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Organic/inorganic hybrids by 'living'/controlled ATRP grafting from layered silicates

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'Living'/controlled radical graft polymerisation *via* the atom transfer radical polymerisation (ATRP) route has been carried out from ATRP initiator-modified layered silicate. The grafted polymer chains were detached from the solid in order to prove the well-known ATRP features. X-Ray diffraction measurements at different times of conversion demonstrate an increase of delamination as a result of increasing chain length of the grafts which finally results in a fully dispersed polymer silicate nanocomposite.

Introduction

Increasing interest in organic/inorganic hybrids as nanocomposites has partially focused on polymer layered silicate nanocomposites due to a wide range of scientific and technological viewpoints.[1–5] Driven by low cost strategies, most of them were prepared by mixing of the components, for example, a layered silicate and an appropriate polymer which is able to intercalate. A second route is the *in situ* polymerisation of the monomer in the presence of the layered silicate. Presently only two papers have been published which deal with a grafting technique using a layered silicate with an anchored initiator. Suter and coworkers[6] have reported about the grafting from high surface mica by ionically binding a peroxide initiator to the surface. This one initiates classical free radical polymerisation. Sogah's group[7] described the *in situ* polymerisation using a silicate-anchored initiator of the 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO) derivative which initiates a so-called TEMPO-mediated, stable, free radical polymerisation (SFRP). In fact, this is one of the few examples of graft polymerisation from a solid surface using the so-called 'living'/controlled radical polymerisation technique reported so far.[8–25] The key features of this technique are the control of polymer graft length and length distribution as well as the possibility of designing grafted block copolymers. Since SFRP requires high reaction temperatures which might become a problem due to thermal initiation and is limited to styrene derivatives as monomers, we used the ATRP[26] process to overcome these problems.

Experimental

Materials and methods

Na^+-montmorillonite (Süd-Chemie AG), 11-bromoundecan-1-ol (Fluka), trimethylamine [33% in ethanol, 4.2 M, (Fluka)], 1,1,4,7,10,10-hexamethyltriethylenetetramine (Aldrich) were used as received. 2-Bromoisobutyryl bromide (Acros) was vacuum distilled. THF was purified by destillation over sodium/benzophenone. Acetone was dried over P_2O_5 and distilled. Methyl methacrylate was vacuum distilled over CaH_2 and stored under nitrogen at −20 °C. CuBr was purified according to the literature.[27]

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer using deuterated solvents with the solvent peak as a reference. FT-IR spectra were recorded on a Bruker Equinox 55 spectrometer. Samples were prepared as KBr pellets or as films between NaCl-plates. TGA thermograms were taken from a Netzsch TG 209 analyser at a heating rate of 20 °C min^{-1} under a nitrogen atmosphere between 30 and 550 °C and in the temperature range from 550 to 700 °C under an air atmosphere. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) using an SDS 9404/SFD 12560 system from Schambeck SFD with two mixed C columns from Polymer Laboratories equipped with a GASTORR 102 vacuum degasser, a Schambeck SFD RI2000-F differential refractometer detector and a Wyatt miniDAWN multi angle light scattering (MALS) detector. Measurements were performed in DMF/0.1 M LiBr as eluent at 80 °C. XRD patterns of poly(methyl methacrylate)–clay nanocomposites were obtained by using a Stoe StadiP theta-theta diffractometer equipped with a Ni-filtered CuKα (1.543 Å) source. Spectra were recorded using a Bragg–Brentanno geometry.

Synthesis

11′-Bromoundecanyl-2-bromoisobutyrate 3. To a solution of 11-bromoundecan-1-ol (5 g, 19.9 mmol) and triethylamine (2.8 mL, 20.1 mmol) in dry THF (100 mL) was added a solution of 2-bromoisobutyryl bromide (2.7 mL, 21.8 mmol) in dry THF (25 mL) at 0 °C. After stirring at 0 °C under argon for 2 h, the cooling bath was removed and stirring was continued for 6 h at room temperature. Triethylamine hydrobromide was separated by filtration and the solvent was removed *in vacuo*. The residue was dissolved in diethyl ether (100 mL) and the solution was washed with aqueous $NaHCO_3$ (saturated, 150 mL), NaCl (saturated, 100 mL) and H_2O (100 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel with petroleum ether–ethyl acetate (10 : 1 v/v) to give the product **3** as a colourless oil. Yield: 5.81 g (73%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.16 (t, 2H, CH_2O), 3.39 (t, 2H, CH_2Br), 1.90 [s, 6H, $(CH_3)_2$], 1.82 (quintet, 2H, CH_2), 1.65 (quintet, 2H, CH_2), 1.35–1.22 [m, 14H, $(CH_2)_7$]; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.71 (RCOOR), 66.11

(CH_2O), 55.97 [$(CH_3)_2CBr$], 33.96 (CH_2Br), 32.80 (CH_2), 30.77 [$(CH_3)_2$], 29.37, 29.36, 29.34, 29.10, 28.71, 28.31, 28.13, 25.74 (CH_2); FT-IR (film) 2928, 2855, 1735, 1461, 1389, 1277, 1146, 1110 cm^{-1}.

11′-(*N*,*N*,*N*-trimethylammonium bromide)undecanyl-2-bromoisobutyrate 4. To a solution of **3** (1.2 g, 3 mmol) in dry THF (5 mL) was added a solution of trimethylamine in ethanol (10 mL, 4.2 M, 42 mmol) at room temperature. The reaction mixture was stirred in the dark under an argon atmosphere for 2 days. Volatile materials were removed *in vacuo*. The crude product was washed three times with dry diethyl ether (20 mL). The product **4** was separated, after decantation of the diethyl ether and drying *in vacuo* over P_2O_5, as a white hygroscopic solid material.

Yield: 1.17 g (85%); ^1H NMR ($CDCl_3$, 400 MHz) δ 4.08 (t, 2H, CH_2O), 3.51 (m, 2H, CH_2N), 3.39 [s, 9H, $N(CH_3)_3$], 1.85 [s, 6H, $(CH_3)_2$], 1.67 (m, 2H, CH_2), 1.60 (quintet, 2H, CH_2), 1.37–1.17 [m, 14H, $(CH_2)_7$]; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.59 (RCOOR), 66.83 (CH_2N), 65.98 (CH_2O), 56.01 [$(CH_3)_2CBr$], 53.29 [$N(CH_3)_3$], 30.67 [$(CH_3)_2$], 29.18, 29.14, 29.13, 29.03, 28.92, 28.16, 26.03, 25.28, 23.05 (CH_2); FT-IR (KBr-pellet) 3001, 2924, 2852, 1730, 1469, 1414, 1389, 1369, 1279, 1163, 1110, 1027 cm^{-1}.

Modification of Na^+-montmorillonite with initiator 4. Na^+-montmorillonite (0.5 g, cation exchange capacity: 0.8 mequiv g^{-1}) was dispersed into deionised water (250 mL) at room temperature. The dispersion was stirred for 30 min. A solution of **4** (230 mg, 0.5 mmol) in deionised water (25 mL) was prepared. It was poured into the montmorillonite–water dispersion under vigorous stirring. Stirring was continued for 4 h and the reaction mixture was left without stirring for additional 12 h. The exchanged clay was filtered and washed with deionised water. It was then dried *in vacuo* over P_2O_5 at room temperature.

The amount of immobilized initiator was determined by TGA: 0.67 mmol immobilised initiator per g montmorillonite.

Typical polymerisation process. Graft reactions were carried out in Schlenk flasks equipped with a magnetic stirring bar. In a typical polymerisation a 10 mL Schlenk flask was charged with montmorillonite modified with **4** (100 mg, 0.067 mmol surface-bound initiator). The flask was capped with a rubber septum and the contents were degassed by applying a vacuum and back-filling with nitrogen three times. Degassed acetone (0.5 mL) was added to the content *via* a syringe that had been purged with nitrogen. The suspension was stirred for 30 min. In a second 10 mL Schlenk flask a solution was prepared containing methyl methacrylate (3 mL, 28 mmol), acetone (1.5 mL), CuBr (9.6 mg, 0.067 mmol) and 1,1,4,7,10,10-hexamethyltriethylenetetramine (18 μL, 0.067 mmol). The contents were then frozen with liquid nitrogen and purged with nitrogen by applying a vacuum and purging with nitrogen gas alternately three times. This homogenous solution was transferred to the montmorillonite/**4**-acetone dispersion *via* a syringe that had been purged with nitrogen. The reaction mixture was stirred in a 60 °C oil bath for 4 h under nitrogen. The viscous mixture was diluted with acetone and the polymer-grafted montmorillonite was precipitated in methanol. The solid material was collected and dried at 50 °C and 10 mbar to constant weight. Yield: 1.6 g poly(methyl methacrylate)-grafted montmorillonite.

Cleavage of polymer grafts from the surface of montmorillonite. The nanocomposite (100 mg) was suspended in toluene (150 mL) and methanol (10 mL). *p*-Toluenesulfonic acid (20 mg) was added and the reaction mixture was heated under reflux for 14 h. The reaction mixture was transferred to centrifuge tubes and the solid material was separated by centrifugation. The supernatant was separated by decantation and the solution was passed through a column of alumina. The solution was concentrated *in vacuo* and the polymer was precipitated in methanol. The polymer was filtered off and dried at 50 °C and 10 mbar to constant weight.

Results and discussion

An appropriate ATRP-initiator which is capable of intercalating between the individual layers of a silicate such as Na^+-montmorillonite must contain an ionic anchor group, see Scheme 1. The ATRP-initiating head group is introduced through esterification of **1** with **2** quite easily. By reaction of **3** with trimethylamine the cationic trimethylammonium anchor group is established in **4**.

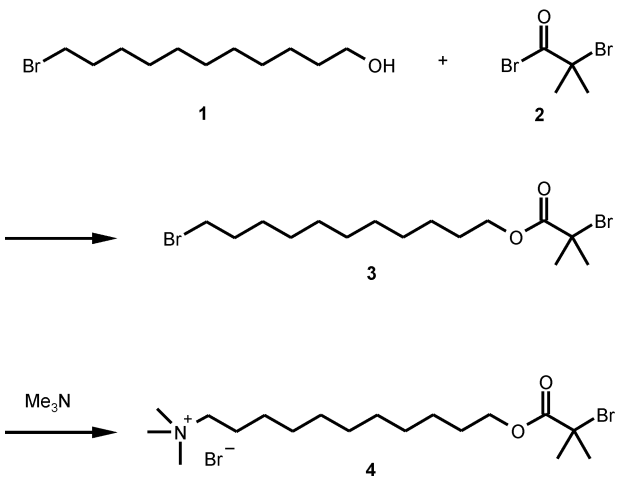
The initiator **4** was ion-exchanged onto Na^+-montmorillonite (Scheme 2), having an ion exchange capacity of 0.8 mequiv g^{-1}.

Fig. 1 displays a representative X-ray diffraction pattern. The resulting interlayer distance increases from $d_{001} = 1.16$ nm for the unmodified silica (a) to finally $d_{001} = 1.88$ nm (b). This is a clear indication of the formation of the initiator-modified silica **5**.

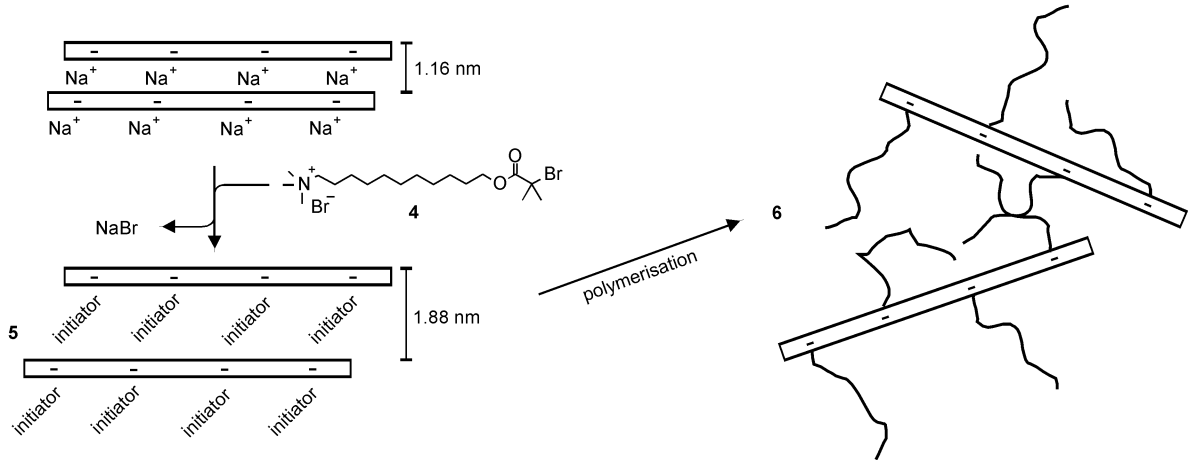
Thermogravimetric analysis (TGA) of **5** reveals a silicate content of 75% which corresponds to 0.67 mmol immobilised initiator per g silicate. This value is slightly lower than for the case of complete ion exchange (70% silicate content and 0.8 mmol initiating sites per g silicate). This is attributed to the greater sterical demands of **4** than for small inorganic ions.

'Living'/controlled ATRP graft polymerisation of methyl methacrylate (MMA) from initiator-modified montmorillonite **5** (Scheme 2) was carried out at 60 °C. CuBr complexed by the ligand 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) was used as the transition metal catalyst. Acetone was used as solvent (MMA : acetone 3 : 2, v/v) for two reasons. First, slightly polar solvents increase the solubility of the catalytic system,[28] which leads to a better control of the polymerisation process. Second, **5** can readily be dispersed in acetone, which is attributed to interaction of the solvent with the remaining polar groups of the layered silicate. This should result in a better accessibility towards the initiating sites in between the layered silicate. After predetermined times, polymerisation was stopped and the resulting composite **6** precipitated into methanol. The grafted polymer chains were detached from the surface to investigate their molecular weight and molecular weight distribution by gel-permeation chromatography (GPC).

As can be seen from Table 1 the molecular weight increases with conversion and the polydispersity index (PDI) remains low. The graft polymerisation shows very good first-order kinetic behaviour (Fig. 2) under these conditions. These results



Scheme 1



Scheme 2

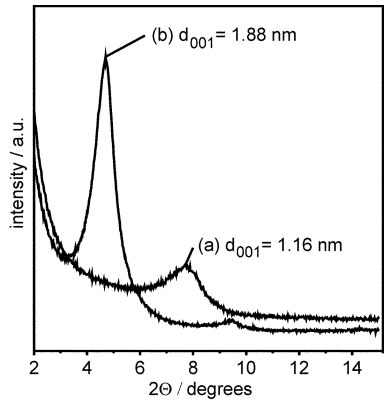


Fig. 1 Plot of X-ray diffraction (in arbitrary units) *versus* scattering angle (in degrees): (a) unmodified Na^+-montmorillonite; (b) initiator-modified silicate **5**.

Table 1 Molecular weight control in the synthesis of PMMA–silicate nanocomposite at different polymerisation times

Entry[a]	Time/ min	Conversion[b] (%)	M_w[c]/ g mol^{-1}	M_n[d]/ g mol^{-1}	PDI[e]
1	30	5	15 100	13 600	1.11
2	60	13	29 500	26 800	1.10
3	120	27	30 800	29 000	1.06
4	240	52	52 400	46 000	1.14

[a]Conditions: 100 mg of **5** (0.067 mmol of initiating sites); $[CuBr]_0$ 0.067 mmol; $[HMTETA]_0$ 0.067 mmol, $[MMA]_0$ 28.2 mmol; MMA : acetone 3 : 2, v/v; 60 °C. [b]Calculated value from determined weight loss of composite during TGA. [c]Weight-average molecular weight by SEC using MALS. [d]Number-average molecular weight by SEC. [e]Polydispersity index, M_w/M_n.

are in good agreement with the proposed mechanism for a 'living'/controlled radical polymerisation.

The precipitated samples of the resulting composite material were further analysed as to whether the graft polymerisation process resulted in delamination of the starting compound **5** (Fig. 3).

XRD of the composite obtained after a polymerisation time of 0.5 h [Fig. 3(b)] shows a weak diffraction peak. The layered structure is retained to a certain extent. After 4 h of polymerisation [Fig. 3(d)] the silicate layers were completely delaminated as evidenced by the absence of any diffraction peak.

In summary, we have demonstrated that 'living'/controlled graft polymerisation from initiator-modified silicate is possible. The increase of molecular weight with conversion and also low

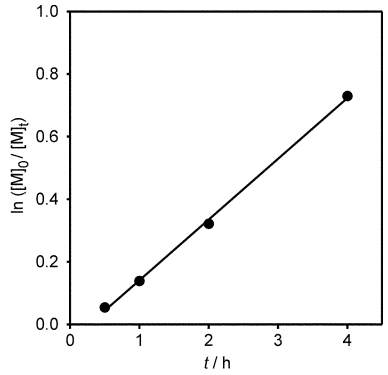


Fig. 2 First-order rate plot for the ATRP graft polymerisation of MMA from initiator-modified montmorillonite **5**.

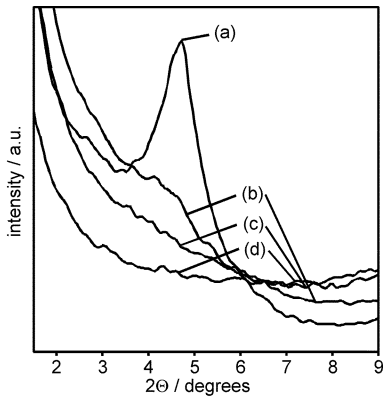


Fig. 3 Plot of X-ray diffraction (in arbitrary units) *versus* scattering angle (in degrees): (a) initiator-modified silicate **5**; (b) composite after 0.5 h time of polymerisation; (c) composite after 1 h time of polymerisation; (d) composite after 4 h time of polymerisation.

polydispersities are in agreement with the proposed mechanism for ATRP. Graft polymerisation in between individual silicate layers is a promising method for the direct synthesis of dispersed silicate nanocomposites. Further efforts to measure physical properties of the polymer silicate nanocomposites are in progress.

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