Surface-initiated nitroxide-mediated radical polymerization of 2-(dimethylamino)ethyl acrylate on polymeric microspheres

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Abstract

2-(Dimethylamino)ethyl acrylate (DMAEA) was grafted from the surface of alkoxyamine-functionalized crosslinked poly(styrene-*co*-chloromethylstyrene) microspheres by nitroxide-mediated radical polymerization (NMRP). Latex particles ($\sim$60 nm diameter) bearing chloromethyl groups were synthesized by emulsion polymerization. *N-tert*-butyl-*N*-(1-diethyl phosphono-2,2-dimethylpropyl)nitroxide (SG1) was then immobilized on the particle surface. Microspheres grafted with the homopolymer pDMAEA, as well as block copolymers poly(styrene-*b*-DMAEA) and poly(butyl acrylate-*b*-DMAEA) were prepared by surface-initiated NMRP in *N,N*-dimethylformamide at 112 °C, with the addition of free SG1 to ensure that control is maintained. Particle size increases with number average molecular weight (M_n) of untethered polymers. The polymerizations exhibit linear first order kinetic plots and slight curvature of evolution of M_n with conversion. The functional microspheres were analyzed by infrared spectroscopy, transmission electron microscopy and thermal analysis, as well as their dispersibility in water; the results support the formation of surface-grafted pDMAEA on the microspheres.
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1. Introduction

The functionalization of microspheres by grafting of polymer chains to the surface provides a powerful and flexible route to improve the physical and chemical properties of particles. Using a ''grafting from'' approach with living/controlled radical polymerization (LRP/CRP) enables preparation of particles with high grafting density, controlled graft structure/composition and applicability to different monomers [1–3]. Most recent research activities in this area have focused on surface modification of polymeric microspheres via Atom Transfer Radical Polymerization (ATRP) [4–12] or Reversible Addition-Fragmentation Transfer (RAFT) [13–16].

However, fewer reports have been published applying nitroxide-mediated radical polymerization (NMRP) for the grafting step. NMRP has the advantage of being a relatively simple process, although it is not as versatile as ATRP or RAFT in the range of monomers suitable for use. Hodges et al. [17] and our group [18] reported the grafting of polystyrene onto a Merrifield resin surface via NMRP. In these works, a pronounced increase of particle size was observed, which was attributed to the formation of chains both at the surface and within the microspheres. Hawker [19], Chaumont [20], Riedl [21], and more recently Bourgeat-Lami [22] also reported the graft polymerization of styrene on the surface of silicon wafers or silica particles by NMRP. While these publications are good demonstrations of NMRP surface-initiated polymerization, only polystyrene is grafted onto the particle surface. Grafting functional monomers to the microsphere surface can bring about enhanced properties such as hydrophilicity, amphiphilicity, and even a smart response to environmental changes, enabling the preparation of particles with more widespread application.

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2-(Dimethylamino)ethyl acrylate (DMAEA) is an important water-soluble monomer. Its polymers and copolymers have wide applications in the pharmaceutical, surfactant, and water treatment industries [23]. Recently, Ignatova et al. reported the synthesis of copolymer brushes from stainless steel by nitroxide-mediated random copolymerization of DMAEA and styrene or *n*-butyl acrylate [24]. However, we have not found reports describing the homopolymerization of DMAEA or its block copolymerization on a microsphere surface applying any controlled polymerization method. The controlled polymerization of DMAEA is relatively difficult since this monomer has low steric hindrance on its substituents and a polar amino group that will interact with catalysts. Recently we reported the first NMRP of DMAEA and the synthesis of block copolymers based on DMAEA [25]. In this work, we report on the surface-initiated grafting of DMAEA to crosslinked polystyrene microspheres using NMRP, including characterization of the functional microspheres.

2. Experimental

2.1. Materials

All the reagents were used as received except as specified. 2-(Dimethylamino)ethyl acrylate (DMAEA, Aldrich, 98%) was purified by vacuum distillation with CaH_2. *n*-Butyl acrylate (BA, Aldrich, 99+%), 4-vinylbenzyl chloride (chloromethylstyrene, CMS, Aldrich, 90%) and divinyl benzene (Aldrich, technical grade, 80%) were purified by passage through a basic alumina column prior to use. Styrene (S, Aldrich, 99%) was washed with 2 wt.% aqueous solution of NaOH and distilled under vacuum. Potassium persulfate (99+%), CuBr (98%), 2,2′-dipyridyl (99+%), Cu powder (99%), and glycine (99+%) were all from Aldrich. Sodium dodecyl sulfate (SDS, 99%) was received from Sigma and sodium bicarbonate (assay 100.2%) from Fisher Scientific. The *N-tert*-butyl-*N*-(1-diethyl phosphono-2,2-dimethyl propyl)nitroxide (SG1, 89% purity) and SG1-based alkoxyamine MONAMS (96% purity) were kindly provided by Arkema Inc. All the solvents were purchased from Fisher Scientific, Canada. Spectrum/Por® membranes (Spectrum Inc.) with an MWCO of 3500 were used for dialysis of the latexes.

2.2. Synthesis of latex particles bearing chloromethyl groups (L-CH$_2$Cl)

Latex particles with chloromethyl (CH_2Cl) groups were synthesized by emulsion polymerization of styrene and chloromethylstyrene (CMS). A typical recipe is shown in Table 1. The procedure is as follows. A 1 L three-neck reactor fitted with an overhead mechanical stirrer and a condenser was immersed in an oil bath. To the reactor were added all the reagents except KPS and 455 mL deionized water (DIW). The reactor was sealed with a septum and stirred at 300 rpm. Oxygen was removed by bubbling the solution with N_2 for 20 min. KPS was dissolved in 10 mL DIW in a separate tube and bubbled with N_2. When the temperature reached 70 °C, KPS aqueous solution

Table 1
Recipe of emulsion polymerization for synthesis of latex particles with CH_2Cl

Components	Weight (g)
Styrene	13.33
Chloromethylstyrene (CMS, 90%)	26.66
Divinyl benzene (DVB, 80%)	2.0
Sodium dodecyl sulfate (SDS)	1.31
Sodium bicarbonate	0.48
Potassium persulfate (KPS)	0.46
Deionized water	465

Polymerization conditions: 70 °C, stirring rate 300 rpm, 2 h.

was added by a syringe. Polymerization was stopped after 2 h. The conversion of monomer was analyzed by gas chromatography, giving conversions of styrene and CMS of 86% and 93%, respectively. The unreacted monomers were removed first by steam distillation and then by dialysis against distilled water for 1 week with a daily change of distilled water. The number average particle size (d_n) was 60 nm with a coefficient of variation (CV) 8%, measured by transmission electron microscopy (TEM).

Surface CH_2Cl groups of latex particles were analyzed as follows. Latex 2.5 g (solid content 8.0 wt.%, measured by gravimetry) was stirred with glycine (12.5 mL, 1.0 M), NaOH (18.3 mL, 0.50 M), and deionized water at 35 °C for 26 h. A blank experiment without the addition of NaOH and glycine was conducted to offset the effect of hydrolysis of CH_2Cl at this temperature. The reaction mixture was then filtered and the solution containing released free Cl^- ion was analyzed by ion chromatography. By analysis of the Cl^- ion content, functionality of the latex particles was determined to be 1.60 mmol/g of CH_2Cl.

2.3. Synthesis of SG1-immobilized latex particles (L-SG1)

The reaction was performed in *N,N*-dimethylformamide (DMF), therefore a solution of latex particles in DMF was first prepared. Water in the latex was removed by evaporation and DMF was gradually added in several batches during the dehydration process. The solution was then dried by 4Å molecular sieves and filtered. Solid content was analyzed by gravimetry. SG1 was immobilized to the particles by an atom transfer radical reaction. To a 1 L reaction flask were added latex particle solution in DMF (340 g, solid content 7.93 wt.%, 0.044 mol by CH_2Cl groups), CuBr (6.34 g, 0.044 mol), 2,2′-dipyridyl (27.5 g, 0.176 mol), Cu powder (2.82 g, 0.044 mol) and SG1 (14.9 g, 0.051 mol). The solution was bubbled with argon for 1 h to remove dissolved oxygen. The reaction was undertaken at 65 °C for 20 h. The final reaction mixture was separated and purified by centrifugation. Copper salts or powders were separated with a rotation speed of 8000–10 000 rpm, while latex particles could only be separated at speeds >16 000 rpm. To facilitate the centrifugation of latex particles, a lower density solvent (tetrahydrofuran, THF) was added to displace DMF. The supernatant solution was discarded and fresh THF was added. Six cycles of serum displacement with THF were performed to remove unreacted reagents. The purified SG1-immobilized particles have an N content of 1.60% by elemental

analysis, corresponding to a functionality of 1.14 mmol/g. L-SG1 was stored in DMF for further use (solid content 8.42 wt.%).

2.4. General procedures for graft polymerization onto microspheres

To a Schlenk tube was added SG1-immobilized latex particles (L-SG1) dispersed in DMF, monomer, free nitroxide SG1, and MONAMS (if applicable). The reaction tube was sealed with a rubber septum. Three cycles of freeze−vacuum− thaw were applied to remove the oxygen, and the tube was then immersed in an oil bath at 112 °C. Samples were taken by syringe at specified time intervals. A portion of each sample was directly dissolved in deuterated chloroform (CDCl$_3$) for the analysis of monomer conversion by ^{1}H NMR. The remainder of each sample was mixed with THF and centrifuged. The supernatant was concentrated and analyzed by gel permeation chromatography after removing excess monomer under vacuum (50 °C). The particles were re-dispersed in THF with the aid of sonication and centrifuged again. After three cycles of serum displacement, the purified microspheres were stored in THF or DMF.

2.5. Synthesis of pDMAEA-grafted microspheres (L-pDMAEA)

L-SG1 dispersion in DMF (12.6 g, 1.21 mmol), DMAEA (21.4 g, 0.149 mol), MONAMS (0.204 g, 0.535 mmol) and SG1 (19 mg, 0.065 mmol) were reacted at 112 °C. Samples were taken at 0.50, 1.25, 2.05, 3.05, 4.27 and 5.75 h, giving conversions of 4.8%, 12.8%, 23.0%, 34.5%, 43.0% and 53.3%, respectively. In another experiment, L-SG1 dispersion in DMF (12.0 g, 1.15 mmol), DMAEA (14.5 g, 0.101 mol) and SG1 (10 mg, 0.034 mmol) was reacted without the addition of initiator MONAMS. Samples were taken at 0.67, 1.0, 2.75, 4.5 and 10.0 h, giving conversions of 2%, 3%, 11%, 18.7% and 35%, respectively.

2.6. Synthesis of pS-grafted microspheres (L-pS)

L-SG1 dispersion in DMF (11.6 g, 1.11 mmol), styrene (31.5 g, 0.303 mol), MONAMS (0.381 g, 0.001 mol) and SG1 (13 mg, 0.044 mmol) were reacted at 112 °C. Polymerization was stopped after 3 h, giving a styrene conversion of 50% as measured by ^{1}H NMR. The number average of molecular weight (M_n) of free pS in solution was 15 250 g/mol and polydispersity index (PDI) was 1.14. These pS-grafted microspheres (L-pS) had a particle size of 84 nm and a CV of 8% as measured by TEM and were used as a macroinitiator.

2.7. Synthesis of p(S-b-DMAEA) grafted microspheres (L-p(S-b-DMAEA))

The above-synthesized L-pS dispersion in DMF (9.5 g, solid content 9.7 wt.%), DMAEA (18.9 g, 0.132 mol), MONAMS (0.137 g, 0.360 mmol) and SG1 (9 mg, 0.031 mmol) were

reacted at 112 °C. Samples were taken at 0.5, 1.15, 1.9, 2.75 and 3.75 h, giving conversions of DMAEA as 6%, 17.7%, 27%, 40% and 51%, respectively.

2.8. Synthesis of pBA-grafted microspheres (L-pBA)

L-SG1 dispersion in DMF (11.2 g, 1.08 mmol), BA (34.0 g, 0.266 mol), MONAMS (0.345 g, 0.906 mmol) and SG1 (16 mg, 0.054 mmol) were reacted at 112 °C. Polymerization was stopped after 3 h, giving a conversion of BA 45%. M_n of free pBA was 12 480 g/mol, with PDI of 1.18. These pBA-grafted microspheres (L-pBA) had a particle size of 73 nm and a CV of 8% (by TEM) and were used as macroinitiator.

2.9. Synthesis of p(BA-b-DMAEA) grafted microspheres (L-p(BA-b-DMAEA))

The above-synthesized L-pBA dispersion in DMF (19.8 g, solid content 4.0 wt.%), DMAEA (19.8 g, 0.138 mol), MONAMS (0.157 g, 0.413 mmol) and SG1 (11 mg, 0.037 mmol) were reacted at 112 °C. Samples were taken at 0.55, 1.13, 1.93, 2.93 and 4.17 h, giving conversions of DMAEA as 7.4%, 21%, 36%, 50% and 61.5%.

2.10. Analytical techniques

The monomer conversion was determined by ^{1}H NMR in CDCl$_3$, using a Bruker AV-400 MHz FT spectrometer. The conversion of DMAEA was determined by comparing the integration of two vinyl protons (β position) of the monomer (H_2C=, 5.6−5.8, 6.2−6.4 ppm) and the integration of protons of the methylene group connected to the carbonyl oxygen (−C(=O)OCH_2−, 3.85−4.3 ppm) for both monomer and polymers. The conversion of styrene was determined by comparing the integration of two vinyl protons (β position) of monomer (H_2C=, 5.2−5.4, 5.7−5.9 ppm) and the integration of both vinyl protons (α position) of monomer and the integration of benzyl protons (=CH− and C$_6H_5$−, 6.3−7.5 ppm). The conversion of BA was determined by comparing the integration of two vinyl protons (β position) of monomer (H_2C=, 5.7−5.9, 6.3−6.5 ppm) and the integration of methyl protons (CH_3−, 0.8−1.1 ppm).

The conversion of styrene and CMS in emulsion polymerization was analyzed by a Varian CP-3800 Gas Chromatography with a Flame Ionization Detector. Samples were diluted in acetone and the area of each component was compared with a standard calibration curve.

Infrared spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer. All samples were prepared as pellets using infrared grade KBr pressed at 10 000 psi.

Elemental analysis was performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada.

Chlorine ion content was analyzed in a Dionex DX300 Ion Chromatography system by the Analytical Services Unit, Queen's University, Canada.

Gel permeation chromatography (GPC) was performed in a Waters 2690 separation module equipped with five Waters

Styragel HR columns (HR5, HR4.0, HR3.0, HR1.0, and HR0.5) in series. A Waters 410 differential refractometer was used as the refractive index (RI) detector and a Wyatt Technology DAWN EOS laser photometer as the light scattering (LS) detector, all set at 40 °C. Tetrahydrofuran (THF) was used as eluent at a flow rate of 1 mL/min. Narrowly distributed polystyrene samples were used as calibration standards for the RI detector. The absolute molecular weight and molecular weight distribution were calculated using ASTRA for Windows (Version 4.90.08) with known specific refractive index increment (dn/dc) and known RI detector calibration constant. Except as specified, we report the number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity (PDI = M_w/M_n) from the LS detector. The dn/dc values of pS, pDMAEA and pBA adopted were 0.18, 0.06, and 0.065, respectively [25].

Transmission electron microscopy (TEM) was analyzed by a Hitachi H7000 TEM at an accelerating voltage of 75 kV. Specimens were prepared by placing a drop of particle dispersion in THF to the Cu grid coated with pure carbon (from Squelec International) and then drying at room temperature overnight. Particle size was averaged from more than 150 particles in more than three different pictures using SigmaScan Pro Image Analysis (Version 5.0.0, SPSS Inc.).

Differential scanning calorimeter (DSC) measurements were carried out on a TA Instruments Q100 DSC. The sample was first heated to 110 °C to remove history, cooled to −80 °C and stayed there for 1 min, and then heated at 15 °C/min to 120 °C. Glass transition temperature (T_g) of polymer was calculated by Universal Analysis 2000 software from TA Instruments, Inc.

Thermal gravimetric analysis (TGA) measurements were performed on a TA Instruments Q500 TGA. Heating was undertaken from room temperature to 650 °C at a rate of 10 °C/min. Weight losses and decomposition temperatures were estimated using Universal Analysis 2000 software.

3. Results and discussion

3.1. Latex particles synthesis by emulsion polymerization

The colloidal latex particles were synthesized by emulsion polymerization. To introduce a reactive chloromethyl group (CH$_2$Cl), chloromethyl styrene (CMS) was chosen as comonomer together with styrene. A temperature of 70 °C was used. Higher temperatures are known to accelerate the hydrolysis of CH$_2$Cl groups in the monomer as well as in the polymer, though it was reported that the polymers have a much lower tendency towards hydrolysis [26]. However, the polymerization rate will be decreased at low temperature, which will prolong the nucleation process and give rise to a broader particle size distribution. More CMS than styrene was added (CMS/S = 2/1 wt/wt), with the intent of increasing the surface density of CH$_2$Cl groups in the final latexes. Further increase in the CMS fraction can lead to instability of the latex during polymerization, possibly due to the low solubility of CMS in water and the effect on the nucleation and particle growth

processes. Final latexes were purified by dialysis to remove unreacted monomers, salts and surfactants. The particle size was 60 nm as measured by TEM. The analysis of hydrolyzed CH$_2$Cl groups by glycine/NaOH solution gave a surface functionality of 1.6 mmol/g, indicating a relatively high surface density. Gradual addition of DMF to latexes was applied to displace the water, as described in Section 2, yielding latex particle dispersion in DMF ready for chemical modification and further graft polymerization.

3.2. Immobilization of nitroxide to the particle surface

To immobilize the nitroxide SG1 on the particle surface, a method similar to that used by Hodges et al. [17] was first tried. In this method, nitroxide was reduced by sodium ascorbate followed by deprotonation with NaH in DMF. The expected sodium salt of nitroxide is then reacted with latex particles to form nitroxide-bound particles. However, while this is a good approach for 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), it was not successful for SG1. By analysis of the sodium salt of SG1 using IR, NMR and mass spectroscopy, it can be concluded that the reduced form of SG1 is not stable in this reaction medium. It was found that a *tert*-butyl group was removed from the SG1. Unlike TEMPO, SG1 has a hydrogen on the α-carbon connected to the O−N bond; this hydrogen is labile to oxidization and other chemical reactions.

The second method of chemical modification, reported by Matyjaszewski et al. [27], was therefore tried for immobilizing SG1 to the latex particle surface and proved to be successful. This method is based on atom transfer radical reaction (ATRA), as shown in Scheme 1. The bipy-Cu(I) reduces the CH$_2$Cl group to methylene radicals, which are captured by SG1, a stable radical, to form alkoxyamine. The oxidized state of copper (Cu(II)) will react with Cu powder to form the reduced form of copper (Cu(I)), which as a result drives the reaction to completion. The reaction was performed in different solvents such as benzene, toluene, and DMF, with DMF giving the highest yield. (The ratios of reagents to latex particles (L-CH$_2$Cl) were increased since the surface reaction is more difficult than in solution.) The SG1-bound latex particles have a functionality of 1.14 mmol/g, by nitrogen elemental analysis, indicating a reaction yield of 71%.

3.3. Graft polymerization of DMAEA on SG1-bound particles

The SG1-bound latex particles (L-SG1) were reacted with DMAEA at 112 °C. Small amounts of free SG1 were added to capture thermally decomposed free radicals in solution in order to maintain control of the polymerization. The additional SG1 is necessary for two reasons; DMAEA is a monomer with
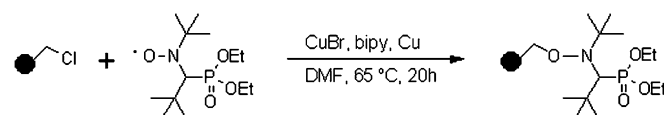
Scheme 1. Immobilization of SG1 onto the microsphere surface.

a high propagation rate therefore making it more difficult to control, and thermal polymerization is pronounced at the temperature used in this work. According to the nitroxide chemistry, the mediating nitroxide radicals are not associated with a single chain end and are free to diffuse throughout the polymerization mixture. If the polymerization in solution is out of control, it is expected that surface-initiated polymerization will also not be in good control. Two degassing methods were compared: one is to bubble the solution with argon for more than 40 min, and the other is to apply three cycles of freeze–vacuum–thaw. It was found that the freeze operation did not have a harmful effect on the dispersion stability of the latex particles in organic solvents (DMF, THF) and particle sizes were almost the same. Therefore, the freeze–vacuum–thaw degassing operation was used throughout this work. The samples taken at different intervals were purified by centrifugation and displacement with fresh solvent. The supernatant was subjected to GPC analysis, which gave the molecular weights and distributions of free polymers (pDMAEA) in solution. Centrifugation is difficult when particles are dispersed in DMF, however, the operation is much easier when a lower density solvent (THF) is used. The experimental results for graft polymerization of DMAEA from SG1-bound latex particles without the addition of MONAMS are shown in Fig. 1.

It can be seen from Fig. 1 that although the kinetic plot shows a first order linearity up to about 35% conversion, the evolution of M_n of the free polymers with conversion shows downward curvature, indicating an increasing number of chains. However, the polydispersity of polymers in solution remained very low (the PDI was 1.04 at 35% conversion), showing that excellent control of the polymerization was preserved. The curvature in the M_n versus conversion occurs because the polymerization in solution is thermally initiated, the number of chains is expected to (and does) continually increase. While no alkoxyamine is added to the polymerization mixture, trapping of thermal polymerization by the free nitroxide present rapidly leads to the formation of alkoxyamine in solution. The Δd_n is the increase of particle size that is measured by TEM. The trend of Δd_n increasing with M_n is clearly shown. The % weight loss of particles was measured by TGA. It will be discussed in Section 3.8.

MONAMS is an SG1-based alkoxyamine $CH_3-O-C(=O)-CH(CH_3)-SG1$ which has been used as an effective unimolecular initiator. Fig. 2 shows the similar results from another experiment in which MONAMS was added to the solution. A linear kinetic plot ($\ln(1/(1-x))$ versus time) was observed to a conversion of around 50%. The evolution of M_n with conversion shows a gentle curvature, indicating the number of chains is still steadily increasing. Compared to thermal initiation in the solution in Fig. 1, the initiation of MONAMS produced more radicals, which leads to the lower M_n. The addition of external initiator also improved the control, especially in the initial period of polymerization. Hawker [19] showed that the addition of "free" alkoxyamine is necessary to control the chains growth of both the immobilized and soluble initiators when they grafted polymers from silicon wafer applying NMRP. Similar to Fig. 1, Δd_n increases with
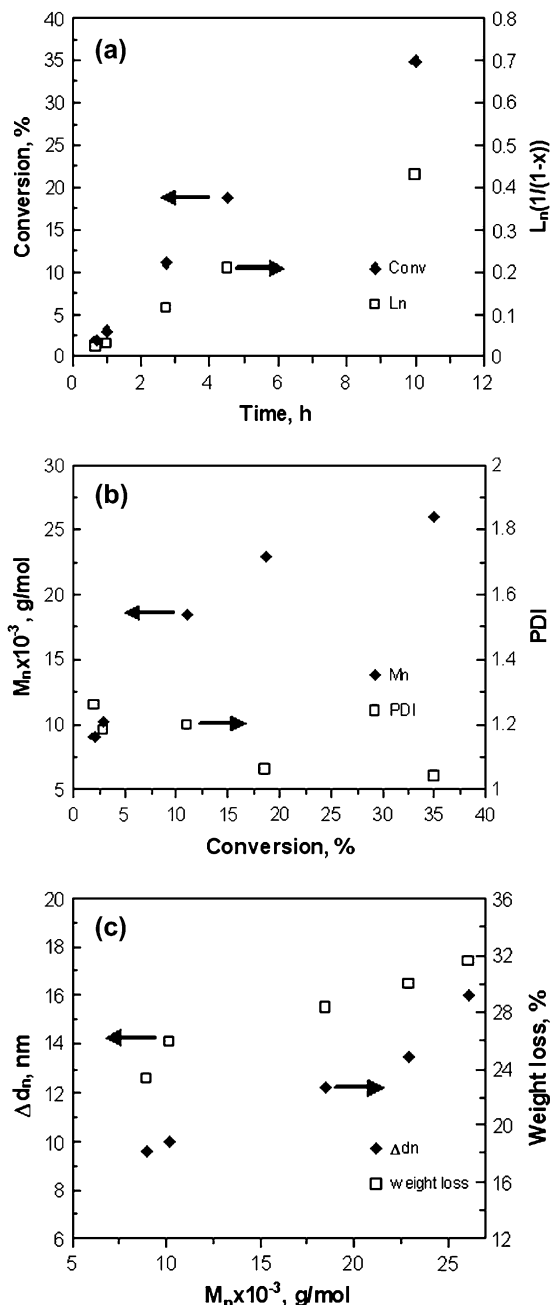

Fig. 1. Graft polymerization of DMAEA from SG1-bound latex particles without the addition of MONAMS. (a) Kinetic plot; (b) variance of M_n of pDMAEA in solution with conversion of DMAEA; (c) variance of particle size increases with M_n of pDMAEA in solution. $[DMAEA]_0/[L\text{-}SG1]_0/[SG1]_0 = 2970/33.8/1$, DMF 43.0 wt.%, 112 °C.

M_n, indicating higher M_n of polymers growing on the surface corresponding with the higher M_n of polymers growing in solution.

It needs to be pointed out that the NMR-based conversion determination was measured based on the ratio of polymers and unreacted monomers in solution, while the polymers grafted on the surface were not included in this calculation. The "real" conversion is in fact higher than the one measured by NMR. Assuming that weight loss of microspheres measured by TGA is only from the contribution of polymer grafted on the
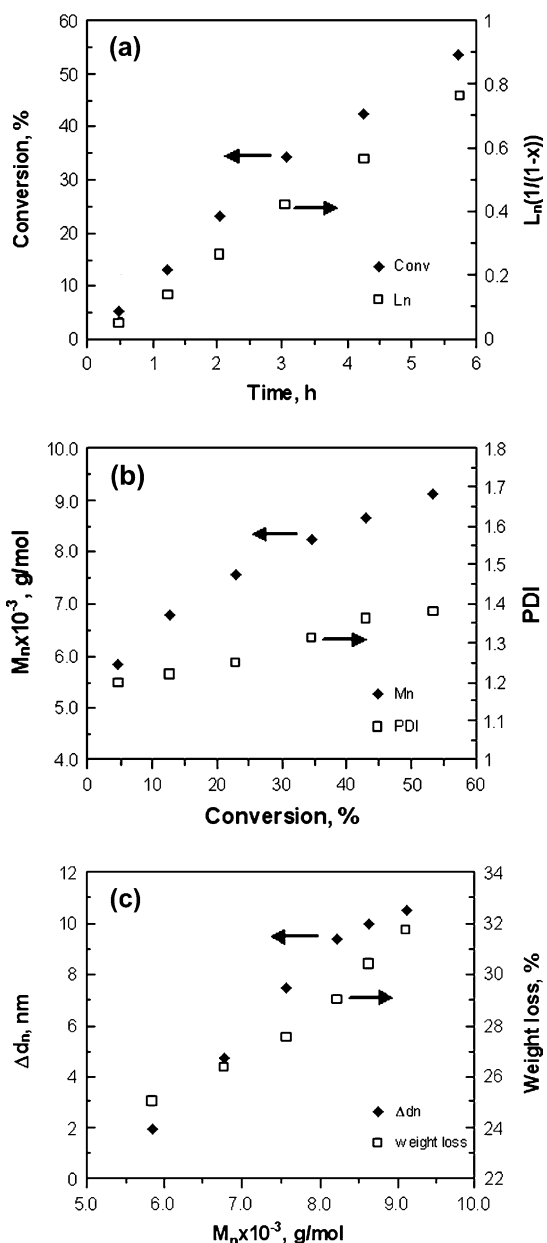
Fig. 2. Graft polymerization of DMAEA from SG1-bound latex particles with the addition of MONAMS. (a) Kinetic plot; (b) variance of M_n of pDMAEA in solution with conversion of DMAEA; (c) variance of particle size increases with M_n of pDMAEA in solution. $[DMAEA]_0/[L\text{-}SG1]_0/[MONAMS]_0/[SG1]_0 = 2292/18.6/8.2/1$, DMF 33.7 wt.%, 112 °C.

microsphere surface, the amount of grafted polymer can be estimated from % weight loss. Based on initial amount of reagents, measured conversions from solution of monomers and free polymers, and % weight loss data, we can approximately calculate the real conversion in each sampling time. For pDMAEA-grafted microspheres (data from Fig. 2), this difference was 35% at the first sampling point (conversion <5%), however, the deviation at low conversions is high. For the second sampling point (conversion 12.8%) deviation was 10%, while at 53.3% measured conversion the deviation was only 6%. This difference between measured conversion and estimated "real" conversion will not have a significant effect on

the evolution of M_n with conversion, and therefore we have only adopted the convention of conversion measured from solution.

3.4. Block copolymer p(S-b-DMAEA) grafting on microspheres

To synthesize block copolymer grafted microspheres, the first block (polystyrene) was grafted to the particle surface. L-SG1 was reacted with excess styrene with the addition of MONAMS and free SG1 ($[SG1]_0/[MONAMS]_0 = 4.4\%$) at 112 °C. A significant increase in particle size (24 nm) was observed after polymerization, with an M_n and a PDI of free pS in solution of 15 250 g/mol and 1.14, respectively.

The synthesized pS-grafted latex particles (L-pS) were reacted with excess DMAEA, with the addition of MONAMS and SG1. The p(S-b-DMAEA) grafted microspheres (L-p(S-b-DMAEA)) were obtained after purification by centrifugation. As can be seen from Fig. 3, similar results were obtained when growing pDMAEA from pS-grafted particles, as compared with the experiment of growing pDMAEA from SG1-bound particles (Figs. 1 and 2). This clearly shows that pS on the particles can initiate polymerization of the second monomer DMAEA, thus forming block copolymer brushes on the microspheres.

3.5. Block copolymer p(BA-b-DMAEA) grafting on microspheres

Microspheres with pBA (L-pBA) grafted on the surface were synthesized by reacting L-SG1 with excess BA, with MONAMS and SG1 added to the solution ($[SG1]_0/[MONAMS]_0 = 5.8\%$). A particle size increase of 13 nm was obtained; the free pBA in the solution has an M_n of 12 480 and a PDI of 1.18. The synthesized L-pBA was used as macro-initiator and reacted with DMAEA to form p(BA-b-DMAEA) grafted microspheres (L-p(BA-b-DMAEA)). From Fig. 4, features such as a linear first order kinetic plot, a gentle curvature of evolution of M_n with conversion, and an increase of Δd_n with M_n are similar to those observed previously. Comparable with the results of L-p(S-b-DMAEA), the block copolymer p(BA-b-DMAEA) grafted microspheres were formed and particle size increased with M_n, though to a lesser extent. The reasons for this will be discussed later.

3.6. Infrared spectroscopic analysis of microspheres

Fig. 5 shows the FT-IR spectra of the microspheres. The spectrum of L-p(BA-b-DMAEA) is almost the same as that of L-pBA because the BA and DMAEA segments give the same characteristic absorption, and therefore it is not shown here. All of the other microspheres show distinct IR absorptions, affirming the formation of new components attached to the particles. For L-CH$_2$Cl, the CH$_2$Cl group has an absorption at 1265 cm^{-1} [28] which was greatly decreased when SG1 is immobilized to the particle surface; instead the strong absorption of the ether C–O bond (1029 cm^{-1}) is apparent.
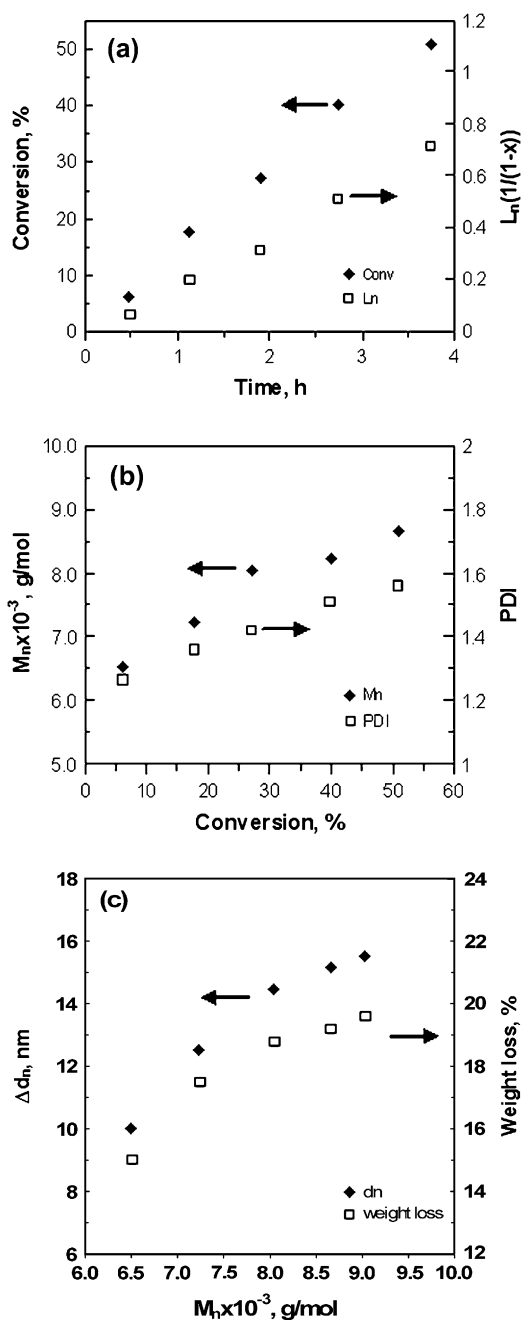
Fig. 3. Graft polymerization of DMAEA from pS-grafted latex particles. (a) Kinetic plot; (b) variance of M_n of pDMAEA in solution with conversion of DMAEA; (c) variance of particle size increases with M_n of pDMAEA in solution. $[DMAEA]_0/[MONAMS]_0/[SG1]_0 = 4260/4.4/1$, DMAEA/L-pS = 20.5/1 wt/wt, DMF 31.0 wt.%, 112 °C.

Fig. 4. Graft polymerization of DMAEA from pBA-grafted latex particles. (a) Kinetic plot; (b) variance of M_n of pDMAEA in solution with conversion of DMAEA; (c) variance of particle size increases with M_n of pDMAEA in solution. $[DMAEA]_0/[MONAMS]_0/[SG1]_0 = 3730/11.2/1$, DMAEA/L-pBA = 25/1 wt/wt, DMF 48.8 wt.%, 112 °C.

Together with absorbance of P=O (1350–1250 cm^{-1}) and P–O–C (1050–990 cm^{-1}), and elemental analysis of P (data not shown here), the formation of SG1-based alkoxyamine is evident. In the spectra of L-pDMAEA and L-pBA, the absorption of a strong carboxyl group C=O (1732 cm^{-1}) and an ester C–O bond (1163 cm^{-1}) clearly shows the existence of DMAEA or BA segments. Comparison of the L-pS and L-p(S-b-DMAEA) spectra show the distinctive formation of copolymers.
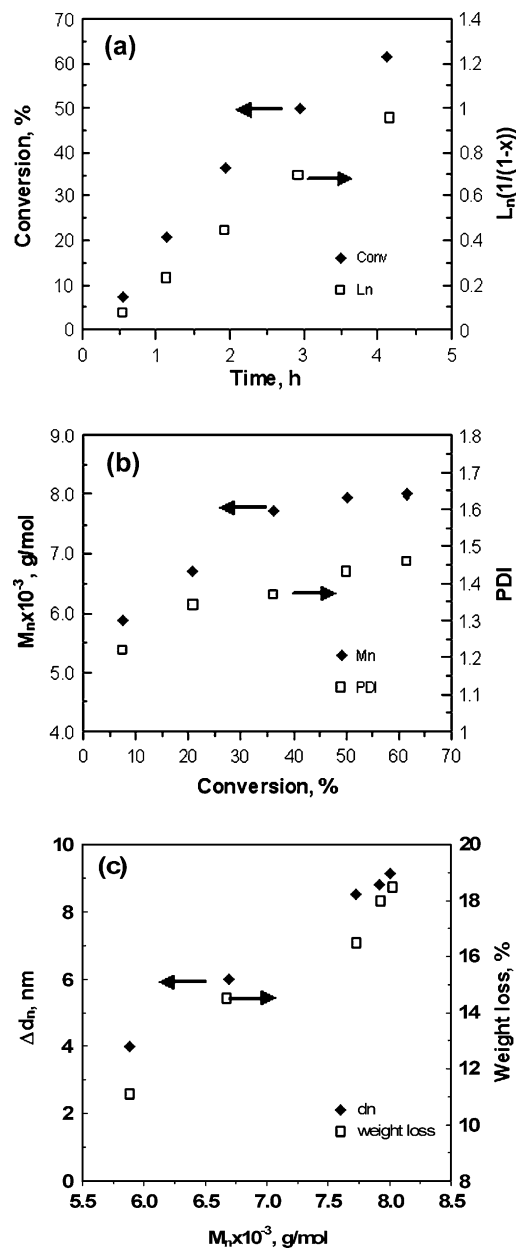
3.7. TEM and particle size analysis

Particles were analyzed by TEM to measure the size, which is averaged from at least 150 particles. The coefficient of variance of particle sizes for all the microspheres is in the range of 8–10%, indicating a very narrow but not monodisperse distribution. Typical TEM pictures of the microspheres are shown in Fig. 6. The original latex particles (a), pS-grafted and pBA-grafted particles (d and f, respectively) are all show a tendency to pack together. However, when pDMAEA is grafted on the particle surface as in the case of L-pDMAEA
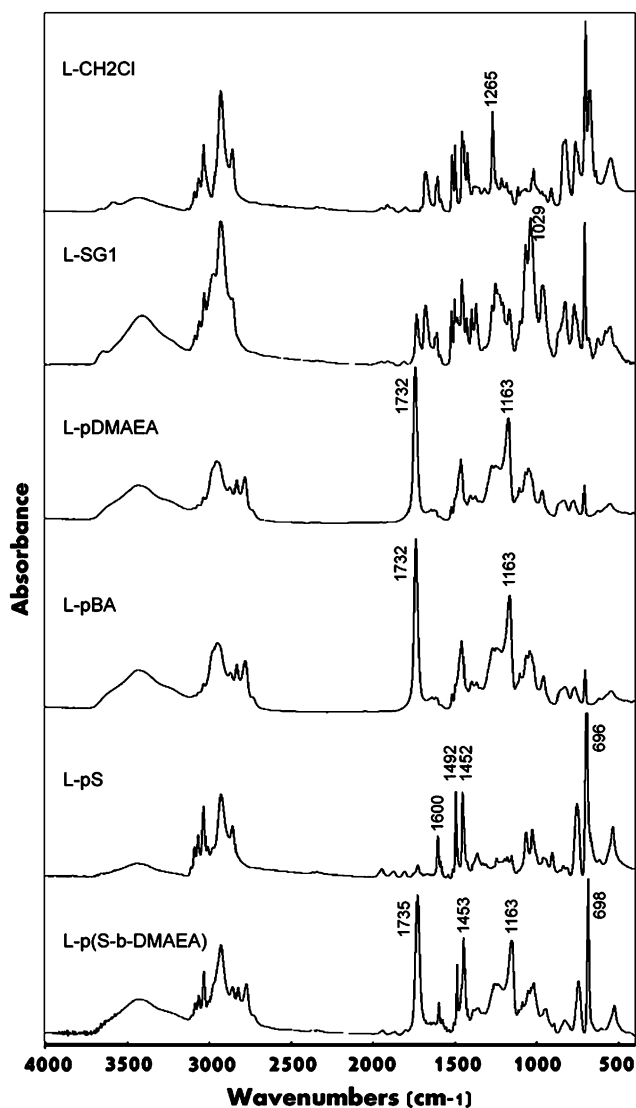
Fig. 5. Infrared spectroscopy of microspheres.

pS and pBA-grafted particles as well as the original latex particles and SG1-bound particles cannot be re-dispersed in water, even with the aid of sonication. These results provide further evidence that the grafting did occur on the surface, yielding block copolymers.

3.8. Thermal analysis of microspheres

The microspheres with homopolymer or block copolymer grafting on the surface were all subjected to thermal analysis. For thermogravimetric analysis (TGA) a heating temperature of 25–650 °C was applied. The microsphere core, which was crosslinked with DVB (5 wt.% with respect to monomers), decomposed in a temperature range of 350–540 °C. The brush-like polymers on the surface of the microspheres decomposed before 335 °C. Table 2 shows data from the analyses. It can be seen from Table 2 that homopolymer grafted microspheres have evident weight loss, ranging from ∼10% for L-pS and L-BA to 23–32% for L-pDMAEA. The weight loss of pS is only 12%, lower than that of L-pDMAEA, while the increase of particle size for pS is 24 nm, much larger than for L-pDMAEA (5–11 nm). This seemingly contradictory observation can be explained by the degree of monomer swelling of the core latex particles. Styrene and low molecular weight pS are good swelling solvents for the microsphere core used in this work, and therefore the graft polymerization of styrene is expected to occur not only on the surface but also on the subsurface, thereby giving a larger increase in particle size as we previously observed [18]. This is possible when taking into account that the degree of crosslinking is not very high, and the similar explanations have been proposed previously [10,18]. For the DMAEA, subsurface swelling is minimal and a more distinct core-shell morphology results. From Table 2, we can see that block copolymer brushes, L-p(S-b-DMAEA) and L-p(BA-b-DMAEA), have increased weight loss when compared to their macroinitiators − homopolymer grafted microspheres. The variance of weight loss of DMAEA-grafted microspheres with M_n of free pDMAEA is shown in Figs. 1c, 2c, 3c and 4c. The weight loss data as described above probably have a higher experimental error, estimated up to 10%, due to the difficulty in determining the upper temperature of decomposition for the grafted polymers. In spite of this, the trend of variance of weight loss with M_n is comparable with the variance of Δd_n with M_n.

DSC data are also shown in Table 2. The pure polymers pS, pBA and pDMAEA have glass transition temperatures (T_g) of 100, −54 and −54 °C, respectively. It is not possible to differentiate BA and DMAEA blocks from DSC experiments. However, DSC analysis can affirm the formation of block copolymers p(S-b-DMAEA) attached to microspheres, as can be seen from two distinct T_g's for L-p(S-b-DMAEA). Since the crosslinked bulk microsphere core will not have a transition at low temperature, the T_g's of the grafted microspheres will be from brush-like polymers attached to the particles.

(c), L-p(S-b-DMAEA) (e), and L-p(BA-b-DMAEA) (g), the particles are well-dispersed in THF. This change in behavior reflects the change in composition of the particle surface due to the presence of pDMAEA grafting on the polystyrene latex particles. A larger increase of particle size for pS-grafted particles is observed compared to either pDMAEA or pBA-grafted particles. This will be discussed further in the next section. When grafted polymers have a large difference of density with the bulk polymeric microspheres (e.g. pDMAEA and p(S-b-DMAEA) grafted particles), a core-shell structure can be seen in the TEM pictures. An example is given in Fig. 6h for p(S-b-DMAEA) grafted particles.

The formation of pDMAEA primarily on the outer particle surface was supported by water-dispersion experiments. The microspheres in a THF dispersion were dried by air-blowing and then applying vacuum (room temperature) for 3 h to remove THF. They were re-dispersed in water after drying. Only pDMAEA, p(S-b-DMAEA) and p(BA-b-DMAEA) grafted particles can be readily re-dispersed in water; while
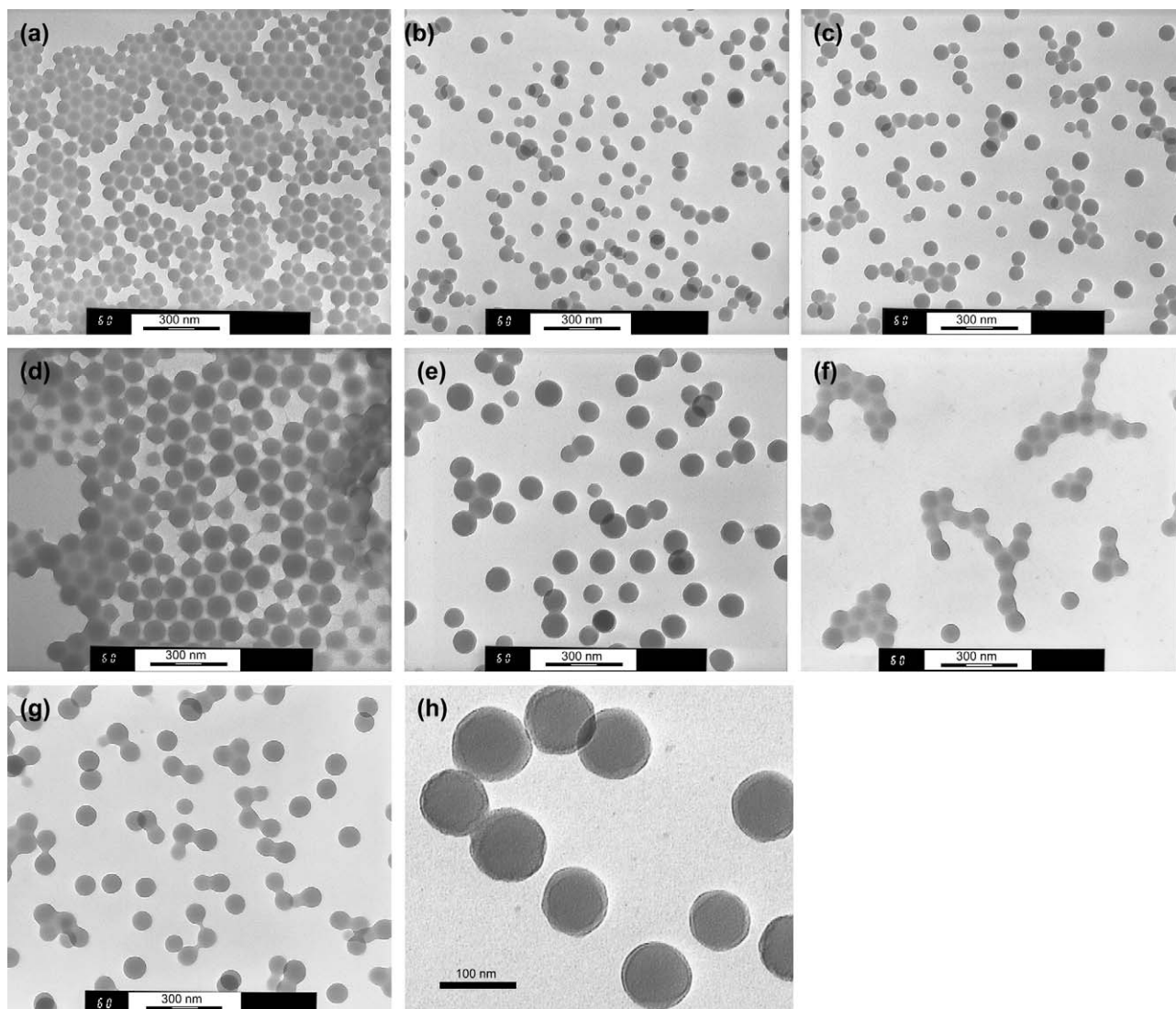
Fig. 6. TEM of microspheres. Scale bar in photos is of 300 nm. (a) L-CH₂Cl; (b) L-SG1; (c) L-pDMAEA; (d) L-pS; (e) L-p(S-*b*-DMAEA); (f) L-pBA; (g) L-p(BA-*b*-DMAEA); (h) enlarged photo of L-p(S-*b*-DMAEA).

Table 2
Thermal analysis of microspheres

Samples	Average particle size (nm)	Decomposition temperature (°C)	Weight loss (%)	T_g (°C)
L-pDMAEA	67	100–330	23–32	−32
L-pS	84	110–335	12	88
L-p(S-*b*-DMAEA)	102	100–335	15–20	−20; 84
L-pBA	73	100–260	8	−44
L-p(BA-*b*-DMAEA)	80	100–330	11–18	−44

4. Conclusion

Surface-initiated NMRP of DMAEA was performed at 112 °C on the surface of microspheres immobilized with SG1. The SG1-mediated polymerization of DMAEA in solution is controlled in the presence of additional SG1, while the particle size and weight loss of microspheres increase with the molecular weight of free pDMAEA in solution. Besides the formation of pDMAEA-grafted microspheres, pS and pBA-grafted microspheres have also been prepared which were subsequently used as macroinitiators to synthesize functional microspheres with block copolymers p(S-*b*-DMAEA) and p(BA-*b*-DMAEA) grafted on the particle surface. A series of analytical techniques including IR, TEM and thermal analysis were applied for the characterization of these microspheres, with the results supporting the formation of brush-like polymers attached to the microsphere surface.

References

[1] Zhao B, Brittain WJ. Prog Polym Sci 2000;25:677–710.
[2] Zheng G, Stover HDH. Chin J Polym Sci 2003;21:639–51.

[3] Edmondson S, Osborne VL, Huck WTS. Chem Soc Rev 2004;33:14–22.

[4] Guerrini MM, Charleux B, Vairon J-P. Macromol Rapid Commun 2000;21:669–74.

[5] Angot S, Ayres N, Bon SAF, Haddleton DM. Macromolecules 2001;34: 768–74.

[6] Ayres N, Haddleton DM, Shooter AJ, Pears DA. Macromolecules 2002; 35:3849–55.

[7] Bontempo D, Tirelli N, Feldman K, Masci G, Crescenzi V, Hubbell JA. Adv Mater 2002;14:1239–41.

[8] Kizhakkedthu JN, Takacs-Cox A, Brooks DE. Macromolecules 2002;35: 4247–57.

[9] Kizhakkedthu JN, Brooks DE. Macromolecules 2003;36:591–8.

[10] Zheng G, Stover HDH. Macromolecules 2002;35:6828–34.

[11] Zheng G, Stover HDH. Macromolecules 2002;35:7612–9.

[12] Zheng G, Stover HDH. Macromolecules 2003;36:1808–14.

[13] Jesberger M, Barner L, Stenzel MH, Malmstrom E, Davis TP, Ostmark E, et al. J Polym Sci Part A Polym Chem 2003;41:3847–61.

[14] Barner L, Li C, Hao X, Stenzel MH, Barner-Kowollok C, Davis TP. J Polym Sci Part A Polym Chem 2004;42:5067–76.

[15] D'Agosto F, Charreyre M-T, Pichot C, Gilbert RG. J Polym Sci Part A Polym Chem 2003;41:1188–95.

[16] Perrier S, Takolpuckdee P, Mars CA. Macromolecules 2005;38:6770–4.

[17] Hodges JC, Harikrishnan LS, Ault-Justus S. J Comb Chem 2000;2:80–8.

[18] Bian K, Cunningham MF. J Polym Sci Part A Polym Chem 2005;43: 2145–54.

[19] Husseman M, Malmstrom EE, McNamara M, Mate M, Mecerreyes D, Benoit DG, et al. Macromolecules 1999;32:1424–31.

[20] Chaumont P, Chapel JP, Devaux C, Beyou E. Polym Prepr 2002;43:74–5.

[21] Kasseh A, Ait-Kadi A, Riedl B, Pierson JF. Polymer 2003;44:1367–75.

[22] Bartholome C, Beyou E, Bourgeat-Lami E, Chaumont P, Zydowicz N. Polymer 2005;46:8502–10.

[23] Alexandridis P, Lindman B, editors. Amphiphilic block copolymers: self-assembly and applications. Amsterdam: Elsevier Science; 2000.

[24] Ignatova M, Voccia S, Gilbert B, Markova N, Mercuri PS, Galleni M, et al. Langmuir 2004;20:10718–26.

[25] Bian K, Cunningham MF. J Polym Sci Part A Polym Chem 2006;44: 414–26.

[26] Subramonia S. React Funct Polym 1996;29:129–33.

[27] Matyjaszewski K, Woodworth BE, Zhang X, Gaynor SG, Metzner Z. Macromolecules 1998;31:5955–7.

[28] Chem Abstr, 113:192294 (Marmara Universitesi Fen Bilimleri Dergisi (in Turkish) 1989;6:105–10).