTAC]/[EB] × conversion/100 × [MW of MTAC]. [d] M_n(obs) of free poly(MTAC) was determined by MALS-SEC calibration using an acetic acid (500 mM) aqueous solution containing $NaNO_3$ (200 mM) as an eluent. [e] Ellipsometry.

All NMR spectra were recorded in methanol-d_4 at 25 °C using a Bruker AV-400 spectrometer (^{1}H 400.13 MHz, ^{13}C 100.61 MHz). The chemical shifts in ppm were referenced to the tetramethylsilane (δ 0) internal standard for ^{1}H NMR and CD_3OD (δ 49.0) for ^{13}C NMR. The thickness of the brush was determined by a spectroscopic ellipsometer MASS-102 (Five Lab Co.) with Xenon arc lamp (wavelength of 380−890 nm) at fixed incident angle of 70°. For the calculation of poly(MTAC) brush thickness, a reflective index of n = 1.495 was used. Atomic force microscopy (AFM) observation was conducted with Agilent 5000 (Agilent Technologies, Inc.) using an ac mode (tapping mechanism) driven dynamic force microscope in air at room temperature. The polymer brush surface was scanned at a rate of 10 μm s^{-1} by a silicon nitride integrated tip on a commercial rectangle cantilever (Nanosensors, Type PPP-NCHR-20) with a normal force constant of 42 N m^{-1} at a driving frequency of 317 kHz in air.

SEC Measurement of Poly(MTAC) Brush on Substrate. To measure the M_n of the surface-grafted poly(MTAC) on a flat substrate by SEC, the polymer brush was prepared on a larger silicon wafer compared with the general-use silicon plates. A sheet of the BHE-immobilized silicon wafer (65 × 65 × 0.5 mm^3), 30.0 mL of MTAC/TFE solution (2.0 M), and 1.50 mL of iPrOH were charged in a specially designed separable flask with a stopcock and degassed by the freeze−thaw process three times. Copper catalyst solution containing CuBr (0.060 mmol), bpy (0.125 mmol), and EB (0.060 mmol) diluted with TFE was prepared in another glass tube and injected to the MTAC solution. The resulting reaction mixture was degassed by repeated freeze−thaw to remove the oxygen and stirred at 60 °C for 48 h under argon. The resulting silicon wafers were washed with TFE using a Soxhlet apparatus overnight to remove the free polymer adsorbed on their surface and were dried under reduced pressure.

The brush-immobilized flat silicon wafers were immersed in concentrated sulfuric acid (20 mL) for 3 days in a glass vessel and carefully and slowly neutralized by sodium hydrogen carbonate aqueous solution. The resulting solution was collected in a dialysis membrane tube (Spectra/Por 3, Standard regulated cellulose membrane, MWCO = 3500 Da) and dialyzed in water to remove inorganic salt ions for 3 days and concentrated to give 0.65 mg of the residue, which was diluted with aqueous solution and injected to SEC. Theoretical yield of the surface-grafted polymer should be 0.18 mg; therefore, the obtained residue still contained salt or impurities.

Results and Discussion

SI-ATRP of MTAC in TFE/iPrOH. In general, well-defined free polymers can be obtained even if ATRP proceeded in a heterogeneous reaction mixture; however, a homogeneous media is preferred for SI-ATRP to produce a high-density polymer brush with narrow MWD because the monomer and catalyst are required to react with the immobilized initiator on the surface. The MTAC monomer is soluble in water and methanol but insoluble in hexane, toluene, benzene, 1,4-dioxane, THF, and acetone, while poly(MTAC) is soluble in aqueous solution and insoluble in a wide range of organic solvents and iPrOH. Armes et al. reported that the ATRP of MTAC in aqueous solution using a hydrophilic free initiator bearing a morpholine group proceeded very rapidly at 20 °C to give a polymer with very broad polydispersity index, M_w/M_n > 1.3, indicating uncontrolled polymerization.[23] They demonstrated that a poly(MTAC) with relatively narrow MWD was obtained by ATRP in a methanol/water mixture at 20 °C for 15−20 h; however, transesterification of MTAC with methanol partially took place during ATRP to give a random copolymer consisting of poly(MTAC) and poly(methyl methacrylate). They eventually found that the ATRP of MTAC using an iPrOH/water mixture (monomer concentration of 20−30%) at 20 °C for 16 h produced a poly(MTAC) with predictable M_n (M_n(SEC) = 1.28× 10^4) and narrow MWD, M_w/M_n = 1.19, without any undesirable side reactions. Therefore, we applied the preferred cosolvent system using iPrOH and water to SI-ATRP of MTAC to prepare a well-defined poly(MTAC) brush on a substrate.

Table 1 shows the M_n's and MWDs of the resulting free poly(MTAC) and thickness of the polymer brushes. All the polymerizations were carried out in the presence of a free initiator and the initiator-immobilized silicon wafer to simultaneously produce the free polymer and the polymer brush on the substrate. We actually obtained well-defined poly(MTAC) with lower M_n than 10^5 by ATRP in a water/iPrOH (1/1.5, v/v) mixture at 25 °C; however, a broader MWD than M_w/M_n = 1.4 was observed for the polymer with higher M_n than 10^5, as shown in runs 1 and 2 in Table 1. The addition of much more iPrOH to the polymerization solution retarded the propagation rate in ATRP to give a polymer with narrow MWD, but an excessively high volume ratio of iPrOH led to a heterogeneous reaction mixture because iPrOH is a poor solvent for poly(MTAC). Expecting a homogeneous polymerization mixture, we tried to use a

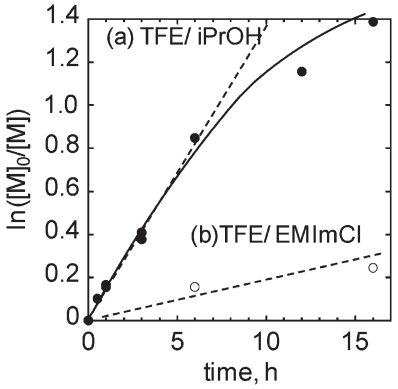


Figure 1. First-order kinetic plots of ln([M]$_0$/[M]) versus time for the ATRP of MTAC at 60 °C (a) in isopropyl alcohol (iPrOH)/2,2,2-trifluoroethanol (TFE) (1/20, v/v) and (b) in 1-ethyl-3-methylimidazolium chloride (EMImCl)/TFE (1/20, wt/wt); [CuBr]/[bpy]/[MTAC]/[EB] = 1/2/500/1 (molar ratio), [EB] = 3.4 mM, where bpy, MTAC, and EB are 2,2′-bipyridyl, 2-(methacryloxy)ethyltrimethylammonium chloride, and ethyl 2-bromoisobutyrate, respectively.

fluoroalcohol, TFE, which is a good solvent for poly(MTAC). Commercially available 80% MTAC aqueous solution was pumped up to remove water, and the white solid residue was diluted with TFE to exchange the solvent. The monomer/TFE solution was passed through the alumina column, filtered off by a PTFE membrane filter, and then collected as a 2.0 mol L^{-1} solution. ATRP of MTAC in TFE at 25 °C for 1 h proceeded homogeneously with an orange color, producing the free polymer with a yield of 73%, M_n of 3.48×10^4, and a rather broad MWD (M_w/M_n = 1.31) (run 3). A small amount of water was added to the polymerization system as a cosolvent, expecting a higher polymerization rate (run 3−8), because ATRP in aqueous solution generally proceeds very quickly. However, increasing the volume ratio of water in TFE ("water/TFE" in Table 1) from 1/50 to 1/1.3 resulted in lower conversions and slower propagation rates. ATRP of MTAC in a 1/50 water/TFE mixture at 25 °C achieved 74% conversion within 1 h (run 3), while only 27% of monomer was consumed by ATRP in a 1/5 water/TFE mixture for 3 h (run 5). In the case of a 1/1.3 water/TFE mixture, it took 20 h to polymerize 50% of MTAC monomer (run 8). The thicknesses of all poly(MTAC) brushes produced by SI-ATRP in a water/TFE mixture were below 10 nm even though the M_n's of the free polymers were 2.3×10^4 to 4.0×10^4. If the M_n's of the free polymer and the brush were the same, the graft density of the brush was estimated to be as low as 0.07 chains nm^{-2}. The graft density of the brush will be precisely described in a later section. Although it is still unclear why the polymerization rate and graft density drastically reduced in a water/TFE mixture, poly(MTAC)s with a narrow polydispersity index below M_w/M_n = 1.2 were obtained.

The additive effect of iPrOH was investigated for the ATRP of MTAC in TFE. ATRP in an iPrOH/TFE mixture with volume ratios of 1/2 and 1/20 at 30 °C proceeded homogeneously and very slowly (runs 9 and 10) compared with ATRP in a water/TFE mixture, resulting in 53−58% conversion after polymerization for 20 h. The MWDs remained at around 1.21−1.23. Controlled polymerization was further improved in the ATRP of MTAC a 1/2 and 1/20 (v/v) iPrOH/TFE mixture at 60 °C to give a free polymer with M_n of 5.37×10^4 to 22.0×10^4 and narrow MWDs of 1.12−1.19 (runs 11−13). The M_n determined by MALS-SEC was slightly higher than the theoretical value based on the yield and the molar ratios of MTAC to EB in the feed, suggesting that initiation efficiency of free initiator EB was 75−85% under the condition. Figure 1 shows a first-order plot of the monomer concentration [M]

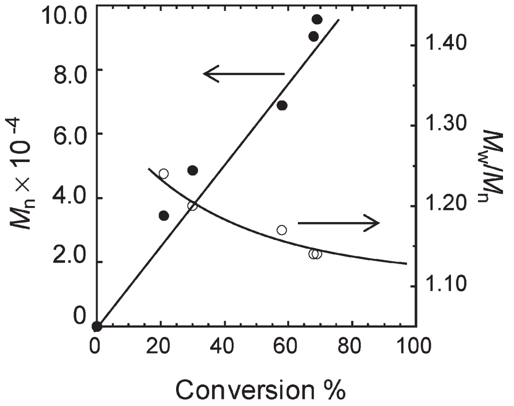


Figure 2. Evolution of the number-averaged molecular weight (M_n) and molecular weight distribution with conversion of ATRP of MTAC in isopropyl alcohol/2,2,2-trifluoroethanol (1/20, v/v) at 60 °C.

(ln([M]$_0$/[M]) vs polymerization time) for the ATRP of MTAC in an iPrOH/TFE mixture at 60 °C. The logarithmic monomer conversion index given by ln([M]$_0$/[M]) increased linearly with polymerization time from the initial stage, indicating that the polymerization rate simply depended on the concentration of monomer and initiator. The apparent propagation rate constant k_p^{app} was 1.0×10^{-2} mol^{-1} L s^{-1}. The plots at higher conversion stage no longer showed a linear relationship; however, the resulting free polymer had a relatively narrow MWD.

As shown in Figure 2, as the monomer conversion increased, the M_n of free poly(MTAC) also linearly increased maintaining narrow MWD by the ATRP in an iPrOH/TFE mixture at 60 °C. With increase in the monomer conversion and the M_n of free polymer from 3.46×10^4 to 9.56×10^4, the thickness of polymer brush also increased from 7 to 24 nm, indicating that the SI-ATRP from surface-immobilized initiator proceeded kinetically similar manner to the ATRP from free initiator EB. The linear relationship between the M_n and the thickness are described in the later section again.

A chain extension experiment was performed for the ATRP in iPrOH/TFE mixture to evaluate the living character of the chain ends. SI-ATRP of MTAC in iPrOH/TFE mixture was carried out at 60 °C to give unbound poly(MTAC) with M_n of 1.94×10^4 and M_w/M_n of 1.06 and the corresponding polymer brush on a silicon wafer. The free resulting polymer was isolated once by precipitation in THF, purified by dialysis in water overnight, and freeze-dried from the methanol/1,4-dioxane (4/1, v/v) mixture. The 5-nm-thick brush substrate was washed with TFE using a Soxhlet apparatus overnight. The purified free poly(MTAC) and the brush substrate were charged into a glass tube again together with a fresh MTAC/TFE solution and degassed by performing freeze−thaw several times. The postpolymerization was carried out at 60 °C for 44 h by the addition of copper catalyst diluted with iPrOH/TFE mixture. As shown in Figure 3, the SEC curve of the postpoly(MTAC) shifted toward the higher molecular side (M_n = 10.6×10^4) than the base-polymer region while maintaining a relatively narrow MWD (M_w/M_n = 1.28). The thickness of the brush was increased to 37 nm by the postpolymerization. These indicate that the halogen group at the propagating chain end of the polymer still retained the ability to reinitiate ATRP. The SEC curve of the postpolymer had a tail at the lower molecular weight region which slightly overlapped with that of the base polymer, although it was at a negligible level.

Molecular Weight and Graft Density of Polymer Brush. It has been reported that a polymer brush prepared by surface-initiated polymerization in the presence of sacrificial free initiator had the same M_n as that of simultaneously produced free

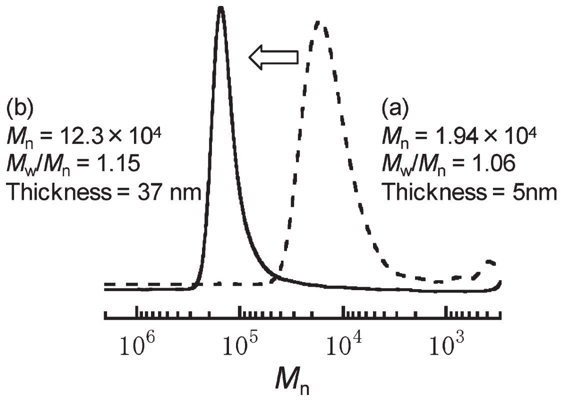


Figure 3. SEC curves for poly(MTAC) produced (a) in the first polymerization in isopropyl alcohol/2,2,2-trifluoroethanol (1/20, v/v) at 60 °C (dot line), M_n(obs) = 1.94×10^4, $M_w/M_n = 1.06$, and (b) in the postpolymerization (solid line), M_n(obs) = 12.3×10^4, $M_w/M_n = 1.15$.

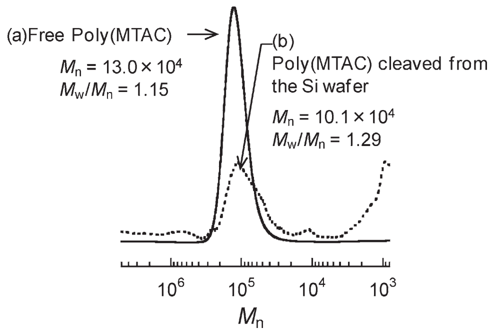


Figure 4. Comparison of SEC traces of (a) free poly(MTAC) produced from ethyl 2-bromoisobutyrate (solid line) and (b) the cleaved poly(MTAC) (dotted line) from the polymer brush generated from surface-immobilized initiator on silicon wafers.

polymer.[39−42] In this work, the surface-grafted poly(MTAC) was cleaved from the substrate to measure the M_n of the brush by SEC. The brush-immobilized flat silicon wafers (65 × 65 mm^2) were immersed in concentrated sulfuric acid for 3 days and carefully neutralized by sodium carbonate aqueous solution. The resulting solution was dialyzed in water to remove inorganic salt ions and concentrated to collect the cleaved polymer. Figure 4 shows the SEC curves of poly(MTAC) generated from the free initiator and the polymer brush isolated from the silicon wafer by acidic hydrolysis, which revealed that both polymers had similar M_n's and relatively narrow MWDs. The SEC curve of the isolated poly(MTAC) brush sample showed low RI intensity and undulation of the baseline due to the extremely low yield of the isolated poly(MTAC) from the substrates. The M_n's of the free poly(MTAC) and the brush were 13.0×10^4 and 10.1×10^4, respectively. The peak of both SEC curves appeared at the same M_n position, although the SEC curve of the polymer brush showed tailing at the lower M_n region. These results indicated that both ATRP from the surface-immobilized initiator and free initiator in a solution proceeded in a controlled manner to give polymers with the same M_n.

The M_n of the polymer brush affects the thickness of the brush. As shown in Figure 5, the thickness of the poly(MTAC) brush was proportional to M_n of the free polymer. The graft density σ of the poly(MTAC) brush prepared by SI-ATRP in TFE/iPrOH solution was estimated to be 0.20 chains/nm^2 on the basis of the relationship between the thickness L (nm) and M_n, as follows:

$$\sigma = d \times L \times N_A \times 10^{-21}/M_n \tag{1}$$

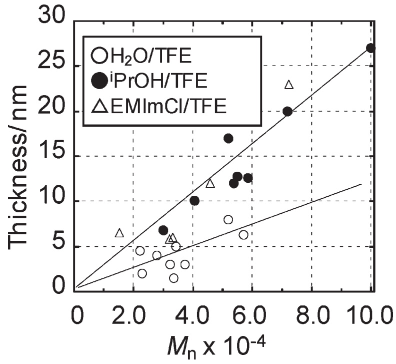


Figure 5. Thickness of poly(MTAC) brushes as a function of the number-averaged molecular weight (M_n) of the corresponding free polymer produced by ATRP in 2,2,2-trifluoroethanol (TFE)/water (open circle), TFE/isopropyl alcohol (filled circle), and in TFE/1-ethyl-3-methylimidazolium chloride (triangle).

where d and N_A are the assumed density of bulk polymer at 293 K and Avogadro's number, respectively. The graft density of the poly(MTAC) brush produced by SI-ATRP in water/TFE mixture was 0.07 chains nm^{-2}, which was lower than that of the brush prepared in the TFE/iPrOH system. If the M_n's of the brush and the corresponding free polymer were the same, a low graft density suggests a low initiator efficiency. The reason for the low graft density of the brush in water/TFE mixture is not clear; densely grafting polymerization might be prevented by the electrostatic repulsion between MTAC monomers in aqueous solution.

SI-ATRP of MTAC in TFE/Ionic Liquid. Imidazolium type ionic liquids are also promising candidates for cosolvents due to their miscibility in MTAC monomer and TFE. For instance, EMImCl and HMImCl are completely miscible in TFE. EMImCl is a solid at room temperature because its melting point is 77−79 °C, while HMImCl is a room-temperature ionic liquid. The reaction mixture of MTAC, TFE, ionic liquid, and copper catalyst gives a red homogeneous and relatively viscous solution compared with the TFE/iPrOH mixture. As shown in Table 2, polymerization in the presence of ionic liquid proceeded very slowly; it took 16 h to achieve 33% conversion by the ATRP of MTAC in EMImCl/TFE (1/20, wt/wt) at 30 °C. However, the resulting polymer had a narrow polydispersity index of 1.12 (run 14). ATRP at 60 °C for 65 h (run 15) gave a polymer with predictable M_n and narrow MWD ($M_n = 11.4 \times 10^4$, $M_w/M_n = 1.13$). A slow polymerization rate can be seen in the first-order plot in Figure 1b. The apparent propagation rate constant k_p^{app} of the ATRP in EMImCl/TFE (1/20, wt/wt) at 60 °C was 1.1×10^{-3} mol^{-1} L s^{-1}, which was much lower than that in the TFE/iPrOH system (1.0×10^{-2} mol^{-1} L s^{-1}). Similar improved control was also observed in the presence of HMImCl (runs 16−20). Poly(MTAC)s with relatively narrow MWDs (M_w/M_n = 1.11−1.28) were obtained by ATPR in TFE containing 10−20 wt % of HMImCl. The graft density of the poly(MTAC) brush estimated from the relationship between the thickness and M_n (Figure 5) was 0.20 chains nm^{-2}, which was the same value as that of the brush prepared in the TFE/iPrOH system.

This is the first case that the ionic liquids were used as additives or cosolvents for ATRP, although the ATRP in a pure ionic liquid has been investigated.[30−36] Therefore, the role of ionic liquids in controlled polymerization of MTAC remains unknown. Several research groups have reported that the polymerization rate of MMA in an ionic liquid was faster than that in bulk or nonpolar organic solvent;[30,33] however, the reduction in rate of the MTAC polymerization was observed by addition of ionic liquid to the reaction mixture in this study. The polymerization rate depends on

Table 2. Surface-Initiated ATRP of MTAC in TFE Containing the Ionic Liquid[a]

run	solvents (weight ratio, wt/wt)	temp, °C	time, h	conv,[b] %	$10^{-4}M_n$ calc[c]	$10^{-4}M_n$ obs[d]	M_w/M_n	thickness, nm[e]
14	EMImCl/TFE (1/20)	30	16	28	2.99	3.32	1.12	6
15	EMImCl/TFE (1/20)	60	65	93	11.0	11.4	1.13	25
16	HMImCl/TFE (1/9)	30	3	21	2.51	3.01	1.16	5
17	HMImCl/TFE (1/4)	30	3	15	1.73	2.21	1.12	3
18	HMImCl/TFE (1/4)	60	6	30	3.18	3.69	1.28	4
19	HMImCl/TFE (1/4)	60	16	39	4.13	4.61	1.24	8
20	HMImCl/TFE (1/9)	60	16	43	5.50	3.22	1.11	5

[a] Atom transfer radical polymerization (ATRP) of [2-(methacryloxy)ethyl]trimethylammonium chloride (MTAC) in 2,2,2-trifluoroethanol (TFE) and 1-ethyl-3-methylimidazolium chloride (EMImCl) or 1-ethyl-3-hexylimidazolium chloride (HMImCl) was carried out with CuBr (0.025 mmol), bpy (0.050 mmol), MTAC (7.2−8.3 mmol), and ethyl 2-bromoisobutylate (EB, 0.025 mmol) in an Ar atmosphere. M_n and M_w represent the number-averaged and weight-averaged molecular weights, respectively. [b] ^{1}H NMR. [c] M_n(calc) = [MTAC]/[EB] × conversion/100 × [MW of MTAC]. [d] M_n(obs) was determined by MALS-GPC calibration using an acetic acid (500 mM) aqueous solution containing $NaNO_3$ (200 mM) as an eluent. [e] Ellipsometry.

the value of the ATRP equilibrium constant, which is the ratio of the rate constants for activation and deactivation established through homolytic cleavage of a C−X bond of dormant species by a Cu^I/ligands complex that generates the corresponding higher oxidation state Cu^{II}/ligands complex deactivator and active species with an organic radical. Therefore, the ATRP equilibrium is governed by a redox process of copper catalyst; a linear correlation has been reported between the logarithm of apparent polymerization rate constant k_p^{app} and the redox potential of Cu^{II}/ligand catalyst.[43,44] We suppose that the imidazolium ionic liquid behaved as an electron-donating solvent enhancing the reducing power of a Cu^{II} complex. As a result, the position of the ATRP equilibrium might be shifted to the dormant species side to result in a slow polymerization rate. On the other hand, not only the coordination of the ionic liquid to copper catalyst but also interaction between MTAC monomer and ionic liquid could occur during the polymerization. Further experiments to explore the effect of ionic liquid on electrolyte monomers are currently in progress.

The surface morphology of the poly(MTAC) brush surface was observed by AFM under air at room temperature (AFM image was shown in Supporting Information). The root-mean-square (rms) of the surface roughness of the poly(MTAC) brushes prepared by SI-ATRP in iPrOH/TFE and ionic liquid/TFE were 0.7 nm in a 2 × 2 μm^2 scanning area. Other polymer brush surfaces prepared in iPrOH/H_2O solution also revealed similar rms values. No significant difference was observed in the surface roughness and morphology of the poly(MTAC) brushes with narrow and broad MWDs in air. The surface roughness of the swollen poly(MTAC) brushes in aqueous solution might be affected by MWD of the polymer. Swollen structures of poly(MTAC) brushes in aqueous solution are characterized by AFM and neutron reflectively measurement,[4,19] which are described in the upcoming paper.

The effect of solvents on the stereochemistry of radical polymerization is attracting great attention in research on controlled polymerization. Okamoto et al. found that free radical polymerization of methyl methacrylate (MMA) in fluoroalcohol at −40 °C afforded a syndiotactic-rich polymer.[45] An enhancement in syndiotacticity was also observed in copper mediated ATRP of MMA in 1,1,1,3,3,3-hexafluoro-2-propanol at −78 °C.[46] Kamigaito et al. prepared stereogradient polymers by ruthenium-catalyzed living radical copolymerization of methacrylate monomers in 2,2,2,2′,2′,2′-hexafluorocumyl alcohol.[47] These stereospecific polymerizations were mainly caused by hydrogen bonding interaction between fluoroalcohols and monomers forming an apparent bulky complex and their large steric effects upon adding monomer to the propagating species. Here, we explore the solvent effect of fluoroalcohol and ionic liquids on the tacticity of poly(MTAC) by ^{13}C NMR. Figure 6 shows ^{13}C NMR signals of carbonyl carbons of poly(MTAC)s produced by ATRP in aqueous solution, TFE/iPrOH, and TFE/EMImCl mixture. Although accurate assignments have not yet been determined for each signal in the spectra, the resonance at 177.6−178.0, 178.0−178.3, 178.2−178.6 ppm may be attributable to *mm*, *mr*, and *rr* triads, respectively, analogous with the case of PMMA.[48] All the samples showed a characteristic sharp peak at 178.4 ppm attributed to the *rr* configuration, indicating that syndiotactic-rich poly(MTAC) was produced by ATRP both in aqueous and in TFE solution. A slight increase in the peak intensity at 177.7 ppm due to the *mm* triad was observed for the polymer produced in TFE/iPrOH; however, the *mm* ratio was lower than 10%. Therefore, the effect of TFE or ionic liquid on the stereoregularity of poly(MTAC) was negligible in this study.

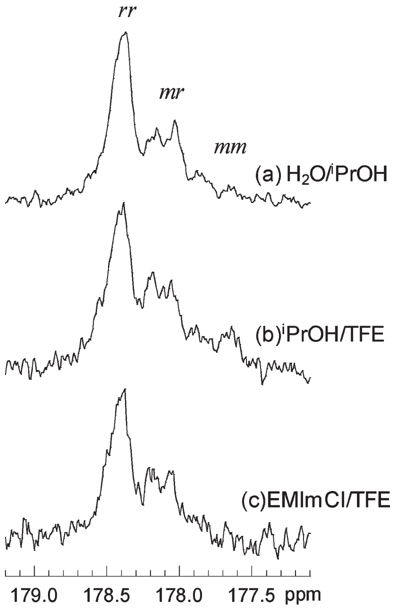


Figure 6. ^{13}C NMR spectra of the carbonyl region of poly(MTAC) synthesized by ATRP in (a) water/isopropyl alcohol (iPrOH) (1/1.5, v/v), (b) iPrOH/2,2,2-trifluoroethanol (TFE) (1/20, v/v), and (c) 1-ethyl-3-methylimidazolium chloride (EMimCl)/TFE (1/20, wt/wt); measured in methanol-d_4 at 25 °C.

Conclusions

In this study, we found that the ATRP of MTAC in TEF in conjunction with a small amount of iPrOH or ionic liquids proceeded in the homogeneous solution state at 60 °C to give poly(MTAC) having narrow MWD (M_w/M_n < 1.19) and predictable M_n even if the M_n was higher than 10^5 g mol^{-1}, indicating satisfactory control of the polymerization. Lower polymerization rates k_p^{app} of 10^{-2} mol L^{-1} s^{-1} in TFE/iPrOH and 10^{-3} mol L^{-1} s^{-1} in TFE/EMImCl were observed than in the aqueous solution. A well-defined poly(MTAC) brush with a graft density of 0.20 chains/nm^{-2} was also prepared on a silicon wafer by SI-ATRP in TFE/iPrOH. Both the resulting free polymer and the corresponding brush can initiate ATRP again smoothly, thus increasing their M_n's and thickness. The combination of TFE and ionic liquid offers good potential is a good candidate solvent for the controlled ATRP and AGET-ATRP of (meth)acrylate monomers bearing various types of polar or charged functional groups.

Supporting Information Available: Surface morphology of the poly(MTAC) brush, including the AFM image. This material is available free of charge via the Internet at http://pubs.acs.org.

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