Grafting of Poly(ϵ-caprolactone) and Poly(ϵ-caprolactone-*block*-(dimethylamino)ethyl methacrylate) from Polymer Microspheres by Ring-Opening Polymerization and ATRP

Guodong Zheng and Harald D. H. Stöver*

Department of Chemistry and Brockhouse Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada L8S 4M1

Received August 8, 2002; Revised Manuscript Received July 24, 2003

ABSTRACT: We report the ring-opening polymerization (ROP) of ϵ-caprolactone catalyzed by $Al(Et)_3$ and $Al[OCH(CH_3)_2]_3$ from lightly cross-linked poly(DVB80-*co*-HEMA) microspheres. The resulting poly(ϵ-caprolactone) grafted particles with active propagating ends were converted to macroinitiators for ATRP and used further to graft (dimethylamino)ethyl methacrylate (DMAEMA) to produce microspheres grafted with block copolymer. The ROP of ϵ-caprolactone from the poly(DVB80-*co*-HEMA) microspheres was carried out both at room temperature and at 70 °C for different reaction times to produce particles with different graft loadings. The subsequent grafting of poly(DMAEMA) blocks using ATRP led to significant particle size increases and to high amine loadings of 5.10 mmol/g of dry particles. The grafted particles were characterized using ESEM, FT-IR, ^{1}H NMR, Coulter particle sizing, and potentiometric titration.

Introduction

Polymers grafted on solid surfaces are being extensively studied, with a range of objectives including improved wetting, friction, adsorption, and adhesion.[1] The grafting-from method has fundamental advantages over the grafting-onto method, such as a higher maximum graft density.[2] To graft polymers from solid surfaces, the initiator groups must be covalently bound to the surface. Living/controlled polymerizations are desirable to limit premature termination of the polymer growing from these surface sites and are required for the formation of block copolymer.

Several living/controlled polymerizations have been used for grafting polymers from solid surfaces.[3] Recently, the most popular living/controlled polymerization used in grafting polymer from solid surfaces has been the atom transfer radical polymerization (ATRP). ATRP[4] allows the synthesis of block copolymers[5] and graft copolymers[6] and is particularly tolerant of water[7] and functional groups. Several groups have reported ATRP grafting from a variety of solid surfaces.[8]

The ring-opening polymerization (ROP) of cyclic esters and related compounds is another living/controlled method suitable for grafting polymer from solid surfaces. The polyester prepared by ROP of ϵ-caprolactone is biodegradable, which is potentially important to different applications.[9] The ROP of cyclic esters can be catalyzed or initiated by organometallic derivatives, with different mechanisms.[10] When metal alkoxides containing free p-, d-, or f-orbitals of a favorable energy are used as initiators, polymer chains grow from the alkoxy group in the initiators, by a two-step "coordination−insertion" mechanism.[11] Among metal alkoxides, aluminum alkoxides such as $Al(OiPr)_3$[12] and $AlOR(Et)_2$[13] have been reported to be efficient initiators toward polymerization and copolymerization of cyclic esters with narrow molecular weight distribution. $AlOR(Et)_2$, prepared by the reaction of $AlEt_3$ with alcohol ROH, has been often used to synthesize α,ω-functional polyester.[14] Using a similar route, Hamaide et al.[15] have reported the heterogeneous ROP of ϵ-caprolactone initiated by $Si-O-Al(OR)_2$ covalently attached to porous silica. This immobilized $Al(OR)_2$ was prepared by reacting Si−OH with $Al(iBu)_3$, followed by replacing the *i*Bu groups with excess ROH. In the heterogeneous ROP process, polymer chains propagated through monomer inserting into the Al−OR bonds, rather than the Al−OSi bonds at the roots of the polymers. However, the $SiO-Al-[(O(CH_2)_5CO)_nOR]_2$ linkage is labile to bases such as water and alcohol. The heterogeneous ROP process was hence only useful for producing tailor-made ω-functionalized (oligo)copolymer and recycling of the silica-bound catalyst. For permanently grafting polymer from particles, the initiating alkoxy group has to be covalently attached to the particle surface through the oxygen, rather than the aluminum.

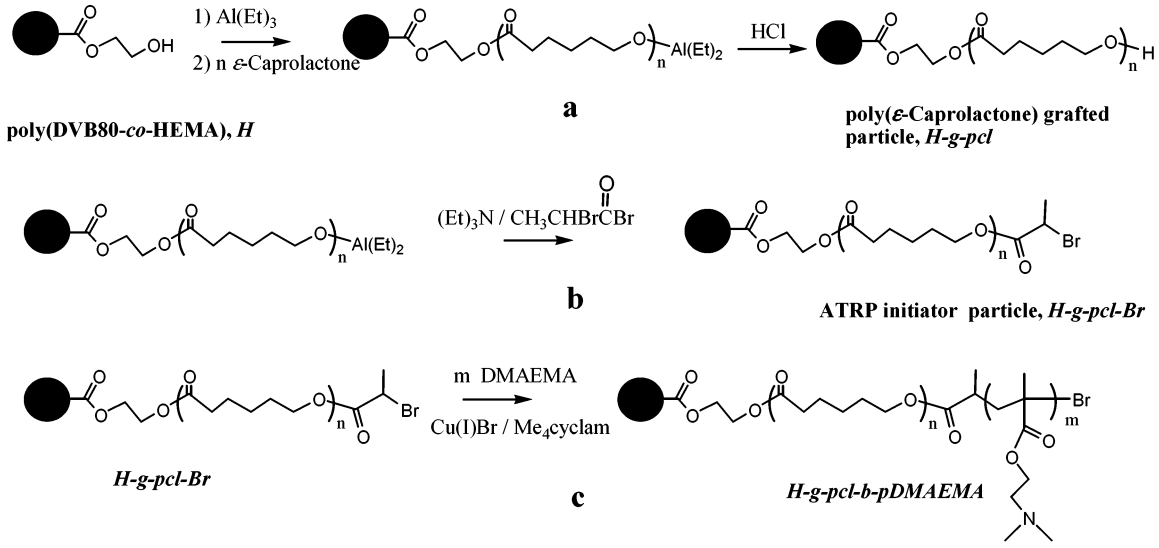
In this paper, we report on the ROP of ϵ-caprolactone from the surface of poly(DVB80-*co*-HEMA) microspheres prepared by precipitation copolymerization in neat acetonitrile. The hydroxy groups of these microspheres were reacted with $Al(Et)_3$ to form $AlOR(Et)_2$ initiating sites. The polyester was then grafted from these initiator sites through monomer insertion at the heads of the polymer chains (Scheme 1a). A subsequent reaction of the chain ends with 2-bromopropionyl bromide (Scheme 1b) permits subsequent graft-ATRP of MMA and DMAEMA. This results in amphiphilic block copolymer grafts combining biodegradable polyester and functional methacrylate blocks (Scheme 1c). Both ROP and ATRP polymerizations could be carried out at room temperature. The present paper describes the synthesis and morphology of these systems. In future work we will investigate to what extent the molecular weight and molecular weight distributions may be controlled in such grafting reactions from swollen cross-linked gels, in both the ROP and ATRP steps.

Experimental Section

Chemicals. Solvents were purchased from Aldrich and used as received unless otherwise specified. Divinylbenzene-80 (DVB80, 70−85% DVB isomers, Fluka, Oakville, Canada), acetonitrile (HPLC grade, Aldrich), 1,4,8,11-tetramethyl-1,4,8,-11-tetraazacyclotetradecane (Me_4cyclam) (98% Aldrich), 2-bro-

10.1021/ma0212902 CCC: $25.00
Published on Web 09/06/2003

Scheme 1. Grafting Poly(ϵ-caprolactone-*b*-DMAEMA) from Poly(DVB80-*co*-HEMA) Microspheres by Subsequent Polymerizations



mopropionyl bromide (97%, Aldrich), triethylaluminum (1.0 M in hexanes, Aldrich), aluminum isopropoxide (98+%, Aldrich), and triethylamine (99%, Aldrich) were used as received. 2,2′-Azobis(2-methylpropionitrile) (AIBN, Eastman Kodak Co.) was recrystallized from methanol. Hydroxyethyl methacrylate (HEMA, 97%), methyl methacrylate (MMA, 99%), and 2-(dimethylamino)ethyl methacrylate (DMAEMA, 98%) were purchased from Aldrich Chemical Co. and purified by distillation under vacuum prior to polymerization. ϵ-Caprolactone (99+%, Aldrich) was dried by storing over active 4 Å molecular sieves. Tetrahydrofuran (THF, 99+%, Aldrich) was refluxed over potassium−sodium alloy and distilled under nitrogen. CuBr was prepared by the reaction of $CuBr_2$ (99%, Aldrich) with dimethyl malonate (99+%, Aldrich).[16]

Syntheses. The poly(DVB-*co*-HEMA) (H_i) starting particles composed of different ratios of HEMA to DVB80 were prepared by precipitation polymerization as reported previously.[17] The particles made with the comonomer ratios $R_{HEMA/DVB}$ of 4.7, 2.7, 1.8, and 1.2 were designated as H_1, H_2, H_3, and H_4.

Typical Procedure To Prepare H_1 Particles. DVB80 (1.05 g, 8 mmol), HEMA (4.95 g, 38 mmol), acetonitrile (200 mL), and AIBN (0.12 g) were placed in a 250 mL polyethylene bottle and shaken vigorously to ensure complete dissolution of the initiator. The bottle was placed in a reactor equipped with horizontal rollers and a programmable temperature controller. The reactor gently agitates the sample by rolling the bottles at approximately 4 rpm. The temperature profile used for polymerization started with a 1 h ramp from room temperature to 60 °C followed by a 100 min ramp to 70 °C and then a further 24 h at 70 °C. The resulting particles were isolated by vacuum filtration over a 0.5 μm membrane filter with three subsequent washings with THF. The yield of clean particles was 3.04 g (50.7%) after drying at room temperature under vacuum for 24 h. The remainder is unreacted monomer.

Grafting ϵ-Caprolactone from H_1 Initiator Particles by ROP. Method A. Poly(DVB-*co*-HEMA) particles H_1 (0.30 g) were dispersed in 8 mL of dry THF together with either $(Et)_3Al$ (2.0 mL of 1.0 M solution in hexanes, 2.0 mmol) or $[(CH_3)_2CHO]_3Al$ (0.41 g, 2.0 mmol) and stirred for 1 h. ϵ-Caprolactone (2.00 g, 17.5 mmol) was rapidly added into the suspension, and the polymerization was continued at 70 °C for 5 h. The resulting grafted particles were filtered on 0.5 μm Teflon filter paper, followed by three washings each with acidic methanol (5% concentrated aqueous HCl) and THF. The yield of the modified particles was 0.64 g ($(Et)_3Al$, Table 1, entry 4). This method was also used for polymerization at room temperature, and the results are listed in Table 1, entries 14−22.

Method B. Poly(DVB-*co*-HEMA) particles H_1 (2.00 g) were dispersed in 50 mL of dry THF for 2 h, and then $(Et)_3Al$ (2.5 mL of 1.0 M solution in hexanes, 2.5 mmol) was added slowly.

Table 1. Weight Gain and Diameter of Poly(ϵ-caprolactone) Grafted Particles Using $(Et)_3Al$

entry[a]	reaction time [h]	weight gain [%]	diameter[c] [μm]
1	1[d]	3	1.40
2	2[d]	65	1.72
3	3[d]	100	1.81
4	5[d]	113	1.89
5	10[d]	106	1.85
6	20[d]	71	1.77
7	30[d]	73	1.77
8[b]	0.5[e]	0	1.56
9[b]	1.5[e]	0	1.56
10[b]	2.5[e]	1	1.56
11[b]	3.5[e]	1.5	1.56
12[b]	4.5[e]	3	1.60
13[b]	5.5[e]	6	1.60
14	0.5[e]	0	1.56
15	1.5[e]	5	1.60
16	2.5[e]	8	1.64
17	3.5[e]	26	1.68
18	4.5[e]	30	1.72
19	5.5[e]	40	1.74
20	6.5[e]	43	1.74
21	8.5[e]	50	1.82

[a] H_1 were used as initiator in the presence of excess $Al(Et)_3$. [b] H_1-$Al(Et)_2$ were used as initiator. [c] 1.40 μm particles were used for polymerization at 70 °C; 1.56 μm particles were used for polymerization at 20 °C. [d] Reaction temperature 70 °C. [e] Reaction temperature 20 °C.

The reaction mixture was stirred at room temperature for 4 h, and the reacted particles were isolated by centrifugation, followed by three washings each with dry THF and diethyl ether. The resulting initiator particles H_1-$Al(Et)_2$ (2.15 g) were dried under vacuum for 12 h (2.15 g). These initiator particles H_1-$Al(Et)_2$ (0.30 g) were subsequently used for the ROP of ϵ-caprolactone as described in method A, for 5.5 h and without adding further $Al(Et)_3$, and yielded 0.32 g of modified particles (entry 13, Table 1).

ATRP Initiator Particles (H_1-g-pcl-Br). Poly(ϵ-caprolactone) grafted particles (1.42 g) made from 1.00 g of H_1 by ROP at room temperature for 5.5 h according to method A were suspended for 2 h in 10 mL of THF containing 0.45 g (4.4 mmol) of triethylamine. 2-Bromopropionyl bromide (0.95 g, 4.4 mmol) was added dropwise into the suspension. An ice−water bath was used during the addition of 2-bromopropionyl bromide, and the resulting mixture was slowly allowed to warm to room temperature and stirred with a magnetic stirrer for 16 h. The resulting ATRP initiator particles were filtered and washed three times each with THF and methanol. The

resulting particles (1.60 g) were isolated and dried at room temperature under vacuum for 24 h.

Grafting DMAEMA from Microspheres H_1-g-pcl-Br by ATRP. The particles H_1-*g*-pcl-Br (0.50 g) were suspended in 5 mL of THF containing 2.0 g (13 mmol) of DMAEMA and purged by passing THF-saturated nitrogen through the solution for 30 min. A degassed solution of CuBr (35 mg, 0.24 mmol) and Me_4-cyclam (62.6 mg, 0.24 mmol) in 2 mL of CH_3CN was transferred into the suspension through a cannula. The mixture was stirred with a magnetic bar at room temperature under nitrogen for 10 h. The resulting grafted particles were centrifuged and redispersed three times each in THF and in aqueous NH_4OH/methanol (1/20 by volume), until the particles became almost white. The particles were finally washed with ether and dried at room temperature under vacuum for 24 h. The yield of the resulting particles was 2.44 g.

Particle Size Analysis. The particle sizes and size distributions were measured using a 256-channel Coulter Multisizer II interfaced with a computer and fitted with a 30 μm aperture tube. A small amount of particles, dispersed in acetone, was added to 25 mL of Coulter Isoton II electrolyte solution and stirred for 1 min with the ministirrer supplied with the instrument. The Coulter Multisizer measurements were confirmed using a Philips ElectroScan 2020 environmental scanning electron microscope (ESEM).

ESEM Analysis. The ESEM samples were prepared by dispersing the particles in THF and casting a drop of the resulting particle suspension on a piece of microscopy cover glass glued onto an ESEM stub. The samples were dried under vacuum for 2 h and sputter-coated with 5 nm gold.

TEM Analysis. The internal structure of the grafted particles was studied using a JEOL 1200EX transmission electron microscope. Here, the samples were embedded in Spurr's epoxy resin and ultramicrotomed to generate 40−60 nm thick slices. The samples had sufficient contrast without staining.

Potentiometric Titration. Acid−base titration was performed on a Mandel PC-Titrate potentiometric titrator. Poly(DMAEMA) grafted particles (typically 0.2 g) were added to 20 mL of 0.1 M aqueous HCl, and 0.1 M NaOH was used to titrate the mixture using an addition rate of 1.0 mL/min. The amount of NaOH consumed between the two equivalent points of HCl and the protonated amine corresponds to the amount of tertiary amine on the particles.

FT-IR Analysis. Fourier transform infrared analysis was performed on a Bio-Rad FTS-40 FT-IR spectrometer. All samples were prepared as pellets using spectroscopic grade KBr in a Carver press at 15 000 psi. The spectra were scanned over the range 4000−400 cm^{-1} in the transmission mode, accumulating 16 scans at a resolution of 2 cm^{-1}.

Results and Discussion

The starting microspheres containing hydroxy groups were prepared by precipitation polymerization of divinylbenzene-80 (DVB80, 70−85% DVB isomer) and hydroxyethyl methacrylate (HEMA) in neat acetonitrile as described earlier.[13] Different ratios $R_{HEMA/DVB}$ of HEMA to DVB80 were used to explore the effects of cross-linking degree and hydroxy loading. Both concentration and availability of hydroxy groups in the particles should depend strongly on the comonomer ratio, since at low values for $R_{HEMA/DVB}$ the remaining HEMA groups would also be less accessible due to the higher degree of cross-linking.

Preliminary experiments showed significant differences in the efficiency of grafting poly(ϵ-caprolactone) from particles having different monomer compositions. The particles H_1, H_2, H_3, and H_4 having $R_{HEMA/DVB}$ values of 4.7, 2.7, 1.8, and 1.2, respectively, were used to initiate the ROP of ϵ-caprolactone in the presence of $Al(Et)_3$. The weights of particles H_1, H_2, H_3, and H_4 after polymerization at 70 °C for 10 h increased by 107, 70, 37, and again 37%, respectively. These results confirm that the particles H_1, with the lowest cross-linker level and the highest HEMA level, give the highest grafting levels based on graft weight. It is not clear why H_3 and H_4 gave identical weight gains. Hence, in this project we focused on particles H_1 as seeds for grafting poly(ϵ-caprolactone) and poly(ϵ-caprolactone-*block*-DMAEMA).

ROP of ϵ-Caprolactone by Using $Al(Et)_3$ and Al(*i*-PrO)$_3$. Two types of reagents, triisopropoxyaluminum $Al[OCH(CH_3)_2]_3$ and triethylaluminum $Al(Et)_3$, were used to generate the initiators for the grafting ROP of ϵ-caprolactone. As mentioned above, ϵ-caprolactone can be activated by Al−O bonds in aluminum alkoxides. When triethylaluminum $Al(Et)_3$ was used, hydroxy groups on the particles first reacted with it to form aluminum alkoxides. Subsequently, the resulting particle-bound aluminum alkoxides started polymer chains growing from the particle. Any excess of triethylaluminum $Al(Et)_3$ in the solution should not affect the grafting ROP polymerization and could in fact be used to remove trace water, if needed. However, the resulting aluminum hydroxides might also initiate ROP of ϵ-caprolactone since a few percent of soluble poly(ϵ-caprolactone) was observed in the present grafting reactions. Table 1 shows the results of ROP grafting poly(ϵ-caprolactone) from H_1 initiator particles using free $Al(Et)_3$ at 70 °C (entries 1−7) and 20 °C (entries 14−21).

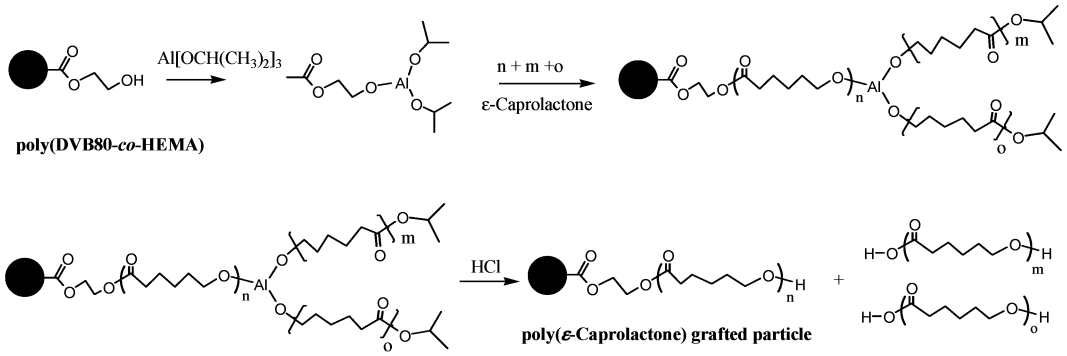
In contrast, triisopropoxyaluminum, $Al[OCH(CH_3)_2]_3$, proved to be a more complicated reagent. Triisopropoxyaluminum can react with primary hydroxy groups on the particles through an alkoxide exchange reaction, resulting in particle-bound aluminum alkoxides. Polymer chains could then grow both from these particle-bound, primary alkoxides, but also from the remaining aluminum isopropoxy moieties, both particle-bound and free. The poly(ϵ-caprolactone) chains originating from isopropoxy groups would be cleaved from the particle-bound as well as from the free initiator upon washing with hydrogen chloride (Scheme 2). This side reaction would account for the significant amount of soluble polymer observed. Therefore, triisopropoxyaluminum, $Al[OCH(CH_3)_2]_3$, is less efficient than $Al(Et)_3$ in terms of grafting polymer from particles.

The ESEM images show that grafting using $Al(Et)_3$ resulted in larger particle sizes (a) compared to grafting using $Al[OCH(CH_3)_2]_3$ (b) (Figure 1). The particle diameter increased by about 31% and 15%, and the weight increased by 82% and 40%, respectively.

Effects of Temperature, Monomer Loading, and Reaction Time on Particle Properties Formed Using Free $(Et)_3Al$. The initial grafting rate for the particles H_1 increased when the ROP of ϵ-caprolactone from the particles was carried out at 70 °C instead of at room temperature. However, at longer polymerization times at this elevated temperature, both weight and size of the grafted particles reached a maximum and subsequently decreased (Table 1, entries 1−7). As well, ESEM images show corresponding morphology changes (Figure 2), where the particles showed fuzzy surfaces after 5 h reaction, with bridges between particles reminiscent of higher molecular weight polymer grafted from a lightly cross-linked surface. At longer reaction times the particle sizes and weights decreased slightly, and the particles showed a smoother surface, with less bridging between particles.

One possible explanation for this observation involves an equilibrium between polymerization and depolym-

Scheme 2. Grafting Poly(ϵ-caprolactone) from Poly(DVB80-*co*-HEMA) Microspheres Catalyzed by Triisopropoxyaluminum



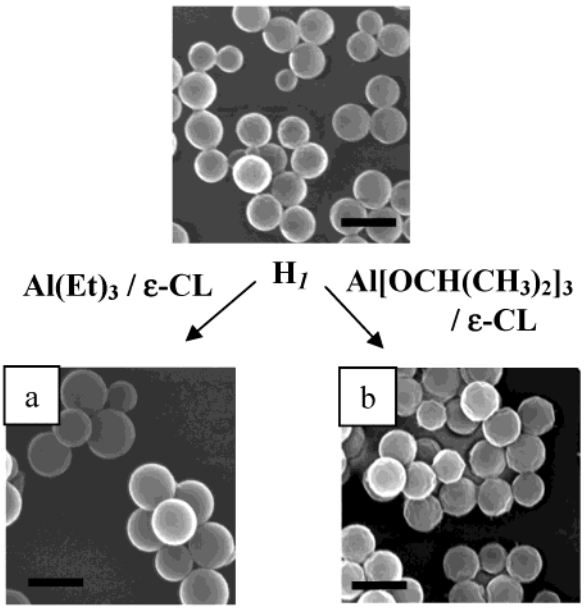


Figure 1. ESEM Images of starting particles (H_1) and of the poly(ϵ-caprolactone) grafted particles formed using (a) $Al(Et)_3$ or (b) $Al[OCH(CH_3)_2]_3$. The scale bar is 2 μm.

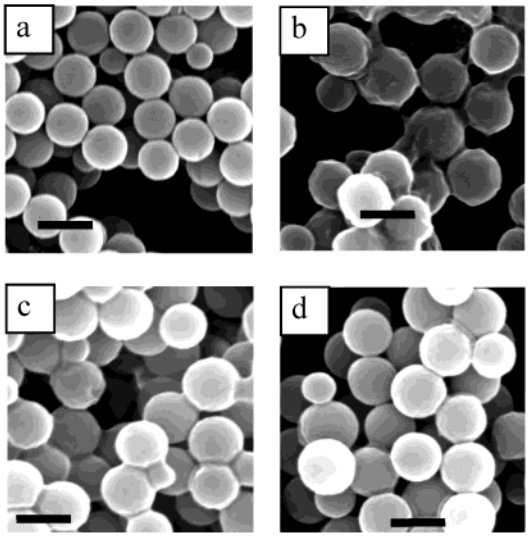
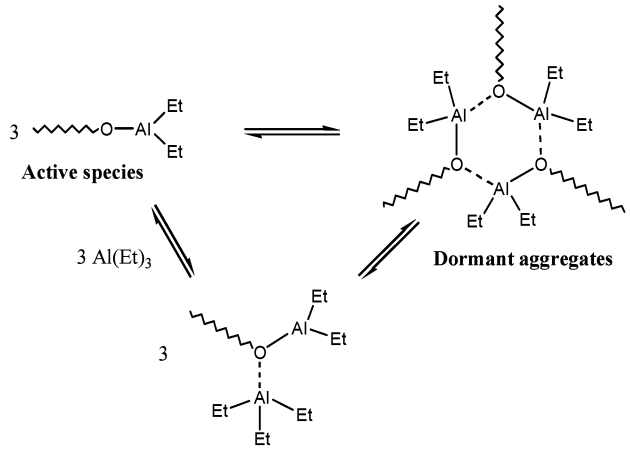


Figure 2. ESEM images of the poly(ϵ-caprolactone) grafted particles after different reaction times at 70 °C: (a) H_1, (b) 5 h, (c) 10 h, (d) 30 h. The scale bar is 2 μm.

erization of ϵ-caprolactone at 70 °C. As the known depolymerization and backbiting reactions generate not only ϵ-caprolactone but also cyclic dimers or oligomers,[18] the equilibrium molecular weight should go through a maximum, as the reaction effectively converts monomer into cyclic oligomers. This could account for the observed reduced particle weight, particle size, and interparticle bridging observed at high reaction times.

Scheme 3. Possible Structure of Aggregated Catalysts



The grafting of ϵ-caprolactone from the particles could also be carried out at room temperature, though at a much slower rate (Table 1, entries 14−21). In contrast to the reaction at 70 °C, the size of the particles grafted at room temperature continued to increase with reaction time throughout the reaction.

To investigate the effect of excess $Al(Et)_3$ on the ROP, initiator particles were prepared by reaction of particles H_1 with $Al(Et)_3$ and isolated following thorough washing with dry THF. The resulting initiator particles were much less active than those formed in situ in the presence of excess $Al(Et)_3$. The particle size increased slowly with reaction time (Table 1, entries 8−13). The lower activity of these preformed initiator particles may be attributed to deactivation by residual moisture or to the formation of nonactive complexes (Scheme 3).

Duda et al. reported the formation of such nonactive aggregates in solution ROP of (di)lactones in the presence of aluminum alkoxides.[19] In fact, only a small fraction of dissociated aluminum alkoxides are active in ROP of (di)lactones. In our case, aluminum alkoxides were tethered on particles, and the local concentration of the aluminum complex should be very high, possibly leading to an even smaller fraction of active complex. The excess $Al(Et)_3$ might prevent the association of the tethered aluminum alkoxides by coordinating to electron pairs on the aluminum alkoxide oxygens. During the preparation of the initiator particles, the excess $Al(Et)_3$

was washed away and the equilibrium would shift to the dormant, aggregated side.

An induction period for solution ROP of lactones was observed by Teyssié et al. with aluminum isopropoxide as the initiator in stoichiometric conditions.[20] The induction period was interpreted in terms of the aggregates that required time to dissociate. The induction period was also observed in this study and could be shortened by adding excess $Al(Et)_3$.

Conversion of the Propagating End into Initiator for ATRP, and ATRP of DMAEMA To Form Block Copolymer. The subsequent grafting of a different polymer using ATRP, from the particles grafted with poly(ϵ-caprolactone), was attempted in order to prepare block copolymer grafted particles having hydrophilic shells. To this end, the propagating aluminum alkoxide ends were directly converted to ATRP initiator groups by reaction with 2-bromopropionyl bromide in the presence of triethylamine. The hydrophilic monomer DMAEMA was then grafted from the resulting 2-bromopropionate-terminated poly(ϵ-caprolactone) grafts, converting the originally hydrophobic particles into polar, ionizable particles that are well dispersible in water.

The poly(ϵ-caprolactone) grafted particles prepared at room temperature for 5.75 h were used for the conversion of initiating groups from ROP to ATRP. The 2-bromopropionate groups on the particles showed a characteristic FT-IR band due to the methyl groups at 1380 cm^{-1}.[14] The intensity of this band became weaker during ATRP due to the decrease in relative concentration of the 2-bromopropionate group.

The ATRP of DMAEMA from the initiator particle H_1-*g*-pcl-Br was carried out at room temperature, using CuBr/Me_4cyclam as catalyst and THF as solvent. The ATRP of DMAEMA catalyzed by CuBr/Me_4cyclam was very effective. Polymers were grafted from the particles H_1-*g*-pcl-Br with 97.0% and 98.4% monomer conversion, for weight ratios of DMAEMA to initiator particles of 4.0 and 2.6, resulting in block-grafted particles H_1-*g*-pcl-*b*-pdmaema (A) and (B), respectively. These particles H_1-*g*-pcl-*b*-pdmaema were hydrophilic and dispersed easily in both polar organic solvents and water. They tended to aggregate upon drying, likely due to the long, polar chains grafted on their surfaces.

Because of the high swellability of the original particles, we expect that the block grafts will be distributed both within and on the surface of the particles, in analogy to similar particle morphologies discussed earlier.[16] Future studies will explore a potential gradient composition due to the core−shell crosslinking gradient expected for the H_1 seed particles.

Aggregation in solution was also observed when a nonpolar solvent such as hexane was added to the suspension of the grafted particles in a good solvent such as THF. The long, surface grafts function as steric stabilizer in good solvents but collapse in poor solvents.

The ESEM images of the block-grafted particles H_1-*g*-pcl-*b*-pdmaema illustrate the morphologies and sizes of the particles (Figure 3). The size of the grafted particles increased dramatically compared to the initiator particles H_1-*g*-pcl-Br. When the particles H_1-*g*-pcl-*b*-pdmaema were cast on a glass piece from a THF suspension, the particles fused into a polymer matrix upon drying, presenting clearly the particle cores and a matrix formed from the surface grafts. Individual, relatively spherical particles were observed when aggregates of the particles made by addition of nonsolvent to a suspension cast on a glass piece. This indicates that the grafted polymer shrinks upon addition of a nonsolvent and collapses down onto the particle surface.

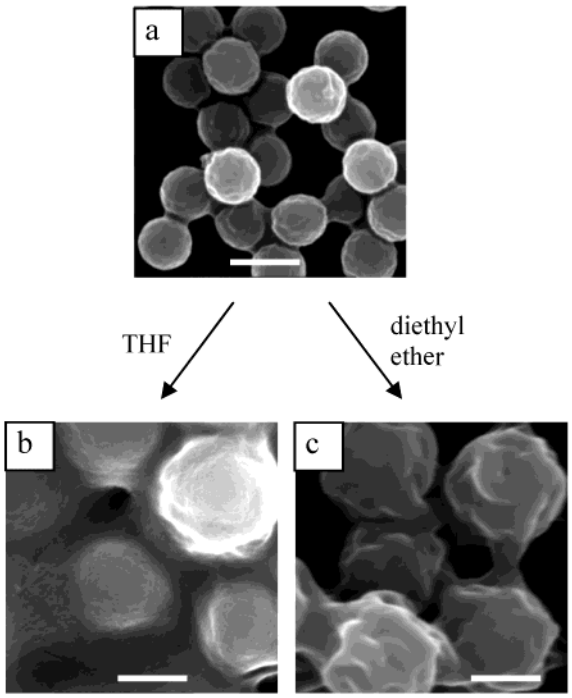


Figure 3. ESEM images of room temperature grafted particles: (a) poly(ϵ-caprolactone) grafted particles; (b) poly(ϵ-caprolactone-*b*-DMAEMA) grafted particles cast from THF; (c) poly(ϵ-caprolactone-*b*-DMAEMA) grafted particles cast from diethyl ether. The scale bar is 2 μm.

The internal structure of the grafted microspheres was studied using transmission electron microscopy. Particles were embedded in Spurr's resin and ultramicrotomed (Figure 4). The particles grafted with poly(ϵ-caprolactone) show a core−shell structure with a dark ring of poly(ϵ-caprolactone) and a light core representing the particle H_1. After the core−shell particles were grafted with poly(DMAEMA), an irregular contour comprised mainly of linear poly(DMAEMA) surrounds each core−shell particle. This corona of poly(DMAEMA) was presumably swollen by the epoxy resin, as indicated by some regions within it having similar contrast to interstitial epoxy resin.

The amount of grafted poly(DMAEMA) on the particles was confirmed by acid−base titration. The particles were added into an excess of 0.1 M HCl and back-titrated by 0.1 M NaOH. Free HCl in solution was first neutralized to give the first equivalent point at pH 4.0, and then the protonated amine was titrated past pH 10. The amount of NaOH consumed between the two equivalent points corresponds to the amount of tertiary amine groups. The titration curve demonstrated a very sharp jump at the second equivalent point, similar to the behavior expected for free tertiary amine (Figure 5), suggesting that the poly(DMAEMA) grafted from the particles is largely accessible and solvated. The amount of grafted poly(DMAEMA) on the particles H_1-*g*-pcl-*b*-pdmaema (A) and (B) as described above was calculated on the basis of the NaOH consumed. Functional amine loadings of 5.10 and 4.53 mmol/g, corresponding to 80.2 and 71.1 wt %, were found, consistent with their weight increase during the grafting polymerization.

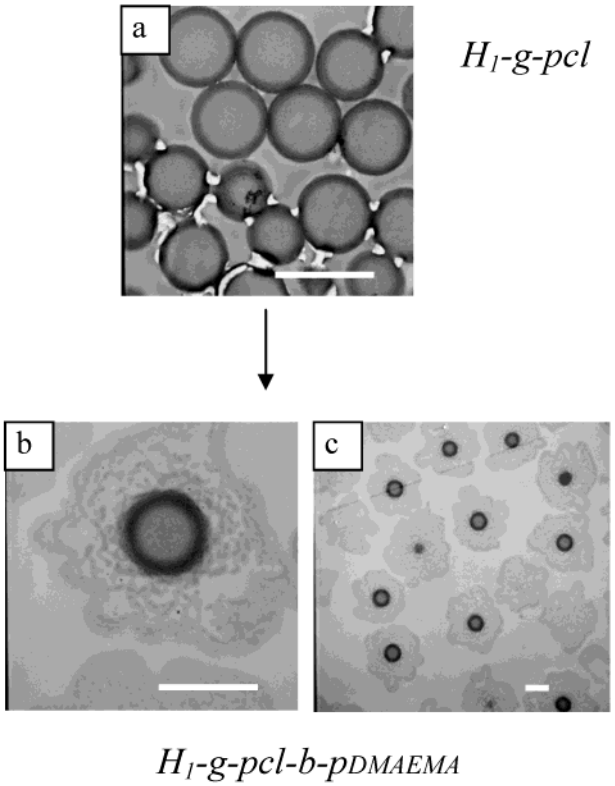


Figure 4. TEM images of sectioned samples of H_1-*g*-pcl and H_1-*g*-pcl-*b*-pdmaema: (a) poly(ϵ-caprolactone) grafted particles; (b, c) poly(ϵ-caprolactone-*b*-DMAEMA) grafted particles at different magnifications. The scale bar is 2 μm.

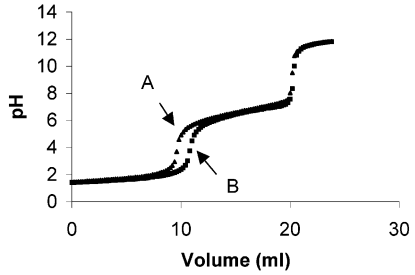


Figure 5. Acid−base titration on the grafted particles: (A) 0.188 g of H_1-*g*-pcl-*b*-pdmaema particles (formed by grafting 1.94 g of poly(DMAEMA) off 0.50 g of H_1-*g*-pcl-Br); (B) 0.238 g of H_1-*g*-pcl-*b*-pdmaema particles (formed by grafting 1.28 g of poly(DMAEMA) off 0.50 g of H_1-*g*-pcl-Br).

FT-IR and NMR Study of the Grafted Particles. The surface modification and the grafted polymer were studied by FT-IR. The starting particles H_1 composed of poly(DVB80-*co*-HEMA) showed the expected hydroxy stretch at 3445 cm^{-1}, as well as the ester group at 1725 cm^{-1} (Figure 6). The ROP of ϵ-caprolactone on the DVB80−HEMA particles H_1 changed the relative ratios, but not the nature of these functional groups. The ratio of hydroxy to ester groups decreased with polymerization, as seen from the gradual decline in intensity at 3445 cm^{-1} in the samples of grafted particles H_1-*g*-pcl generated at increasing reaction time (not shown). Similarly, the absorptions at 1605 and 1511 cm^{-1} due to aromatic carbon−carbon double bond stretches decreased during polymerizations, and the poly(ϵ-caprolactone) C−H stretching band at ca. 3000 cm^{-1} became more pronounced.

When the ATRP initiator was introduced onto the particles H_1-*g*-pcl, the characteristic methyl stretch of 2-bromopropionate at 1380 cm^{-1} was observed (not shown). The adsorption can be used as a probe to monitor the ATRP, with the band becoming weaker during ATRP of DMAEMA due to the relative reduction in the methyl group concentration. The new functional groups arising from the tertiary amine in DMAEMA show two C−N stretching bands at 1272 and 1239 cm^{-1}. The hydroxyl and aromatic stretching bands further diminished during ATRP.

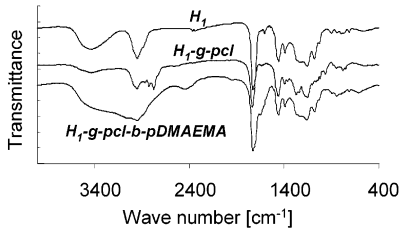


Figure 6. FT-IR spectra of grafted particles. H_1: poly(DVB80-*co*-HEMA) particles made using 82.5 mol % HEMA; H_1-*g*-pcl: poly(ϵ-caprolactone) grafted from particles H_1 particles using free $Al(Et)_3$ at 70 °C for 30 h; H_1-*g*-pcl-*b*-pdmaema: poly(DMAEMA) grafted from the corresponding particles H_1-*g*-pcl-Br.

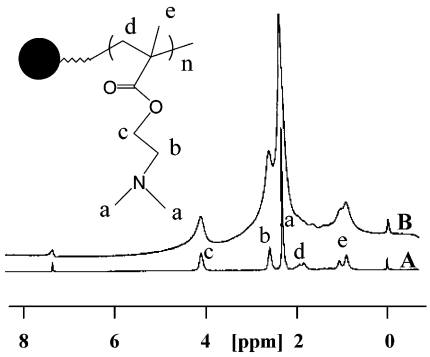


Figure 7. Gel ^1H NMR of H_1-*g*-pcl-*b*-pdmaema: (A) linear poly(DMAEMA) in $CDCl_3$; (B) H_1-*g*-pcl-*b*-pdmaema swollen in $CDCl_3$.

A gel ^1H NMR spectrum of the grafted particles H_1-*g*-pcl-*b*-pdmaema swollen in $CDCl_3$ is shown in Figure 7. The chemical shift at 2.2 ppm is attributed to the methyl groups on the tertiary amine. The shape of the peak is very typical of soluble polymers, which indicates that the grafted particles dispersed well in CD_3OD and that the grafted polymer on the particles behaved like soluble polymer.

Conclusion

Poly(ϵ-caprolactone) was grafted from lightly cross-linked poly(DVB80-*co*-HEMA) particles using ring-opening polymerization (ROP) in the presence of $Al(Et)_3$. The poly(ϵ-caprolactone) grafted particles with active propagating ends were subsequently converted to ATRP initiators, followed by the ATRP of DMAEMA to generate grafted block copolymer. The grafting of a hydrophilic polymer block from hydrophobic polymer blocks on the particles poly(DVB80-*co*-HEMA) dramatically increased the particle size from 1.57 to 2.24 μm with high amine functional loading of 5.10 mmol/g. The grafted particles were characterized using ESEM, FT-IR, ^1H NMR, Coulter particle sizing, and potentiometric titration.

References and Notes

(1) Böttcher, H.; Hallensleben, M. L.; Nuss, S.; Wurm, H. *Polym. Bull. (Berlin)* **2000**, *44*, 223−229. Perruchot, C.; Khan, M.

A.; Kamitsi, A.; Armes, S. P.; von Werne, T.; Patten, T. *Langmuir* **2001**, *17*, 4479−4481. Huang, X.; Wirth, M. J. *Macromolecules* **1999**, *32*, 1694−1696. Angot, S.; Ayres, N.; Bon, S. A. F. Haddleton, D. M. *Macromolecules* **2001**, *34*, 768−774. Prucker, O.; Rühe, J. *Macromolecules* **1998**, *31*, 592−601, 602−613.

(2) Jordan, R.; Graf, K.; Riegler, H.; Unger, K. K. *Chem. Commun.* **1996**, *9*, 1025.

(3) Zheng, G.; Stöver, H. D. H. *Chin. J. Polym. Sci.*, in press.

(4) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721−1723. Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614−5615. Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28*, 7970−7972.

(5) Zhang, X.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 1763−1766. Jankowa, K.; Kops, J.; Chen, X.; Gao, B.; Batsberg, W. *Macromol. Rapid Commun.* **1999**, *20*, 219−223. Braumert, M.; Fröhlich, J. Stieger, M.; Frey, H.; Mülhaupt, R.; Plenio, H. *Macromol. Rapid Commun.* **1999**, *20*, 203−209. Robinson, K. L.; de Paz-Báñez, M. V.; Wang, X. S.; Armes, S. P. *Macromolecules* **2001**, *34*, 5799−5806.

(6) Grubbs, R. B.; Hawker, Dao, J.; C. J.; Fréchet, J. M. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 270−272.

(7) Wang, X. S.; Armes, S. P. *Macromolecules* **2000**, *33*, 6640−6647. Wang, X.-S.; Jackson, R. A.; Armes, S. P. *Macromolecules* **2000**, *33*, 255−257. Perruchot, C.; Khan, M. A.; Kamitsi, A.; Armes, S. P.; von Werne, T.; Patten, T. E. *Langmuir* **2001**, *17*, 4479−4481. Sarbu, T.; Pintauer, T.; McKenzie, B.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3153−3160. Lowe, Andrew, B.; McCormick, Charles, L. *Aust. J. Chem.* **2002**, *55*, 367−379.

(8) von Werne, T.; Patten, T. E. *J. Am. Chem. Soc.* **1999**, *121*, 7409−7410. Huang, X.; Doneski, L. J.; Wirth, M. J. *Anal. Chem.* **1998**, *70*, 4023−4029. Shah, R. R.; Mecerrecyes, D.; Husemann, M.; Rees, I.; Abbott, N. L.; Hawker, C. J.; Hedrick, J. L. *Macromolecules* **2000**, *33*, 597−605. Luzinov, I.; Minko, S.; Senkovsky, V.; Voronov, A. *Macromolecules* **1998**, *31*, 3945−3952. Husemann, M.; Malmström, E. E.; McNamara, M.; Mate, M.; Mecerrecyes, D.; Benoit, D. G.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J. *Macromolecules* **1999**, *32*, 1424−1431. Ejaz, M.; Yamamoto, S.; Ohno, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* **1998**, *31*, 5934−5936. Angot, S.; Ayres, N.; Bon, S. A. F.; Haddleton, D. M. *Macromolecules* **2001**, *34*, 768−774. Huang, W.; Kim, J.-B.; Bruening, M. L.; Baker, G. L. *Macromolecules* **2002**, *35*, 1175−1179. Zhao, B.; Brittain, W. J. *Macromolecules* **2000**, *33*, 8813−8820. Sankhe, A. Y.; Husson, S. M.; Kilbey, S. M. *Mater. Res. Soc. Symp. Proc.* **2002**, *710* (Polymer Interfaces and Thin Films), 277−282.

(9) Nouvel, C.; Ydens, I.; Degee, P.; Dubois, P.; Dellacherie, E.; Six, J. L. *Macromol. Symp.* **2001**, *175*, 33.

(10) Mecerreyes, D.; Jérôme, R.; Dubois, P. *Adv. Polym. Sci.* **1999**, *147*, 1−59.

(11) Nijenhuis, A. J.; Grijpma, D. W.; Pennings, A. J. *Macromolecules* **1992**, *25*, 6419−6424.

(12) Duda, A.; Penczek, S. *Macromolecules* **1995**, *28*, 5981−5992. Ropson, N.; Dubois, P.; Jérôme, R.; Teyssié, P. *Macromolecules* **1995**, *28*, 7589−7598.

(13) Dubois, P.; Jérôme, R.; Teyssié, P. *Polym. Bull. (Berlin)* **1989**, *22*, 475−482.

(14) Barakat, I.; Dubois, P.; Jérôme, R.; Teyssié, P. *J. Polym. Sci., Polym. Chem.* **1993**, *31*, 505−514. Dubois, P.; Degee, P.; Jérôme, R.; Teyssié, P. *Macromolecules* **1992**, *25*, 2614−2618.

(15) Miola, C.; Hamaide, T.; Spitz, R. *Polymer* **1997**, *38*, 5667−5676. Tortosa, K.; Miola, C.; Hamaide, T. *J. Appl. Polym. Sci.* **1997**, *65*, 2357−2372.

(16) Zheng, G.; Stöver, H. D. H. *Macromolecules* **2002**, *35*, 6828−6834.

(17) Zheng, G.; Stöver, H. D. H. *Macromolecules* **2002**, *35*, 7612−7619.

(18) Nelissen, M.; Keul, H.; Hoecker, H. *Macromol. Chem. Phys.* **1995**, *196*, 1645−1661.

(19) Duda, A.; Penczek, S. *Macromol. Chem. Macromol. Symp.* **1991**, *47*, 127−140.

(20) Ouhadi, T.; Stevens, C.; Teyssié, Ph. *Makromol. Chem. Suppl.* **1975**, *1*, 191−201.

MA0212902