

Direct Synthesis of Dispersed Nanocomposites by in Situ Living Free Radical Polymerization Using a Silicate-Anchored Initiator

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We wish to report that anchoring a living free radical polymerization (LFRP) initiator inside the galleries of layered silicate hosts followed by intercalation and polymerization of styrene gives directly dispersed polystyrene(PS)-silicate nanocomposite, which has hitherto proved elusive. The technique permits the molecular weight (MW) to be varied while keeping constant the silicate content of the nanocomposite.

Organic–inorganic nanocomposites continue to generate much interest,^{1–4} principally because of the potential they offer for applications in tough and high temperature-compatible, particle-reinforced polymers,³ coatings,⁴ electronics,⁴ catalysis,⁵ and the study of polymers in confined environments.^{1b} Two types of nanocomposites have emerged: intercalated or layered nanocomposites consisting of well-ordered and stacked polymer multilayers within the host^{1,2} and delaminated nanocomposites in which the host is well-dispersed in the polymer matrix.^{3,6,7} The seminal work of the Toyota group in Japan shows that dispersed nanocomposites give the best improvements in properties such as modulus, strength, heat distortion temperature, and permeability even at extremely low silicate content.³ However, unlike intercalated nanocomposites, for which excellent synthetic methods exist,^{1,2,8} there is no corresponding general method for the preparation of dispersed nanocomposites. Even in cases where the latter are formed,^{3,7,9} the synthetic methods used are incapable of controlling the overall polymer architecture. The best way to achieve such control is to use an appropriate living polymerization method.¹⁰ However, most such methods, for example, group transfer and ionic polymerizations, are sensitive to moisture and minute impurities and therefore will be difficult to perform inside the silicate host that typically contains waters of hydration and, sometimes, trace impurities, especially the naturally occurring silicates.² In contrast, LFRP can tolerate water, air, and some impurities and is applicable to a broad spectrum of monomers.¹¹

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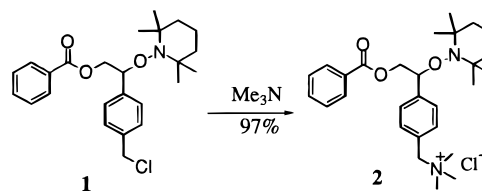
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Scheme 1



Our initial approach to a general synthesis of dispersed nanocomposites focuses on the design and synthesis of a LFRP initiator that can be tethered to the galleries of layered silicates (Scheme 1). Our hope is that, as the polymerization inside the galleries progresses and the polymer chain density increases, the layers will be pushed gradually apart and eventually delaminate, leading to a well-dispersed nanocomposite. Intergallery initiation of living polymerizations will provide an unprecedented opportunity to control not only such crucial characteristics as MW, polydispersity, block copolymer formation, and functionality directly inside the hosts but also the overall architecture of the nanocomposite. O'Hare and co-workers recently reported the polymerization of propylene using silicate-intercalated homogeneous catalysts. However, the MW of the polymer was very low (M_n , 860–2000) and, more importantly, a dispersed nanocomposite was not obtained.¹² The concept of intergallery initiation should be distinguished from the previously demonstrated purely surface initiation.¹³

Recognizing that nitroxyl-mediated LFRP works extremely well for styrene polymerization, we selected the elusive dispersed PS-silicate nanocomposite as the target to illustrate our concept. The appropriate initiator **2** (Scheme 1), which was synthesized from the previously reported **1**,¹⁴ was ion-exchanged^{2c} onto a commercially available montmorillonite, a mica-type layered silicate,^{2a–c} having a cation exchange capacity of 1.2 mequiv·g⁻¹ to give **3a** (Scheme 2). The evolution of X-ray diffraction (XRD) patterns (Figure 1) revealed that the registry spacing increased from 1.26 nm for the unmodified silicate (**1a**) to 2.35 nm (**1b**), thus providing unambiguous evidence for intercalation of **2**. The silicate content of **3a** was found by thermogravimetric analysis (TGA) to be 72.5 wt %; the calculated value for complete ion exchange was 72.0%, suggesting that essentially all exchangeable cations (including surface cations) were replaced.

The LFRP was effected by heating a dispersion of **3a** (0.39 g) in styrene (9.09 g) at 125 °C. The system solidified completely after 8 h to yield **4a** (6.15 g, 65% yield) as a homogeneous transparent solid. XRD of **4a** revealed that the layers were completely delaminated as evidenced by the absence of any diffraction peak (Figure 1c). This was further confirmed by transmission electron microscopy (TEM, Figure 2) which showed the silicate to be randomly dispersed spatially and directionally. Furthermore, differential scanning calorimetry (DSC) revealed no T_g probably because the random and uniform dispersion of the silicate in the polymer matrix prohibited formation of large domains of PS. This level of uniform dispersion is not achievable

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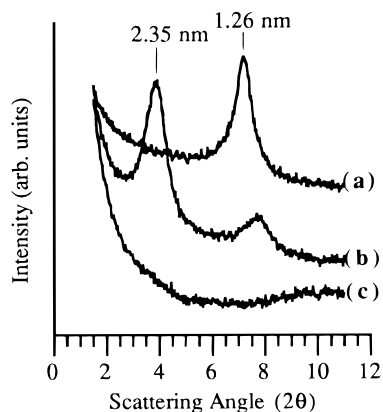
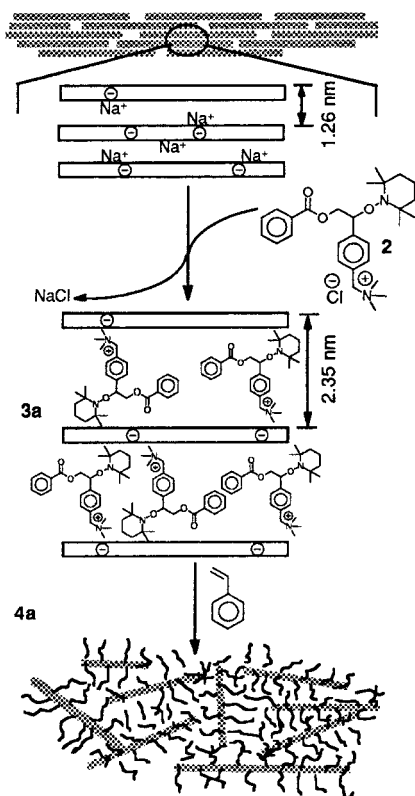


Figure 1. Plot of X-ray diffraction intensity (in arbitrary units) versus scattering angle (in degrees). (a) Original layered silicate. (b) Silicate-anchored initiator **3a**. (c) PS-silicate nanocomposite **4a**.

Scheme 2



by either melt or solution intercalation of a preformed polystyrene (PS). Previous efforts involving in situ polymerization of styrene also did not produce a dispersed nanocomposite.¹⁵

To determine the extent to which other characteristics are controlled, the polymer was desorbed from the silicate in a reverse ion exchange by refluxing the nanocomposite in a THF solution of LiBr. The low polydispersity index (PDI) of 1.3 and the agreement between the calculated number-average molecular weight (M_n) of 24 400 and observed M_n of 21 500, indicate a remarkably well-behaved reaction even under such heterogeneous conditions (Table 1). Using intergallery-anchored initiator samples containing different mole fractions of **2** (samples **3b–d**) prepared from the appropriate mixture of **2** and a noninitiating salt, benzyltrimethylammonium chloride (**5**), led to a library of dispersed nanocomposites (**4b–d**) of constant silicate content and PS of varied but controlled MW. As can be seen from Table 1, at constant styrene weight, the MWs of the polymers increased with decreasing **2/5** molar ratio, thus confirming MW control by the mole fraction of **2**. To obtain conclusive evidence for

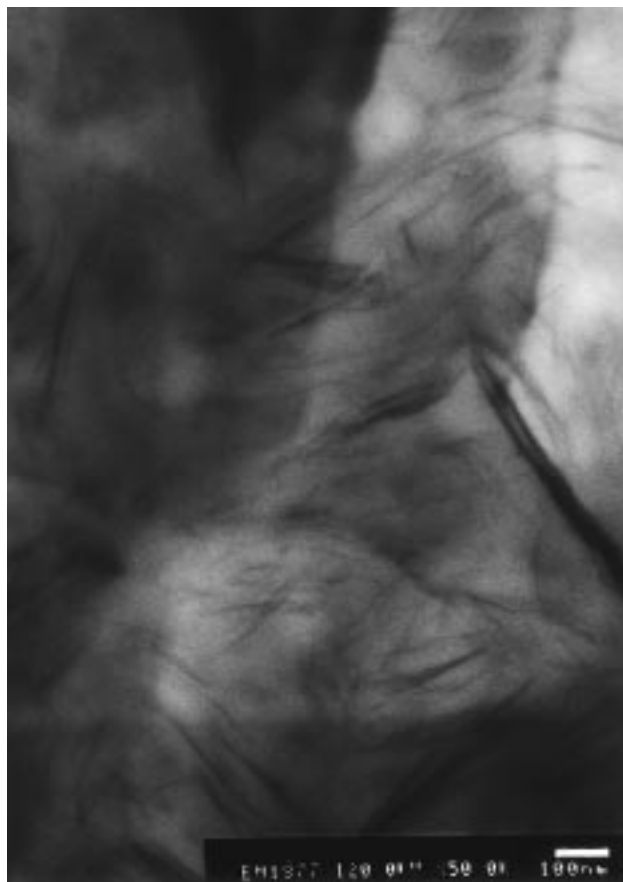


Figure 2. Transmission electron micrograph of **4a**.

Table 1. MW Control in the Synthesis of PS–Silicate Nanocomposite Having Approximate Constant Silicate Content

silicate-anchored initiator	molar ratio of 2/5 in 3a–d	nanocomposite yield (%)	M_w (SEC) ^c × 10 ⁻³	M_n (SEC) ^d × 10 ⁻³	PDI ^e
3a ^a	100/0	65	27.0	21.5	1.3
3b ^b	70/30	80	43.0	25.3	1.7
3c ^b	50/50	84	53.3	38.1	1.4
3d ^b	30/70	81	66.9	47.8	1.4

^a Reaction scale: 9.09 g of styrene, 0.39 g of **3a** (4.1% w/w silicate). ^b Reaction scale: 3.63 g of styrene and 0.17 g of **3b–d** (4.5% w/w silicate). ^c Weight-average molecular weight determined by size-exclusion chromatography (SEC) with PS standard. ^d Number-average molecular weight by SEC. ^e Polydispersity index, M_w/M_n .

livingness and determine block copolymerization feasibility, a chain-extension experiment was performed on 0.38 g of **4a** (PS M_n 21 500, PDI 1.3, SEC peak molecular weight (M_p) 30 000) and 1.36 g of styrene to give 1.63 g (93% yield) of the nanocomposite. The SEC peak MW of the desorbed PS increased to 74 800 (M_n 43 500, PDI 1.6) compared with the estimated theoretical MW of 75 300. Hence, block copolymer formation using the appropriate monomers is feasible.

In summary, we have demonstrated that intergallery polymerization via a silicate-anchored initiator is a viable approach to direct synthesis of dispersed silicate nanocomposites. In addition, critical polymer characteristics such as MW and polydispersity are controlled, and block copolymer formation appears possible. These results constitute the first example of a dispersed PS-silicate nanocomposite. Efforts to extend the strategy to other living polymerizations and measure physical properties are in progress.

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