Atom Transfer Radical Polymerization of *n*-Butyl Acrylate from Silica Nanoparticles

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ABSTRACT: This article reports the synthesis of atom transfer radical polymerization (ATRP) of active initiators from well-defined silica nanoparticles and the use of these ATRP initiators in the grafting of poly(n-butyl acrylate) from the silica particle surface. ATRP does not require difficult synthetic conditions, and the process can be carried out in standard solvents in which the nanoparticles are suspended. This "grafting from" method ensures the covalent binding of all polymer chains to the nanoparticles because polymerization is initiated from moieties previously bound to the surface. Model reactions were first carried out to account for possible polymerization in diluted conditions as it was required to ensure the suspension stability. The use of *n*-butyl acrylate as the monomer permits one to obtain nanocomposites with a hard core and a soft shell where film formation is facilitated. Characterization of the polymer-grafted silica was done from NMR and Fourier transform infrared spectroscopies, dynamic light scattering, and DSC. © 2001 John Wiley & Sons, Inc. J Polym Sci Part A: Polym Chem 39: 4294–4301, 2001 **Keywords:** atom transfer radical polymerization (ATRP); grafting from; inorganic materials; nanocomposites; self-assembly; silicas

INTRODUCTION

Nanoparticle/polymer composites attract strong interest because of the combination of both the properties of the inorganic nanoparticles (optical, electronic, or mechanical) and those of the polymer (solubility, film formation, and chemical activity).¹⁻⁴ However, the exploitation of these properties requires a homogeneous dispersion of the particles in the polymer matrix. One way to avoid agglomeration is to covalently graft polymer chains onto the particles.^{5–7} Grafting does not only improve the stability of the nanoparticles in suspension but also increases the compatibility of the nanoparticles with the polymer matrix.

In the context of this work, we are particularly interested in the mechanical and thermal properties of polymeric materials that can generally be improved by the addition of inorganic fillers such as silica nanoparticles.^{8,9} It has been shown that hybrids having covalently bound polymer chains tend to form well-defined nanodomains and show superior performance (higher storage modulus, better stability, hardness, and abrasion resistance) as compared with particles that are blended and that allow more macroscopic phase separation.⁹

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The "grafting onto" technique, that is, grafting polymer chains onto nanoparticles, is generally used for that purpose,^{10,11} but contamination from nongrafted chains usually occurs. Then, purification of the solutions, that is, separation of the grafted chains from the nongrafted ones, remains difficult. Also, strong hinderance between grafted polymer chains prevents attachment of further ones and then limits the graft density.

One way to overcome this problem is to use the "grafting from" method as shown by Prucker and Rühe^{12,13} who used azo initiators for free-radical polymerization. This method consists of immobilizing initiator molecules onto the surface of the particles and performing the polymerization at the particle surface. In this case, particles can be purified (dialysis or centrifugation), and the graft density can be determined prior to polymerization.

Nevertheless, free-radical polymerization does not control chain growth, and a non-negligible amount of polymer is produced in solution. Welldefined polymer chains are necessary if we want to form well-dispersed nanoparticle/polymer films. A controlled radical polymerization method such as atom transfer radical polymerization (ATRP) is therefore preferred.¹⁴ ATRP has already been successfully used for the functionalization of planar surfaces or porous silica using the "grafting from" method.¹⁵⁻²¹ Recently, first attempts to use silica particles as substrates for ATRP have been demonstrated by von Werne and Patten.²² Methyl methacrylate and styrene have been polymerized from these entities bearing appropriate functionalization. In this article, a very well presented study showed that polymerization is controlled with small particles (75 nm) but not in the case of larger ones (300 nm). The lack of control was attributed to the very high monomerto-initiator ratio in the polymerizations from large silica particles. Addition of a small amount of free initiator permitted to induce molecular weight control.

In the present work, the silica particles were even smaller (12 nm in diameter), and this size is comparable to a bulky molecule such as multifunctional initiator.²³ Moreover, *n*-butyl acrylate was chosen as the monomer for polymerization from silica nanoparticles where the initiator molecules were previously immobilized. Because the corresponding polymer has a low glass-transition temperature ($T_{\rm g}$), then the solvent evaporation is slower and the rearrangement of chains is favored. This leads to formation of homogeneous

films at ambient temperature. Indeed, the ultimate objective was to form nanocomposite films by mixing these poly(n-butyl acrylate) grafted particles in a polymer matrix. The resulting dispersion is thought to be improved as a result of the better compatibility between the matrix and the particle's surface.

EXPERIMENTAL

Reagents

Pyridine and triethylamine (Aldrich) were purified by distillation. *n*-Butyl acrylate (Aldrich) was purified by extraction with 5% aqueous sodium hydroxide and distilled from calcium hydride prior to use. Karstedt catalyst (platinum-divinyltetramethyldisiloxane complex) was provided from ABCR. 2-Bromo-2-methylpropionyl bromide, ethyl 2-bromo-2-methylpropionate, chlorodimethylsilane, N,N,N',N',N"-pentamethyldiethylenetriamine (PMDETA), copper(I) bromide (99.999%, stored in a glovebox), and copper(II) bromide were used as received from Aldrich. Membranes used for Soxhlet extraction were from Whatman (cellulose-extraction thimbles). Silica nanoparticles, 15% by weight in dimethylformamide (DMF), with an average diameter of 12 nm, were a gift from Bayer (Germany).

Synthesis of Initiator

Synthesis of Hex-5-enyl,2-bromo-2methylpropionate¹⁶

To a three-necked round-bottom flask were added 10 mL of 5-hexen-1-ol (83.4 mmol), 44.5 mL of dry methylene chloride, and 16.74 mL of triethylamine (110 mmol). 10.8 mL of 2-bromo-2-methylpropionyl bromide (87.4 mmol) were then added dropwise at 0 °C. The reaction proceeded under nitrogen at 0 °C for 1 h and then at room temperature for 2.5 h. The crude product was then isolated by filtration and extraction from an aqueous-saturated ammonium chloride solution. The alkene was then distilled at 55 °C under reduced pressure (6–7 mm Hg) to yield a clear colorless product (yield: 75%).

This product was analyzed by ¹H NMR (CDCl₃): δ 1.44 (quintet, 2H, CH₂), 1.65 (quintet, 2H, CH₂), 1.92 [s, 6H, (CH₃)₂], 2.08 (quartet, 2H, CH₂), 4.16 (t, 2H, CH₂), 4.9–5.07 (multiplet, 2H, CH₂), 5.68–5.85 (m, 1H, CH).

Hydrosilylation of Hex-5-enyl,2-bromo-2methylpropionate¹⁷

To a flame-dried three-necked round-bottom flask were added, in the following order, 1.2 g of alkene (3.9 mmol), 6.0 mL of chlorodimethylsilane (79.344 mmol), and 100 μ L of Karstedt's catalyst (10⁻⁴ Pt per Si). This mixture was reacted in the dark for 1 h at 40 °C under nitrogen and then overnight at room temperature under air. The catalyst was removed by quickly filtering the product through a short plug of dry silica. The excess chlorodimethylsilane was removed under reduced pressure, and the product was then used directly for the silanization step (purity >90%).

Product was analyzed by ¹H NMR: $\delta 0.2$ [s, 6H, (CH₃)₂], 0.8 (t, 2H, CH₂), 1.3 [m, 6H, (CH₂)₃], 1.65 (q, 2H, CH₂), 1.90 [d, 6H, (CH₃)₂], 4.15 (t, 2H, CH₂).

Binding of ATRP Initiator to Silica Particles

To a flame-dried three-necked round-bottom flask was added 10 mL (15% silica nanoparticles by weight) of a silica nanoparticle solution in DMF. Then, 0.25 g of the hydrosilylated product was introduced through a cannula followed by the dropwise addition of 1.25 mL of triethylamine. The reaction was stirred overnight under nitrogen and purified by Soxhlet extraction. In the Soxhlet extractor, the particles were put in a membrane and exposed to refluxing 50/50 v/v methylene chloride/diethyl ether for 6 h. The purified particles were then redispersed in 10 mL of DMF. This solution was used for the ATRP on the particles. Percentage grafting was determined by elemental analysis. The percentage weight of the OH groups at the surface of the particles was determined by Karl-Fisher titration, and the surface area of the nanoparticles was determined by the Brunauer, Emmett, Teller (BET) method.

Polymerizations

Model Polymerizations

Model ATRP of *n*-butyl acrylate was performed using ethyl 2-bromo-2-methylpropionate as an initiator and the CuBr/PMDETA catalyst system in 25 and 80% DMF solution by volume. A typical polymerization procedure with 80 vol % of DMF follows. All liquids were deoxygenated by purging with nitrogen for 30 min. To a three-necked round-bottom flask were added, in the following order (final concentration is given in brackets), 97.5 mg (0.012 M) of Cu^IBr (stored in a glovebox until use), 9.75 mL (1.17 M) of n-butyl acrylate, and 0.15 mL (0.012 M) of PMDETA. The mixture was stirred at room temperature until all copper bromide was solubilized. After the reaction mixture was considered to be homogeneous, 48 mL of DMF and 0.34 mL (0.04 M) of ethyl 2-bromo-2methylpropionate (E2BIB) were added. The CuBr/PMDETA/E2BIB ratio was 0.3/0.3/1. An initial sample was taken via a nitrogen-purged syringe; then the reaction flask was heated to 50 °C and remained under continuous nitrogen purge. The color of the solution changed rapidly from a light green to dark emerald green color. Kinetic samples were taken via purged syringes and used to determine conversion by gravimetry and molar-mass evolution by size exclusion chromatography (SEC). Samples were dissolved in tetrahydrofuran and purified through an alumina column to remove the copper complexes prior to SEC analysis.

Polymerization from Nanoparticles

All liquids were separately purged under nitrogen for 30 min. To a three-necked round-bottom flask were added, in the following order, 0.012 g (0.08 M) of $Cu^{I}Br$, 2.9 mL (1.57 M) of *n*-butyl acrylate, and 0.02 mL (0.08 M) of PMDETA. The reaction mixture was then allowed to stir until a homogeneous medium had formed. Then 10 mL of a solution of functionalized particles (1.5 g) in DMF were added to the reaction flask by cannula transfer. An initial sample was taken with a purged syringe; then the reaction mixture was heated to 50 °C and remained under continuous nitrogen purge. No immediate aggregation of the particles was observed at the start of polymerization. In this case, the color evolved from light green to turquoise blue, indicating a change in the nature of the copper complexes. Kinetic samples were taken via nitrogen-purged syringes and used to determine conversion by gravimetry. After the reaction, the solution was transferred to a dialysis tubing (Spectra/Por, cutoff of 12-14 kDa) and dialyzed against DMF.

Analysis

Products were analyzed by nuclear magnetic resonance spectroscopy, ¹H and ¹³C, using a Bruker AC200 FT-NMR spectrometer using the solvent peak as a reference [CDCl₃ or deuterated dimethyl sulfoxide (DMSO)]. Polymer molar mass



Scheme 1. Synthesis of the ATRP initiator.

was analyzed by SEC with tetrahydrofuran as the eluent at a flow rate of 1 mL/min with an injection volume of 100 μ L per sample. The columns were from Shodex (KF 802.5L, KF 804L, and KF 805L) and thermostated at 30 °C. The apparatus was equipped with a pump (515 high-pressure liquid chromatographer by Waters) and an autosampler (S5200, from Viscotek). A differential refractometer/viscometer detector (model 200 by Viscotek) was used to analyze samples. Molar masses were derived from a calibration curve on the basis of polystyrene standards. Fourier transform infrared spectra were collected on an Avatar 320 ESP spectrophotometer from Nicolet.

RESULTS AND DISCUSSION

A hybrid ATRP initiator containing a silane function was synthesized so that it could then be grafted onto silica particles (Scheme 1). The first step of the synthesis was the formation of an allylic initiator fragment (1) by the esterification of 2-bromo-2-methylpropionyl bromide and 5-hexen-1-ol, following the procedure of Husseman et al.¹⁶ The product was then used in a hydrosilylation reaction with dimethylchlorosilane, as described by Matyjaszewski et. al.,¹⁷ to yield a preinitiator (2) that could be condensed with the silica nanoparticles. Both products 1 and **2** were purified as described in the literature and analyzed by ¹H NMR.

The silane reactant 2 was then condensed with the silica nanoparticles to form the hybrid ATRP initiators (Scheme 2). The particles were purified by Soxhlet extraction. Similar purification has been performed on functionalized ceramic particles of the same size.²⁴ The percentage of grafted initiator molecules as compared with the total amount of starting material was determined from elemental analysis on the basis of carbon. The weight percentage grafting is described in the following equation:

Grafting (%) =
$$\frac{C_{\rm S}}{C_{\rm I} \times 100}$$

where C_S is the weight fraction of carbon in the sample, and C_I is the weight fraction of carbon in the initiator.

The grafting efficiency is estimated from the percentage of hydroxy groups initially available at the surface of the particles

Grafting efficiency (%) =
$$\frac{Grafting (\%)/M_{I}}{\% OH/M_{OH}} \times 100$$

where $M_{\rm OH}$ and $M_{\rm I}$ are the molar masses of the hydroxy group and initiator, respectively.

Elemental analysis gave a percentage of carbon in the sample of 2.80 wt %. This corresponds to a grafting percentage by weight of 6.23 wt % and a grafting efficiency of 61%. It represents 61% of grafted initiator segments as compared with the initial amount of OH groups on the surface of the SiO_2 particles. This percentage is translated into a grafting density of 1.4 initiators/nm². Such a grafting density would be expected because the initiator (2) is much bigger than a hydroxyl group and, consequently, would occupy a larger surface area per unit. This also indicates that a monolayer of initiator is formed. These particles were then redispersed in DMF and used as ATRP initiators to form hybrid nanoparticles by polymerization of *n*-butyl acrylate in a "grafting from" method.

To confirm that the concentration conditions imposed by the suspensions of silica particles permit one to conduct ATRP in DMF, model polymer-



Scheme 2. Grafting of the initiator to silica nanoparticles.

izations were performed. Although numerous studies have been performed on the solvent effects of ATRP,^{25,26} there has been no well defined kinetic study of ATRP of that *n*-butyl acrylate in dilute DMF solution. It has been $shown^{26,27}$ that the polarity of the solvents can affect the rate and behavior of ATRP. Thus, it is expected that solution polymerization in a high percentage of DMF will display novel kinetic behavior. Polymerizations have been performed in 25 and 80% DMF solutions. Results showed that the polymerization of n-butyl acrylate in 25% DMF was almost complete after 4 h of reaction (Fig. 1). The reaction is fast, but the polymerization is still controlled. The molar masses obtained were close to the theoretical values, and the polydispersity index (M_w/M_p) remained small [Fig. 2(a)]. Under diluted conditions (Fig. 1), polymerization is slower because of the lower concentrations of initiator, monomer, and catalyst. The conversion is limited to 70%

after 24 h of reaction. However, the reaction is still controlled, and the molar mass evolves linearly with conversion and follows the theoretical line [Fig. 2(b)]. As previously stated, the $M_{\rm w}/M_{\rm n}$ decreases during the reaction to the value of 1.1. These results thus permitted us to conclude that the diluted conditions did not affect molecular weight control in the ATRP process, but only slowed down the overall rate of polymerization.

Polymerization from the functionalized silica nanoparticles was much slower than in the analogous homogeneous conditions (80 vol % DMF; see Fig. 1). In this case, the color evolved from light green to turquoise blue, indicating a change in the nature of the copper complexes, and the viscosity increased rapidly (after 2 h of reaction the suspension was clearly more viscous). The reaction was stopped after 20% conversion, and after that point, physical microgel formation be-

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gan to occur (Fig. 1). The fact that the concentration of reagents was slightly lower than in the analogous model experiment is not sufficient to explain the large difference in polymerization rates. The initial monomer-to-initiator ratio was 30/1 for the model reactions, whereas it was 75/1in the case of polymerization from the particles. It was necessary to increase this ratio to obtain a similar dilution factor as that of the model reactions. Such slow polymerization might be the consequence of various factors. First, the activation by Cu^IBr of the grafted initiating species might be slowed down by the difficulty of these reactants to reach the particle surface as a result of physical size constraints. Second, due to radical confinement, irreversible termination reactions might be fast, leading to an increase in the deactivator concentration [Cu(II) complex] in the medium and then to a shift in the activation-deactivation equilibrium, thereby favoring the formation of dormant species. This result is supported by the fact that addition of 5% of $Cu^{II}Br_2$ at the beginning of polymerization decreased drastically the reaction rate, and no polymer was formed within a reasonable polymerization time (24 h). In model reactions (the diluted case), we found that addition of 5% of $Cu^{II}Br_2$ decreases the conversion from 70% to less than 50% after 5 h of reaction.

As a result of the inherent viscosity of the reaction media and the relatively large weight of the particles, even a small amount of bimolecular coupling could cause gelation. Because it is well



Figure 1. Conversion of monomer versus time plot: \blacktriangle model p(BuA) polymerization in 25% DMF, [*n*BA] = 4.98 M, [E2BIB] = 0.166 M, [Cu^IBr] = 0.049 M, [PMDETA] = 0.049 M; \blacksquare model p(BuA) polymerization in 80% DMF, [*n*BA] = 1.17 M, [E2BIB] = 0.039 M, [Cu^IBr] = 0.012 M, [PMDETA] = 0.012 M; and \bigcirc polymerization of (PBuA-*g*-SiO₂), [*n*BA] = 1.57 M, [SiBr] = 0.021 M, [Cu^IBr] = 0.007 M, [PMDETA] = 0.007 M.



Figure 2. Kinetic plots of model polymerizations in (a) 25% DMF and (b) 80% DMF: — theoretical M_n , \blacklozenge experimental M_n , and $\blacktriangle M_w/M_n$.

known that butyl acrylate is able to terminate by combination of polymer radicals, it was necessary to stop the polymerization at relatively low conversion. However, the formation of physical microgels instead of chemical crosslinking is supported by the possible redispersion of the poly(*n*-butyl acrylate)-*grafted*-silica particles (PBuA-*g*-SiO₂) by vigorous stirring or dilution.

The PBuA-g-SiO₂ suspension was further purified by dialysis to remove the ATRP catalyst and any possible ungrafted chains. ¹H NMR and SEC analyses of the counter-solution residue after removing the solvent indicated that no free poly(*n*-butyl acrylate) was detected (only the unreacted monomer was present). Dynamic light scattering measurements showed that the modified particles remained unagglomerated with an increase in the hydrodynamic diameter (28 nm).

To account for the polymerization of *n*-butyl acrylate from the surface of the silica particles, ¹³C NMR, IR, and DSC measurements were carried out. Figure 3(a) shows the ¹³C NMR spectrum of the dialyzed PBuA-*g*-SiO₂ in deuterated DMSO. The spectrum of the free poly(*n*-butyl acrylate) prepared classically in solution, in CDCl₃,

is displayed in Figure 3(b). The PBuA-g-SiO₂ could not be properly redispersed in chloroform; therefore, deuterated DMSO was used as the solvent. By comparing the two spectra, it is clear that PBuA chains are grafted to the particles. Five distinct carbons can be identified in the second spectrum as belonging to the PBuA part of the modified silica. The other characteristic peaks of the polymer, a and b, are hidden by the DMSO peak. Peaks widths are enlarged as a result of covalent bonding at the particle surface and the resulting lack of freedom of the polymer chains, as compared with the PBuA prepared in solution.

Comparison of the IR spectra also indicates that PBuA has been polymerized from the particle's surface (Fig. 4). Spectrum 4c (PBuA-g-SiO₂) clearly reveals the existence of new bands characteristic of PBuA (spectrum 4a). The band of the ester carbonyl at 1735 cm⁻¹ is particularly intense in spectra 4a and 4c. The other characteristic bands between 1150 and 1250 cm⁻¹ are hidden by the large band due to the Si—O stretch.



Figure 3. ¹³C NMR characterization of the nanocomposite after dialysis: (a) (PBuA-g-SiO₂) hybrid particles in DMSO- d_6 and (b) model PBuA in CDCl₃.



Figure 4. Fourier transform infrared spectra of (a) PBuA, (b) the unmodified SiO_2 nanoparticles, and (c) the (PBuA-g-SiO₂) hybrid particles.

The spectrum of the unmodified particles shows no peaks in these areas.

DSC measurements in one case showed an increase in the $T_{\rm g}$ of the PBuA-g-SiO₂ composite ($T_{\rm g} = -40$ °C) when compared with the model poly-(butyl acrylate) ($T_{\rm g} = -52$ °C). In other cases, the difference was even larger, and the glass transition is usually very broad. Others have also observed that grafted chains show a higher and broader $T_{\rm g}$ than free chains.²⁸ These differences can be explained by the decrease in mobility of the grafted chains. Solvent-cast films formed from the pure polymer are sticky and rubbery-like, whereas those of PBuA-g-SiO₂ look like polymer films below its $T_{\rm g}$. Although these observations need to be confirmed by characterization of the mechanical properties, they suggest that the particles are held by the grafted polymers.

CONCLUSION

Formation of a new example of polymer/nanoparticle composites with a soft corona of PBuA and a hard sphere consisting of SiO_2 nanoparticles has been described. ATRP was used as the technique to polymerize the *n*-butyl acrylate from the surface of 12-nm-silica particles. This method has the advantage of avoiding the presence of nongrafted chains and leads to individual coated particles. It also provides the possibility to control the molar mass of the grafted polymer chains. This factor is important for the control of SiO_2 nanoparticle dispersion in the polymer matrix. Moreover, the very small size of the particles represents a great advantage in the possibility of a better dispersion. The corresponding increase of the specific area will also help to improve the mechanical properties of the resulting films.²⁹

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