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Living Anionic Surface Initiated Polymerization (SIP) of Styrene from Clay Surfaces

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Surface initiated polymerization (SIP), in which the initiator is directly bound onto inorganic surfaces and then activated for polymerization, has been investigated to improve the stabilities and grafting density of polymers on "fillers" and flat substrate surfaces. This includes polymerization by free radical,[1] atom-transfer radical polymerization (ATRP),[2] 2,2,6,6-tetramethyl-1-piperidyloxy (TEMPO),[3] cationic polymerization,[4] and anionic polymerization[5,6] mechanisms for polymer composite materials[7] and surface modifiers. Living anionic polymerization is an excellent method for preparing near monodispersed homopolymers and various block and graft copolymer architectures.[8,9] However, it has not been reported in methodologies for SIP directly on clay (silicate) particle lamellar hosts.[10] This is directly related with the difficulties associated with the anionic polymerization mechanism[11] and the presence of adventitious H_2O molecules as in the case of silicates and clay particles.[7]

This communication reports our initial results on the living anionic polymerization initiated directly from lamellar clay surfaces and differentiates surface initiation from intergallery initation.[5,12] We have used a 1,1-diphenylethylene (DPE) derivative as an initiator precursor in order to avoid self-polymerization.[13] DPE was modified to be an organic cation by functionalizing with a triethylammonium bromide group.[14] The immobilization of the DPE on clay and partial exfoliation were done by a cation-exchange and centrifugation procedure (Supporting Information). The ion-exchange capacity for clay (Montmorillonite, Na^+) is 90 mequiv/100 g.[15] The exact molar-mass ratio of initiator to clay should be 0.9 mmol/g of clay, that is, ~27.56% initiator on clay. This value was a little higher than the experimental result of 23.9% as determined by thermogravimetric analysis (TGA). X-ray diffraction (XRD)[16] showed a basal spacing of the initiator-intercalated clay to be 2.34 nm, calculated from a sharp first-order Bragg peak. The initiator layer thickness would amount to an ~1.2 nm increase based on the basal spacing of pure clay, which is 1.14 nm.[10] The procedure for immobilization of DPE and polymerization of styrene is shown in Figure 1.

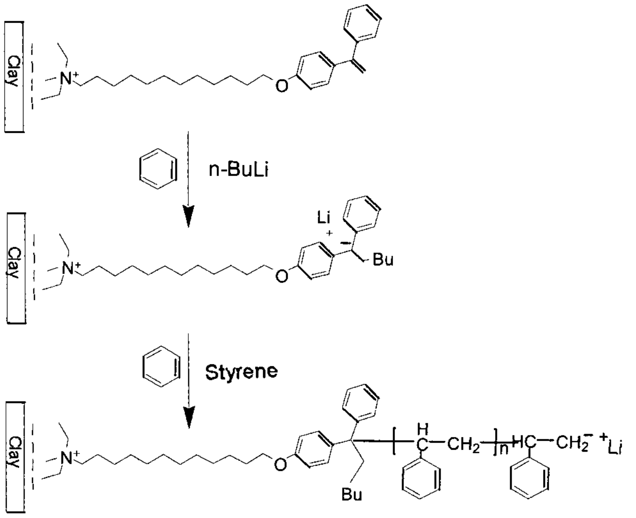

Figure 1. Chemical structure of the cationic DPE initiator. Immobilization of DPE and polymerization of styrene from clay surfaces was done by cation exchange. Polymerization was initiated after reacting with *n*-BuLi.

Polymerization was carried out in a specially designed reactor under high vacuum in which an attached filter allows the separation of clay from excess initiator.[17] We have found that room temperature and high vacuum conditions were not enough to remove trace impurities such as H_2O, which can result in a broadened molecular weight distribution or polydispersity index (PDI =

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[10] Giannelis, E. P.; Krishnamoorti, R.; Manias, E. *Adv. Polym. Sci.* **1999**, *138*, 108. Values ranging from 0.98 to 1.26 nm have been reported in the literature for the basal (lamellar) spacing of various polymorphs of clay (phylosilicates). This is believed to be largely dependent on bound cations in the interlayers.

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[14] The full name for the cationic DPE is triethyl{12-[4-(1-phenylvinyl)phenoxy]dodecyl}ammonium bromide. The synthesis will be reported in a future publication: Zhou, Q.; Mays, J.; Advincula, R. In preparation.

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[16] X-ray diffraction was done with a Phillips, X′pert system, PW3040-MPD, with Cu Kα = 0.1543 nm.

[17] The sequence of the polymerization procedure is as follows: After the DPE initiator-coated clay was placed into the reactor, the system was put on the vacuum line and the reactor was heated to 120 °C for at least 8 h and then cooled. Excess *n*-BuLi in benzene was then added to the initiator−clay, followed by extensive washing and filtration in vacuo to remove extra *n*-BuLi and any unattached DPE initiator. Since *n*-BuLi initiates DPE very slowly in hydrocarbon solvents, we paid careful attention as to how long the reaction was allowed to proceed. The monomer in benzene solution was added and the polymerization carried out up to 8 h and terminated with MeOH. After several washings with toluene to remove free polymer, the polymer bound on clay was cleaved off by refluxing polymer−clay with LiBr in tetrahydrofuran (THF) with stirring. The cleaved polymers were separated from solid clay by centrifugation. Analysis by NMR, FT-IR, size-exclusion chromatography (SEC), and thermogravimetric analysis (TGA) was carried out on the polymer−clay composite and detached polymer. The results are summarized in Table 1.

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Table 1. Summary of SEC Results for Anionic Polymerization of Styrene on Clay Surfaces

sample	styrene/DPE (g/mmol)	$10^{-3}M_n$ (SEC)[a] (solution)[b]	PDI[c] (solution)[b]	$10^{-3}M_n$ (SEC)[a] (cleaved)[d]	PDI[c] (cleaved)[d]	bound PS/clay (PS/g of clay) (g)
CP-1	14.6	78.6	1.09	11.9	1.44	0.62
CP-6	19.9	58.5	1.30	21.8	1.30	0.81
CP-3	9.6	35.5	1.20	7.4	1.31	0.45
CP-4[e]	21.8	100.1	1.10	23.6	1.40	0.79

[a] Number average molecular weight (M_n) and weight average molecular weight (M_w) were determined by size exclusion chromatography (SEC) with PS standard. [b] Polymer formed in solution. [c] Polydispersity index, M_w/M_n. [d] Polymer cleaved from clay surfaces. [e] Cumyl potassium was used as initiator instead of *n*-BuLi.

M_w/M_n).[18] Successful polymerization of styrene from clay was *only* realized by using a higher temperature and high vacuum. TGA did not show any decomposition of the DPE derivative at 120 °C, which is an advantage of DPE as initiator precursor because a high temperature was used for drying the initiator-clay completely. This ensured that the initiator-clay is free from any trapped H_2O that can terminate the living anion. Excess *n*-BuLi must be used to efficiently initiate DPE and react with any bound OH groups. Another reason is that BuLi tends to form aggregates in benzene solvent. The familiar red color (activated anionic DPE)[13] was observed on the solution and subsequently only on the clay particles (suspension) after several washings with solvent and filtration to remove excess BuLi from the reactor. It is essential to remove free *n*-BuLi because this will compete with the tethered initiator for monomers and strongly affects the reproducibility of polymerization (unpredictable molecular weight). Nevertheless, a small amount of polymers still formed in solution either from unremoved *n*-BuLi or cleaved DPE initiators (Table 1). No significant differences in results were observed when the larger cumyl potassium (instead of *n*-BuLi) was used to activate DPE (CP-4 in Table 1), which lead us to conclude that no significant cation exchange could be attributed to BuLi or its aggregates.

After several washings to remove free polymer, the cleaved polymers were separated from solid clay by refluxing with LiBr in THF with stirring followed by centrifugation.[17] SEC analysis of the free polymer (formed in solution) and bound polymer (formed on clay surface) are summarized in Table 1. A linear correlation between the monomer concentration and the M_n for the cleaved polymers, CP-3 < CP-1 < CP-6, is indicative of a living anionic polymerization mechanism.[11] The polymers initiated by the free initiator in the solution have a very narrow molecular weight distribution. This also demonstrates that styrene was polymerized via the living anionic mechanism in solution and that the amino end group introduced no side reactions to the anionic polymerization. The bound polymer has a much lower molecular weight and broader distribution, PDI, than the polymer formed in solution. We believe that the tight *intergallery* spacing between clay platelets may have prohibited the styrene monomer from reaching the DPE anionic sites in the interlayers when the monomer was added to the suspension of clay.[12] Akelah et al. have also reported the effect of the initial amount of styrene inserted in the interlayers on the intercalation of growing polymer.[19] In principle, the polymer can only grow within the lamellae of clay when the monomer diffuses inside the interlayers and is initiated by the activated surfaces. However, the monomer needs time to diffuse inside the interlayers while the free initiator exhausted most of the monomer in solution. Wittmer et al.[20] predicted that in surface initiated living polymerization longer chains will compete more effectively for monomer than shorter chains, resulting in a broadened molecular weight distribution. *We believe that the key factor which makes the monomer more accessible to DPE anionic sites (inside interlayer) is to disperse the intercalated clay more efficiently in the solvent.* Clearly, further experiments are needed to distinguish the role of the solvent toward intergallery polymerization.

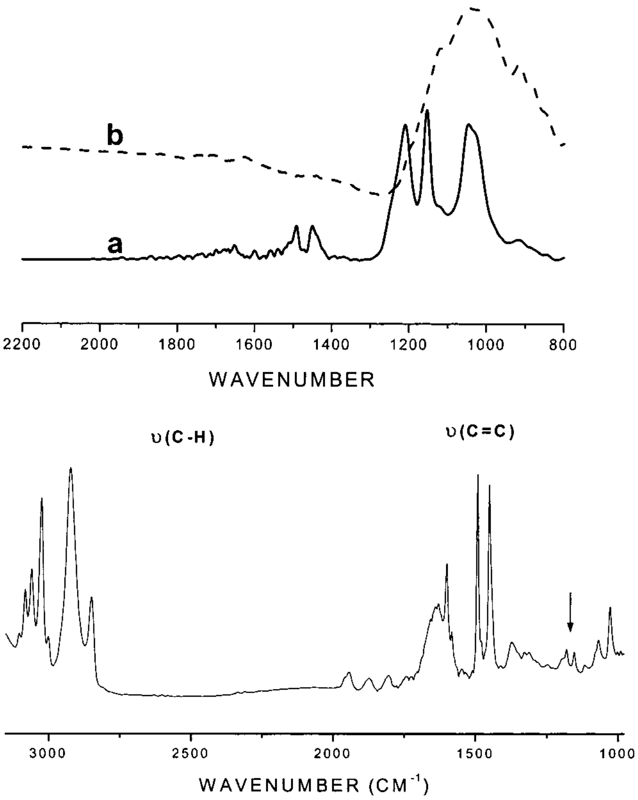

Figure 2. (Top) FTIR spectra of (a) polymer-bound clay (0.42 g/g of clay) and (b) pure clay. (Bottom) FTIR spectrum of cleaved polymer. FT-IR analysis showed C=C double bond stretching vibrations at 1600, 1549, and 1458 cm^{-1} compared to the pure clay IR spectrum, which has a broad peak centered at 1050 (Si−O−Si antisymmetric stretch) in the top spectra. The vibrational bands typical for bound polystyrene, such as the CH stretching vibrations around 3000 cm^{-1}, were also observed (bottom).

Nevertheless, FT-IR analysis confirmed the presence of polystyrene on clay (Figure 2).[21] Prominent peaks

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around 1200 cm^{-1}, which do not exist in pure clay, are attributed to the C−N−C antisymmetric stretch of the ∼$C(C_2H_5)_3N^+Br^-$ group and are noticeable on the detached polystyrene, albeit at much lower intensity, which indicates its presence only as end groups for the polymer. ^{1}H NMR of the cleaved polymer shows the broadened proton signal of the styrene phenyl ring at 7.04 ppm, CH_2 protons at 1.28 ppm, and triethylamine group protons at 3.22 ppm.

A two-step decomposition of the clay-initiator was observed by TGA at 330 and 580 °C. The 580 °C process is due to decomposition of the DPE group while degradation at 330 °C is consistent with the alkyl spacer. For the bound polymer, the decomposition temperature increased to 418 °C. However, the percentage by weight of the polymer−clay (decomposition) or PS/g of clay (Table 1) was low compared to the amount of bound polymers given the theoretical value calculated for clay surfaces.[22] We believe that this is indicative of low initiation efficiency. Together with the low molecular weight and higher dispersity (by SEC) observed with the detached polymers, we believe that most of the initiation occurred at the surface of the clay rather than at the intergallery spaces of the clay lamellae.[10] This was further supported by XRD in which the polymer−clay composite showed a lowering of the *d*-spacing on the basis of a very broad peak centered at 1.58 nm.[12] We supposed that a large part of the intercalated initiator on the clay lamellae was not activated for anionic polymerization and most of the initiation took place at the outer surface (perimeter). Our initial atomic force microscopy (AFM, Molecular Imaging, MAC mode) images showed the partially exfoliated clay platelets with ∼1−5 nm in thickness and a very wide distribution of diameter ∼35−300 nm. After polymerization, the polymer-bound clay showed very smooth edges as compared to the initial platelet's sharp edges. This indicates that a range of exfoliated and unexfoliated particles make up the clay sample. Future studies are currently being focused on determining a living anionic SIP mechanism from such surfaces and the feasibility of block copolymerization.

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Supporting Information Available: Text describing the experimental procedures, and figures showing the vacuum polymerization apparatus, weight loss versus temperature for polymer-bound clay, and AFM images of clay and polymer composites (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) FT-IR analysis showed C═C double bond stretching vibrations at 1600, 1549, and 1458 cm^{-1} compared to the pure clay IR spectrum, which has a broad peak centered at 1050 (Si−O−Si antisymmetric stretch). The vibrational bands typical for bound polystyrene, such as the CH stretching vibrations around 3000 cm^{-1}, were also observed.

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