Water-Dispersible Carbon Black Nanocomposites Prepared by Surface-Initiated Atom Transfer Radical Polymerization in Protic Media

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ABSTRACT: The synthesis of hydrophilic carbon black composites by grafting 2-(dimethylamino)ethyl methacrylate (DMAEMA) from functionalized carbon black using atom transfer radical polymerization (ATRP) is reported. The polymerizations were performed in methanol/water mixtures near ambient temperatures using $CuBr/CuBr_2$/2,2′-bipyridine as the catalytic system. Under acidic conditions or upon quaternization with ethyl bromide, the polymer-bound carbon black can form stable dispersions in water. TGA, light scattering, and AFM were used to characterize the polymer bound carbon black. 2-Hydroxyethyl methacrylate (HEMA) was random and block copolymerized with DMAEMA to form functional carbon black nanocomposites.

Introduction

Carbon blacks are structurally complex particles containing 90−99% of elemental carbon. The smallest dispersible units of carbon black are irregularly shaped aggregates ranging in size from 50 to 500 nm. The aggregates are composed of chemically coalesced spherically shaped primary particles with diameters of 10−75 nm. Beyond the basic structures, aggregates of carbon black can easily form agglomerates that are physically held together. Carbon black is widely used in rubber industry as a reinforcing agent and in the plastics industry for its antistatic, conductive, and UV-protective capacities.[1−4] Recently, carbon black/polymer composites have been studied as vapor-sensing materials.[5,6] Carbon black is also an important pigment used for plastics,[1,2] packaging,[7] coatings,[8] ink,[9] inkjet,[10,11] and toner applications.[12,13] To apply carbon black in waterborne coatings, ink, and toners, a stable dispersion of carbon black in aqueous medium is desired.

Despite its hydrophobic nature, carbon black can be dispersed in water by using ionic or nonionic surfactants.[14−17] In these systems, the hydrophobic parts of surfactants adsorb onto carbon black and the hydrophilic parts interact with water, providing steric/static repulsions between carbon black aggregates.[18] The colloidal stability of these systems depends on the amount of adsorbed surfactants and the hydrodynamic thickness of the adsorbed layer.[19] The stability of dispersed carbon black decreases upon addition of some solvents or prolonged storage due to desorption of the surfactant molecules from the carbon black surface.

The surfactants or polymers that chemically linked to carbon black should provide higher dispersion stability. Nagai and co-workers copolymerized acrylonitrile with a polymerizable surfactant by a radical initiator in the presence of carbon black in water and achieved higher dispersion stabilization due to the successful immobilization of the surfactant on the carbon black surface.[20,21] Carbon black is known to be a strong radical scavenger due to the presence of polycondensed aromatic rings and quinonic and phenolic oxygens. Propagating polymeric or oligomeric radicals can be easily trapped during polymerization by the carbon black surface. Tsubokawa[22] took advantage of this feature and achieved water-dispersible poly(ethylene oxide)-grafted carbon black by trapping poly(ethylene oxide) radicals formed by the redox reaction of ceric ions with the polymer's hydroxy chain ends.

Instead of grafting in-situ formed or preformed polymers onto the surface of carbon black, which is a diffusion-controlled process, water-soluble polymers can be grafted from carbon black surface. Li et al.[8] introduced hydroxymethyl groups onto the carbon black surface and polymerized acrylic acid and 2-hydroxyethyl methacrylate (HEMA) from surface-immobilized radicals generated by ceric ions. They observed that the grafted carbon black displayed much better dispersion stability and stronger resistance to electrolytes as well as long-term storage stability in soap-free waterborne coatings.

Although conventional radical polymerization methods are good for growing homopolymers or random (co)polymers under mild conditions, controlled radical methods are more desirable to achieve interesting functionalities and architectures with controlled molecular weight and low polydispersities.[23] ATRP is among most successful controlled radical polymerization methods because it is applicable to readily available initiators, ligands, and monomers and allows for the preparation of polymers with interesting functionalities and architectures.[24−37] ATRP has also proved to be one of the most versatile methods to functionalize surfaces as shown by a number of recent reviews.[38−43] Among the publications, grafting polymers from surface in protic media has received continued attention and has been done not only on planar surfaces[44−51] but also on inorganic[52] and organic particles.[53−57]

In our previous communication, we successfully employed ATRP to synthesize poly(*n*-BA)-grafted carbon black.[58] Jin and co-workers also demonstrated that ATRP can be used to polymerize three monomers from functionalized carbon spheres.[59] To our knowledge, there has been no report to date on synthesizing water-dispersible carbon black by employing ATRP

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in protic media. Herein we report our results on polymerizing 2-(dimethylamino)ethyl methacrylate (DMAEMA) from the carbon black surface using ATRP in protic medium and subsequent quaternization of the polymer to achieve water-dispersible carbon black. The polymer-grafted carbon black samples were analyzed by thermogravimetric analysis (TGA), light scattering, and atomic force microscopy (AFM). Random and block copolymers of DMAEMA and HEMA were also grafted from carbon black to achieve functionalized carbon black nanocomposites.

Experimental Section

Materials. 2-(Dimethylamino)ethyl methacrylate (DMAEMA) and 2-hydroxyethyl methacrylate (HEMA) were purchased from Aldrich and passed through basic alumina column prior to polymerization. CuBr (97%) was obtained from Aldrich and purified and dried as reported before.[60] $CuBr_2$, 2,2′-bipyridine, 4-(dimethylamino)pyridine (4-DMAP), and 1,3-dicyclohexylcarbodiimide (DCC) were obtained from Aldrich and were used as received. Difunctional initiator, 2,2-dimethyl-3-hydroxypropyl α-bromoisobutyrate, was synthesized according to literature.[61] All the other chemicals were purchased from Aldrich.

Carbon black (Monarch 700) and carbon black aqueous dispersions (carboxylate-stabilized carbon black, CB−COONa) were supplied by Cabot Corp. (Billerica, MA).

Functionalization of Carbon Black with ATRP Initiator Moiety. 15 g of CB−COONa (0.52 mmol of carboxylate per gram of carbon black, 0.0078 mol) was acidified to pH 2 to precipitate the carbon black. After the carbon black was washed with DI water and isolated by centrifugation several times, it was dried under vacuum at 60 °C for 12 h prior to further modifications. The carbon black sample was homogenized by a rota-stator in 250 mL of dry THF. To this dispersion, DCC (0.156 mol, 32.2 g), DMAP (0.039 mol, 4.76 g), and 2,2-dimethyl-3-hydroxypropyl α-bromoisobutyrate (0.156 mol, 39.5 g) were added. The reaction was homogenized for 5 h and allowed to proceed overnight while stirred by a magnetic stirbar. The functionalized carbon black was then purified by multiple centrifugations in THF and methanol.

Polymerization of DMAEMA from Functionalized Carbon Black Surface (CB−PDMAEMA). Before the polymerization, a predetermined amount of carbon black (CB−Br, 0.87 g, 0.17 mmol of bromine per gram of carbon black that corresponds to 0.15 mmol of initiator) was added into a Schlenk flask and dried under vacuum at room temperature for 1 h. To the Schlenk flask were added DMAEMA (11.8 g, 75.0 mmol), MeOH (11 g), water (1.4 g), DMF (1.0 mL), bipyridine (0.15 g, 0.96 mmol), and $CuBr_2$ (0.040 g, 0.18 mmol). The flask was then degassed by four freeze−pump−thaw cycles. While the contents were frozen in liquid nitrogen, the flask was back-filled with nitrogen and CuBr (0.043 g, 0.30 mmol) was added. The flask was then degassed and back-filled with nitrogen twice and then allowed to warm to room temperature, and an initial sample ($t = 0$) was collected by syringe. The flask was then placed in an oil bath thermostated at 30 °C. Aliquots were taken out of the flask periodically. Conversion of the monomer was monitored by GC in conjunction with NMR. The reaction was stopped at desired conversions.

Polymerization of DMAEMA from 2,2-Dimethyl-3-hydroxypropyl α-Bromoisobutyrate with/without Carbon Black. As shown in the above example, the same amount of reagents were used. The difference is the use of a small molecular ATRP initiator, 2,2-dimethyl-3-hydroxypropyl α-bromoisobutyrate (0.038 g, 0.15 mmol), instead of CB−Br. For the experiment with unfunctionalized carbon black present, the same amount of unmodified Monarch 700 was used instead.

ATRP of DMAEMA from Functionalized Carbon Black (CB−Br) in the Presence of a Sacrificial Initiator. 2,2-Dimethyl-3-hydroxypropyl α-bromoisobutyrate (0.0127 g, 0.050 mmol) and CB−Br (0.58 g, 0.17 mmol of bromine per gram of carbon black, which corresponds to 0.10 mmol of initiator) were used as the sacrificial and surface initiator, respectively. The other components of the polymerization remained the same. Three parallel reactions were performed in the same thermostated oil bath after the same freeze−thaw cycles. Reactions were stopped by opening the flasks to air at predetermined intervals. Monomer conversion was determined as before. Molecular weight of the polymers generated in solution was obtained by GPC using DMF as the eluent.

Purification of CB−PDAEMA by Centrifugation. The products from the synthesis were isolated by centrifugation and sonification in methanol. The sample was then centrifuged at 39 000*g* force for 2 h. The process was repeated until there was no polymer detectable in the supernatant by GPC.

Quaternization of CB−PDMAEMA with Ethyl Bromide. The above CB−PDMAEMA (0.50 g) was dispersed in 20 mL of THF by sonication and was treated with 10 mL of ethyl bromide. The mixture was allowed to stir overnight. The precipitated product was isolated by removing the solvent and excess alkyl halide.

Polymerization of DMAEMA and HEMA from Functionalized Carbon Black Surface. Before the polymerization, a predetermined amount of carbon black (CB−Br, 0.87 g, 0.17 mmol of bromine per gram of carbon black that corresponds to 0.15 mmol of initiator) was added into a Schlenk flask and dried under vacuum at room temperature for 1 h. To the Schlenk flask were added DMAEMA (9.83 g, 62.5 mmol), HEMA (1.63 g, 12.5 mmol), MeOH (11 g), water (1.4 g), bipyridine (0.15 g, 0.96 mmol), and $CuBr_2$ (0.040 g, 0.17 mmol). The flask was then degassed by four freeze−pump−thaw cycles. While the contents were frozen in liquid nitrogen, the flask was back-filled with nitrogen and CuBr (0.043 g, 0.30 mmol) was added. The flask was then degassed and back-filled with nitrogen twice and then allowed to warm to room temperature, and an initial sample ($t = 0$) was collected by syringe. The flask was then placed in an oil bath thermostated at 30−32 °C. Aliquots were taken out of the flask periodically. Conversion of the monomer was monitored as shown before. The reaction was stopped at desired conversions.

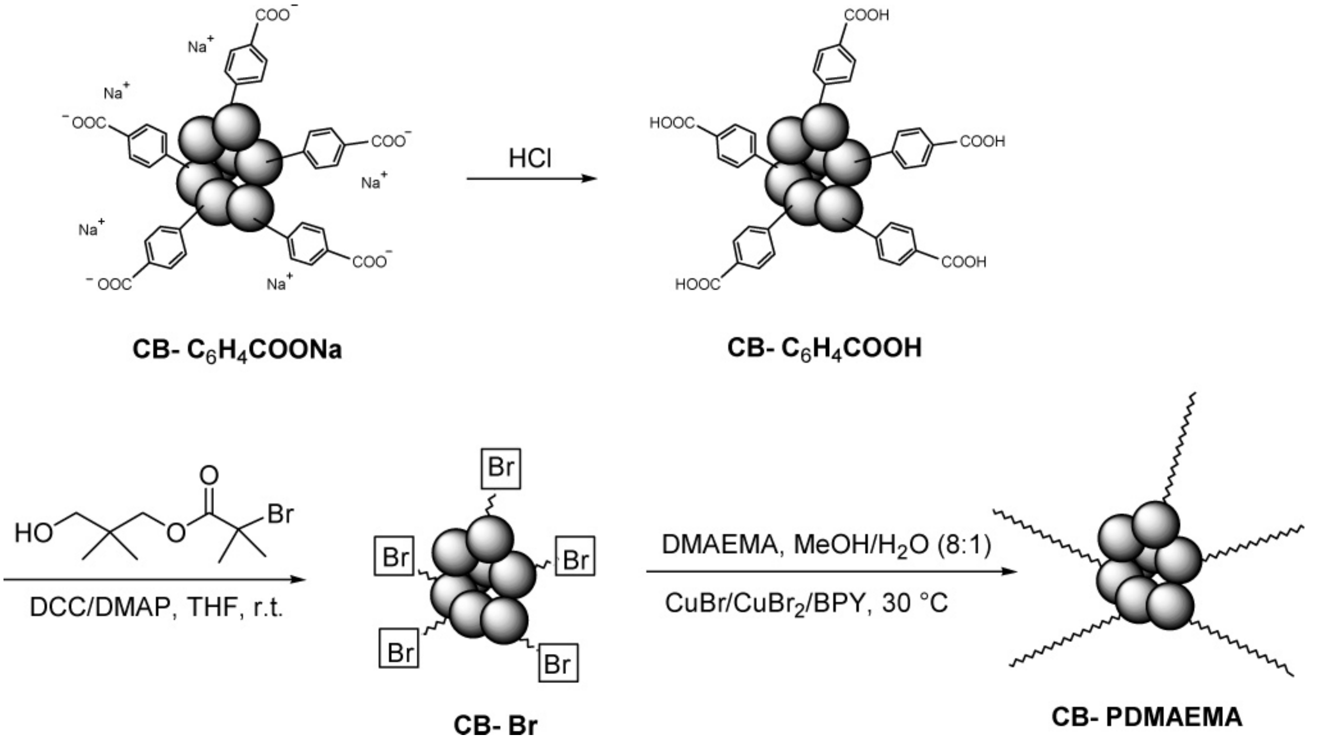
Polymerization of HEMA from CB−PDMAEMA. Before the polymerization, a predetermined amount of CB−PDMAEMA (0.35 g) was added into a Schlenk flask and dried under vacuum at room temperature for 1 h. To the Schlenk flask were added HEMA (6.52 g, 50 mmol), MeOH (8 g), water (1.0 g), bipyridine (0.075 g, 0.48 mmol), and $CuBr_2$ (0.020 g, 0.085 mmol). The flask was then degassed as described as before.

Characterizations. Monomer conversion was determined from the concentration of residual monomer by gas chromatography (GC) or NMR with DMF as internal standard. For GC measurement, aliquots from the reaction were diluted with acetone or methanol and injected directly into a Shimadzu GC-14 gas chromatograph equipped with a J&W Scientific 30 m DB-WAX column with a Shimadzu CR501 Chromatapac. Analysis conditions: injector/detector temperature: 250 °C; temperature program: 2 min 40 °C, 20 °C/min until 160 °C, 3 min 160 °C. The conversion was calculated by detecting the decrease of the monomer peak area relative to the internal standard peak area. GC measurements were repeated three times for each sample to reduce errors. For NMR measurements, ^1H NMR was performed on a Bruker 300 MHz or a Varian 300 MHz spectrometer.

Molecular weights of the kinetic samples were measured by GPC (Waters 717) by dissolving the polymer samples in DMF with a drop of toluene as the internal standard using DMF as the eluent at a flow rate of 1 mL/min. The molecular weight and polydispersities of the samples were determined on the basis of a calibration curve generated from poly(methyl methacrylate) standards in conjunction with a refractive index detector.

AFM measurements were carried out with the aid of a Nanoscope III (Digital Instruments, Santa Barbara, CA) equipped with phase extender module and vertical engage J scanner. The images were acquired in the tapping mode (light tapping mode near resonance frequency) under ambient conditions with standard silicon cantilevers with a nominal spring constant of 50 N/m and a resonance frequency around 300 kHz. The polymer-grafted carbon black samples were dispersed in a solvent (THF or water) and diluted to

Scheme 1. Functionalization of ATRP Initiator on Carbon Black Surface



a concentration of ∼0.001 wt %. 1−2 drops of the THF dispersions were dripped onto freshly cleaved mica (Ruby clear mica, New York Mica Co.) spinning at 4000 rpm at room temperature. For aqueous samples, 1 drop of the sample was put on mica surface and allowed to dry at room temperature overnight.

Centrifugation of the samples was performed in a refrigerated Sorvall RC 5C plus centrifuge at 16 500 rpm (corresponding to 39 000*g* force) at 4 °C.

Fourier transform infrared measurements were performed on an ATI Mattson Infinity Series FTIR spectrometer. The spectra were obtained after accumulation of 128 scans at a resolution of 2 cm^{-1} between 500 and 4000 cm^{-1}.

The determination of grafted polymer on carbon black was performed on AutoTGA 2950 (TA Instruments). About 10 mg of the dried samples was placed in a Pt pan under nitrogen. The samples were kept at 110 °C for 10 min before being heated to 650 °C at 10 °C/min. Finally the samples were kept at 650 °C for 15 min.

The size of the polymer-grafted carbon black particles was obtained on a MICROTRAC particle size analyzer (UPA). The measurement technique is based on dynamic light scattering. The dispersions of carbon black particles were diluted in a suitable solvent until the final concentrations were as low as few parts per million (ppm). The sample cell was a 316 stainless steel cell with a capacity for samples 3−8 mL in volume, and the acquisition time for the sample measurement was 360 s.

Results and Discussion

ATRP of DMAEMA from Functionalized Carbon Black Surface. The starting carbon black (CB−COONa) was dispersible in water due to electrostatic repulsions from surface carboxylate groups. The particles can be destabilized and isolated by either adding electrolytes or adjusting pH of the solution. In our experiments, the particles were collected by acidifying the solution to pH ∼ 2. The ATRP initiator with hydroxy group was then attached to the surface via DCC/DMAP facilitated coupling reaction, as shown in Scheme 1. The content of attached initiator was determined on the basis of bromine content from elemental analysis.

The functionalized carbon black particles (CB−Br) with 0.17 mmol of bromine per gram of carbon black were then used for ATRP of DMAEMA. ATRP of DMAEMA in water/alcohol mixtures is known to afford good control and fast polymerizations.[62−65] In the experiments, a methanol/water mixture (8:1 w/w) was used to obtain a fast rate as well as good control over molecular weight. As shown in Figure 1, the polymerization of DMAEMA initiated by the functional initiator, 2,2-dimethyl-3-hydroxypropyl α-bromoisobutyrate, afforded a relatively fast polymerization rate at 30 °C. The semilogarithmic kinetic plots indicated a constant radical concentration in the reaction system. Carbon black is known to be a strong radical scavenger, and when unfunctionalized carbon black was put into the system, a

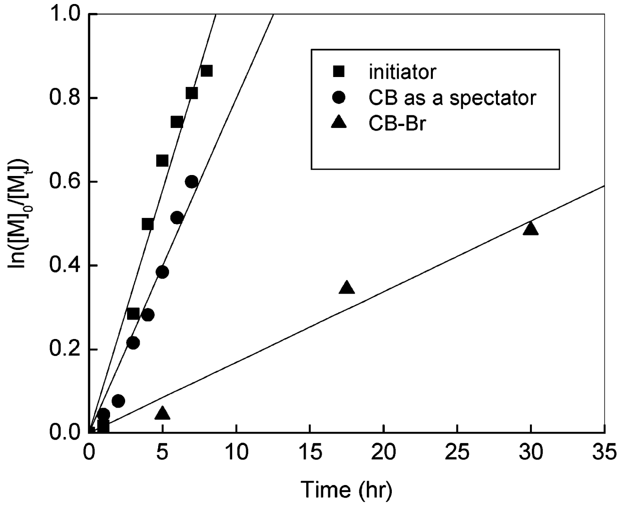


Figure 1. Kinetics of ATRP of DMAEMA initiated by 2,2-dimethyl-3-hydroxypropyl α-bromoisobutyrate (■), by the same initiator in the presence of carbon black (●), and by surface-anchored initiator CB−Br (0.17 mmol of bromine per gram of carbon black) (▲). [DMAEMA]:[initiator]:[CuBr]:[$CuBr_2$]:[BPY] = 500:1:2:1.2:6.4, [DMAEMA] = 50 wt %, $MeOH/H_2O$ = 7.9:1 (w/w). The reactions were conducted at 30−32 °C.

slight decrease of polymerization rate was observed in the kinetics. The lower slope indicates a slight decrease in radical concentration in the system, proving the radical trapping effect of carbon black. Then the reaction was stopped by opening the reaction medium to air, and the carbon black was easily collected by centrifugation. After multiple sonification−centrifugation cycles in methanol, the supernatant layer in the centrifuge tube was found to be free of poly(DMAEMA) by GPC. The sedimented carbon black was then analyzed by TGA and found to contain only 8.4% of polymer at 45% monomer conversion. Previously, we observed a much higher polymer content when carbon black was present in the ATRP of *n*-butyl acrylate (*n*-BA): at a conversion of 62% (monomer-to-initiator ratio = 375), TGA revealed a volatile content of 27.7%.[58] The difference can be explained by a stronger affinity of the in-situ generated polymer toward hydrophobic surface and a better dispersibility or more available surface area for unmodified carbon black in *n*-BA/anisole compared with MeOH/water. When ATRP of DMAEMA was initiated from functionalized carbon black, despite a linear relationship observed in the semilogarithmic plot, the reaction was 7 times slower compared to that initiated by the small molecule initiator. Three factors can contribute to this observation: first, radicals tethered on surface can couple with neighbors or get trapped by the surface. Second, carbon black is hydrophobic in nature, and it is harder to obtain discrete aggregates under normal magnetic stirring conditions when hydrophilic methanol/H_2O mixtures are used. Third, the surface initiator density was calculated on the basis of the bromine content obtained from elemental analysis; however, the initiator accessible for the copper catalyst could be lower than analyzed by elemental analysis due to the aggregated structure of carbon black particles, more complicated than discrete well-separated spherical particles. Because of the long reaction time in this case, a noticeable amount of methyl methacrylate (MMA) was formed as shown in GC chromatograph as a new peak. This is attributed to the transesterification reaction between methanol and DMAEMA, which was previously reported by Armes,[66] and the tranesterification was believed to be self-catalyzed by the tertiary amine groups in DMAEMA. However, when pure poly(DMAEMA) was placed in the same reaction medium in our control experiment at 30 °C, no transesterification was observed for 2 days, which was also reported by Armes.[66] This can be explained by the decreased basicity of the amine groups in the polymer chain. Poly(DMAEMA) has a lower pK_a compared to that of DMAEMA[67] due to charge repulsions between neighboring groups once the amines on the side chain are protonated. In our case, after 30 h, the content of MMA in the monomer and solvent mixture was calculated to be around 40 mol % by GC and confirmed by NMR. The presence of MMA also led to the formation of statistical copolymers of DMAEMA and MMA on carbon black.[66] NMR analysis of the polymer-grafted carbon black indicated that around 33% PMMA was present.

To monitor the molecular weight evolution of the polymer grafted on carbon black, the functional initiator used in the kinetic studies was added to the system as a sacrificial initiator because it was reported that free polymers formed in the solution have the same molecular weight as those formed on the surface assuming fast exchange between the two populations of polymers in the same system.[68,69] As shown in Figure 2, the molecular weight of the free polymers were measured by GPC at different conversions in the polymerization with $^{1}/_{3}$ of the total initiator being the sacrificial initiator in the solution. A linear increase of molecular weight vs conversion was observed (Figure 2B), indicating negligible transfer in the polymerization. However, polydispersities increased, suggesting presence of termination processes.

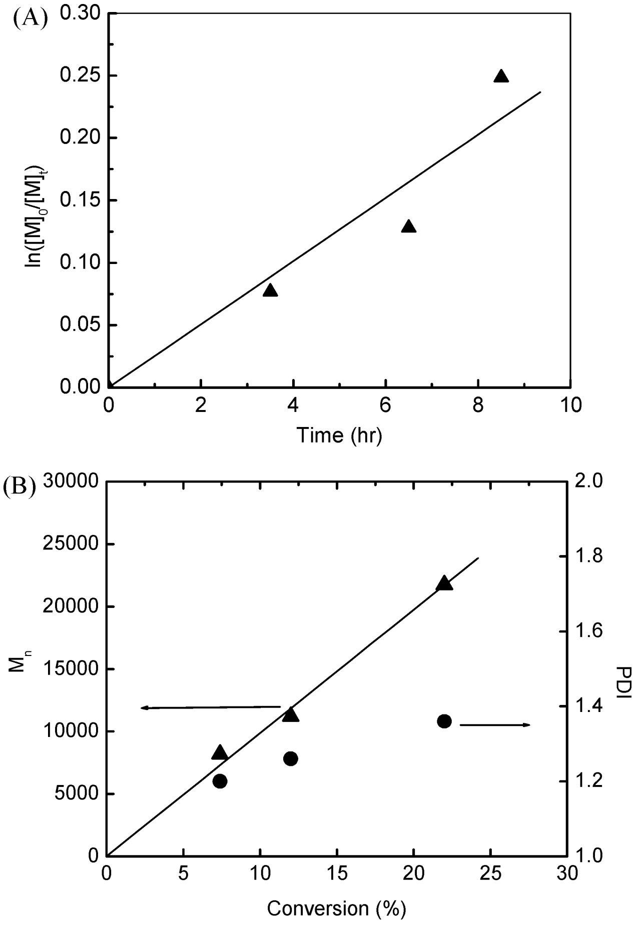


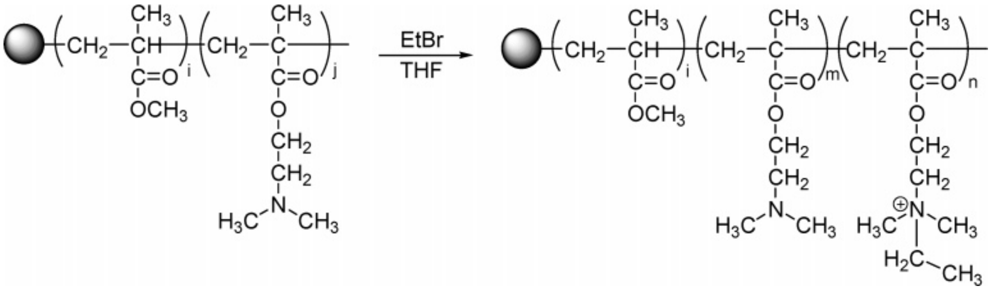
Figure 2. Kinetics (A) and molecular weight vs conversion (B) in the ATRP of DMAEMA from functionalized carbon black surface in the presence of sacrificial initiator. [CB−Br]:[sacrificial initiator] = 2:1. [DMAEMA]:[total initiator]:[CuBr]:[$CuBr_2$]:[BPY] = 500:1.5:2:1.2:6.4, [DMAEMA] = 50 wt %, MeOH/H_2O = 7.9:1 (w/w). The reactions were conducted at 30−32 °C. CB−Br (0.17 mmol of bromine per gram of carbon black) was used together with sacrificial initiator.

Quaternization of CB−PDMAEMA. Poly(DMAEMA) belongs to a family of hydrophilic polymers exhibiting reverse temperature-dependent solubility in water with an LCST around 50 °C.[65,70,71] Once attached to carbon black, the resulting CB−PDMAEMA was not dispersible in water even after prolonged sonification but formed good dispersions in methanol, THF, and DMF. Therefore, the sedimentation of CB−PDMAEMA by centrifugation was performed in MeOH/H_2O (3:1 v/v) mixture, which dissolved free unattached polymer as indicated by GPC chromatograms.

However, CB−PDMAEMA was dispersible in acidified water, which protonates the amino groups on the polymer chains resulting in a layer of surface-anchored polyelectrolytes surrounding the carbon black cores. Because of charge repulsions, CB−PDMAEMA can form stable dispersions at low pH. When the pH of the solution was adjusted to a pH ~ 9, CB−PDMAEMA immediately precipitated out from the aqueous solution.

Poly(DMAEMA) was linked to the surface of carbon black by ester bonds, which may not be stable under acidic conditions during prolonged storage. An alternative way to form stable CB−poly(DMAEMA) aqueous dispersions is to quaternize the

Scheme 2. Quaternization of Poly(DMAEMA)-Grafted Carbon Black by Ethyl Bromide



nitrogen groups on the polymer side chain with alkyl halide to achieve a layer of strong cationic polyelectrolytes around carbon black. As shown in Scheme 2, ethyl bromide was used in the quaternization reaction after CB−PDMAEMA was dispersed in THF. Poly(DMAEMA) homopolymer quaternized by ethyl bromide displayed strong antibacterial activities against *E. coli.*[72] As the reaction proceeded, the polymer-grafted carbon black was found to precipitate out from the solution. After removing the solvent, the particles were readily dispersible in water after sonication. The dispersions were stable throughout the pH range and even in boiling water. Armes reported a complete elimination of LCST for block copolymers of DMAEMA with (diethylamino)ethyl methacrylate even when the degree of quaternization was as low as 15%.[73] To explain the good solubility of the particles in water, the degree of quaternization on one of the PDMAEMA bound carbon black samples was studied by ^{1}H NMR in D_2O, and the original sample in deuterated acetone is shown in Figure 3 for comparison. The original unquaternized sample displayed the peaks from not only poly(DMAEMA) but also PMMA (methyl ester at 3.65 ppm), proving tranesterification occurred during the ATRP process. The relative integration area of *d* vs *h* revealed that 28% MMA was incorporated in the poly(DMAEMA). When the sample was quaternized with ethyl bromide, it was not soluble in acetone but in water. In D_2O, new peaks due to the two methyl groups attached to nitrogen shifted to lower magnetic field (from 2.5 to 3.4 ppm). New peaks labeled *c*, *e*, *f*, *j*, and *k* appeared due to the presence of quaternary amines. The efficiency of quaternization was estimated to be around 92% based on the relative peak area of *b* vs *f* ($[(f/3/(f/3 + b/6)] \times 100\%$). The result explained the good solubility and stability of the polymer-grafted particles in water.

The polymer content and particle size of the original CB−PDMAEMA and quaternized CB−PDMAEMA were compared

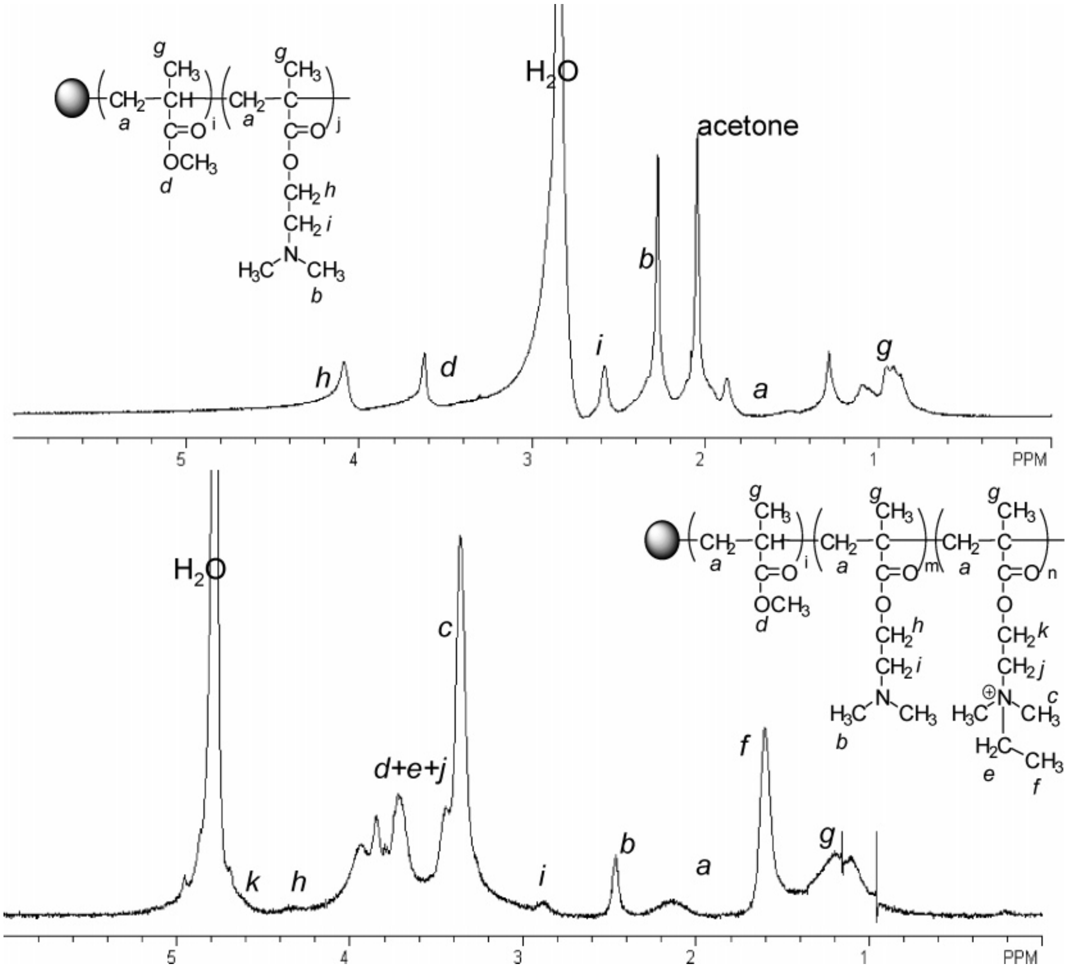


Figure 3. ^{1}H NMR spectrum of a poly(DMAEMA)-grafted carbon black sample before (in CD_3COCD_3, top spectrum) and after quaternization with ethyl bromide (in D_2O, bottom spectrum).

Table 1. Characterizations of CB−PDMAEMA and Quaternized CB−PDMAEMA

	CB−PDMAEMA		quaternized CB−PDMAEMA	
polymer content by TGA under N_2	57%		74%	
mean volume particle size (nm)	MeOH	H_2O (pH = 2)	H_2O (pH = 7)	H_2O^a (pH = 7)
	342	462	784	682

[a] Particles were filtered through a 0.45 μm filter.

using dynamic light scattering (DLS) and TGA, as shown in Table 1. The original sample afforded an organic volatile content of 57% by TGA analysis. After quaternization, the polymer content increased to 74%. On the basis of the degree of quaternization and the MMA content in the polymer, the polymer fraction for the quaternized sample was calculated to be around 69%, which is close to the experimental value. The size of initial water-dispersible carbon back (CB−COONa) was 120 nm by DLS. After polymer grafting, the particle size of CB−PDMAEMA dispersed in methanol was found to increase to 342 nm. When CB−PDMAEMA was dispersed in low pH water, an even larger size increase was observed (462 nm), which can be explained by the charge repulsions by the polymer side chains. After quaternization, the size of the CB−PDMAEMA was found to be 784 nm, much larger than the unquaternized sample. It was also bigger than the size of acidified sample (pH ∼ 2) To rule out the possibility of particle agglomeration, the aqueous sample was filtered through a 0.45 μm filter, and despite the fact that some of the particles were trapped by the filter, an average size close to 700 nm was observed again. Therefore, we assume the size increase of quaternized carbon black was not due to agglomeration of the carbon black particles. It was proved by studying the morphology of the composites using AFM.

Characterization of CB−PDMAEMA and Quaternized CB−PDMAEMA by AFM. AFM is an excellent tool for characterization of nanostructures[74−79] and was also employed in this study to directly visualize the poly(DMAEMA)-grafted carbon black particles. Samples for AFM observations were prepared by spin-coating very dilute (10 wt ppm) CB−PDMAEMA dispersion onto mica which assured sufficiently low coverage (individual isolated particles on mica surface). As shown in Figure 4, the image clearly shows curly polymer brushes surrounding the carbon black core, proving that poly(DMAEMA) was grafted onto carbon black. However, this picture differs from what was observed for poly(*n*-BA)-grafted carbon black particles, where the poly(*n*-BA) chains formed dense brushes extending out onto the substrate from the carbon black core.[58] The difference in morphology of the attached polymers can be attributed to the difference in T_g of the materials. Poly(*n*-BA) has a $T_g = -50$ °C, i.e., much lower than room temperature and is much softer and more likely to conform to the contours of the hard carbon black cores. In the case of quaternized CB−PDMAEMA, it was first dispersed in water to obtain a dilute solution as usual, then one drop of the solution was cast on mica, and water was allowed to evaporate at room temperature. As shown in Figure 5, almost all the particles in the field of view are surrounded by polymer brushes, and the polymer chains stretch out more than in the unquaternized CB−PDMAEMA, which is consistent with the result obtained from light scattering experiments. In Figure 5, a second layer of polymers can be seen close to the irregular-shaped carbon black core as indicated by a different color in the height profile. This is due to polymer chains grown on the top of the particles "draping" down onto the polymer chains grown from the lower half of the particles.

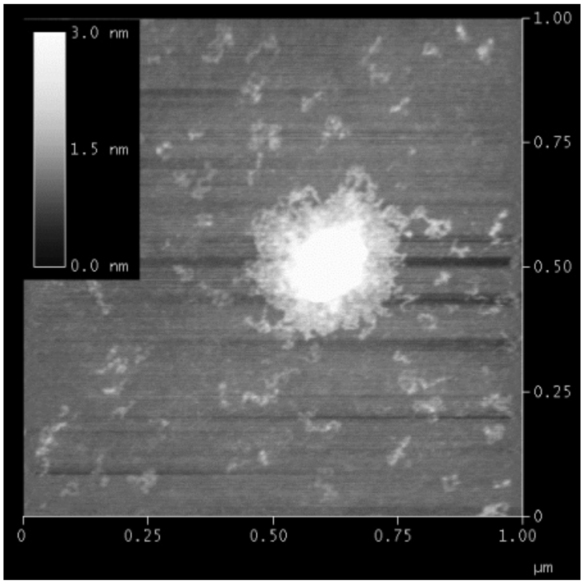


Figure 4. AFM height image of an air-dried original poly(DMAEMA) bound carbon black particle spin-cast from THF on mica before quaternization.

Copolymerization of DMAEMA and HEMA. HEMA is a functional monomer, and incorporation of HEMA in polymer structure can afford materials for chromatography,[80] implants,[81,82] membranes,[83] and polymer supports for catalysis.[84] HEMA has also been incorporated into carbon nanotube-based amphiphilic core−shell structures.[85] Despite the fast polymerization rate of HEMA in pure water, the same methanol/H_2O cosolvents were applied to the copolymerization of DMAEMA and HEMA because it has been reported that poly(HEMA) produced by aqueous ATRP was not soluble possibly due to transesterifications.[44,86]

As shown in Figure 6, linear kinetics was observed in the semilogarithmic plot of conversion vs time for both DMAEMA and HEMA monomers, indicating good control of the reaction. The simultaneous copolymerization of HEMA and DMAEMA initiated by AIBN was reported to produce a Bernouillian-type of random copolymers,[87] and in Figure 6, a similar rate of monomer consumption was also observed although the ratio between DMAEMA and HEMA was 5:1, which also suggested random copolymerization of the two monomers.

One of the advantages of controlled radical polymerization over conventional radical polymerization is the possibility of preparation of block copolymers as well as other well-defined architectures. To prove that the chain end of the poly(DMAEMA)-grafted carbon black (a CB−poly(DMAEMA) sample with 51% volatile was used) was still living, HEMA was polymerized as a second block. The same polymerization conditions were used, and after 18 h of reaction, a monomer conversion around 5.7% was detected by GC. The formation of block copolymers was confirmed by a solubility test: previous CB−PDMAEMA kinetic samples were dissolved in acetone which was used for GC analysis. In contrast, the block

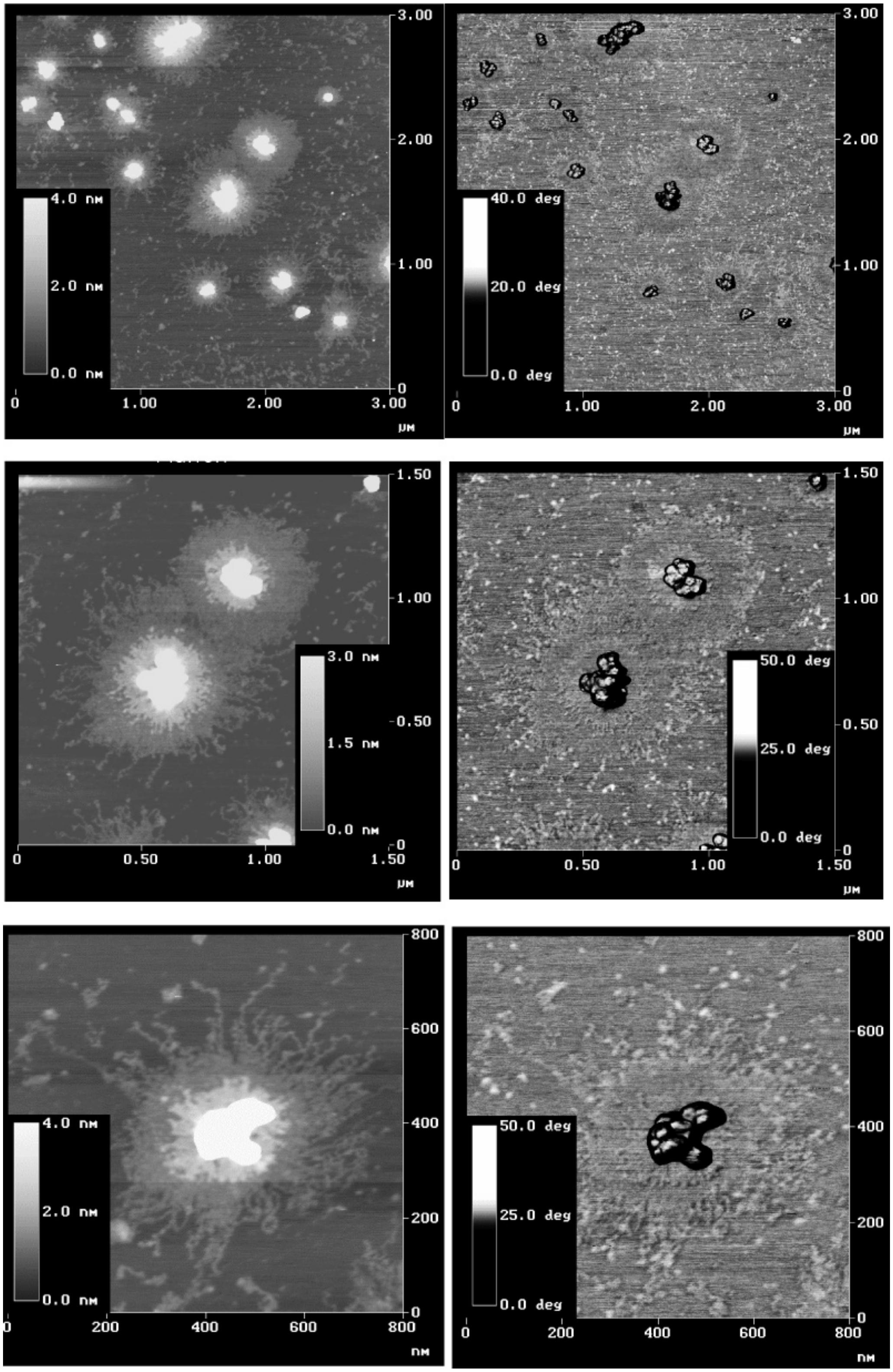


Figure 5. AFM height (left) and phase (right) images of quaternized poly(DMAEMA) bound carbon black particles on mica at different magnifications. Samples were first dispersed in water, and one drop of the dilute dispersion (∼10 ppm) was placed on mica and air-dried at room temperature.

copolymer-grafted carbon black was no longer soluble in acetone, which is not a good solvent for poly(HEMA). Instead, methanol was used in place of acetone for the GC analysis.

The final product was purified by centrifugation in methanol. The formation of block copolymers was confirmed by infrared spectroscopy, as shown in Figure 7. For poly(DMAEMA)-grafted carbon black, the peaks appearing at 2819 and 2767 cm^{-1} are characteristic of the symmetric and asymmetric stretching of the methyl groups on nitrogen. After block copolymerization, a strong peak around 3400 cm^{-1} due to O—H stretching and an increase in the intensity around 2930 cm^{-1} due to C—H stretching were observed, which correlated with the structure of poly(HEMA). Consistently with the IR results, TGA indicated the volatile content increased from 51% to 68%,

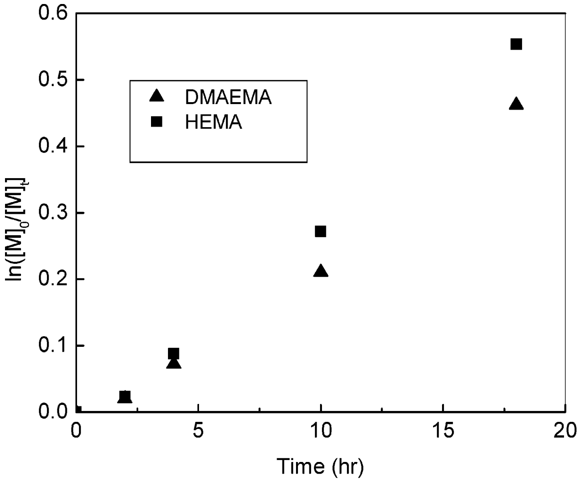


Figure 6. Kinetics of random copolymerization of DMAEMA and HEMA from functionalized carbon black. [DMAEMA + HEMA]:[CB−Br initiator]:[CuBr]:[$CuBr_2$]:[BPY] = 500:1:2:1.2:6.4, [DMAEMA]/[HEMA] = 5:1 (mol), $MeOH/H_2O$ = 7.9:1 (w/w). The reactions were conducted at 30−32 °C. CB−Br (0.17 mmol of bromine per gram of carbon black).

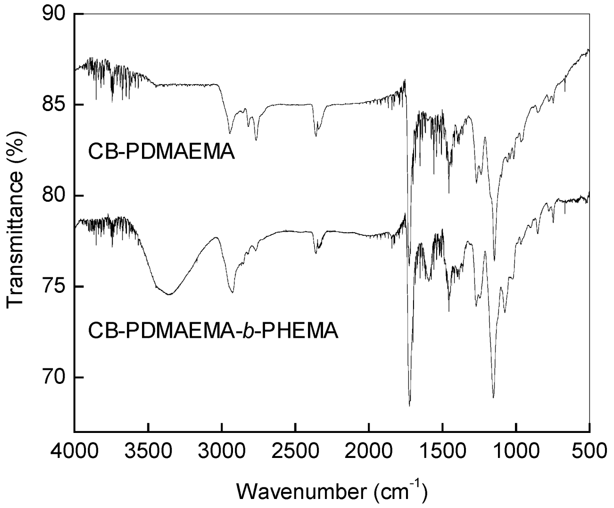


Figure 7. Infrared spectra of poly(DMAEMA) and poly(DMAEMA)-*b*-poly(HEMA)-grafted carbon black (CB−PDMAEMA and CB−PDMAEMA-*b*-PHEMA, respectively). CB−PDMAEMA was dispersed in acetone and cast on a KBr pellet. CB−PDMAEMA-*b*-PHEMA was dispersed in methanol and cast on a KBr pellet. Both samples were dried under high vacuum overnight at room temperature.

and light scattering study in methanol showed the particle size increased from 198 to 283 nm.

Conclusions

DMAEMA was grafted from functionalized carbon black surface via ATRP catalyzed by CuBr/$CuBr_2$/bipyridine in protic media. When the polymerization was conducted in the presence of a sacrificial initiator, good control of the reaction was confirmed by the linear evolution of molecular weight vs monomer conversion. Despite the incorporation of MMA in the polymerization due to transesterification of DMAEMA in methanol/H_2O, the polymer-grafted carbon black formed stable water dispersions under acidic conditions or upon quaternization using alkyl bromide. The successful attachment of polymers to carbon black surface was proved by TGA, dynamic light scattering, and AFM. The AFM image of quaternized sample showed polymer chains grafted from carbon black extended on mica much further due to charge repulsions between chains. HEMA was copolymerized with DMAEMA on the carbon black surface, providing functional sites for further modifications. The poly(DMAEMA)-bound carbon black was also chain-extended by block copolymerization of HEMA.

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