Polymer-Layered Silicate Nanocomposites: *In Situ* Intercalative Polymerization of ε-Caprolactone in Layered Silicates

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Introduction

In situ polymerization of monomers confined within spaces of molecular dimensions has been studied in the past as a means of synthesizing macromolecules of known stereospecificity.[1-3] Synthesis of the confined polymer is typically accomplished by adsorption of a guest molecule (monomer) into a host compound containing intraplanar spaces, channels or other cavities, followed by *in situ* polymerization of the monomer. The resulting polymers are said to be intercalated or occluded but may be liberated by dissolution or decomposition of the host and often exhibit stereospecific sequences not observed in bulk or solution polymerized macromolecules. For example, predominantly isotactic poly(methyl methacrylate) is obtained from the polymerization of methyl methacrylate intercalated in the galleries of layered silicates.[1,2] The stereospecific nature of the polymerization is believed to be the result of preferred molecular orientation of the intercalated monomers induced by chemical interactions with interlayer cations and the silicate surface. Similar results have also been obtained from the polymerization of diene monomers occluded within the channels of perhydrotriphenylene.[3]

Recent research suggests that polymer/inorganic nanocomposites can be obtained by intercalative polymerization of suitable monomers in the galleries of layered solids and that the resulting hybrids often exhibit unique mechanical, thermal, and electrical properties.[4-13] Intercalative polymerization of conducting polymers in the galleries of layered inorganic materials, for example, results in composites possessing highly anisotropic electrical conductivity.[4-9] Furthermore, intercalated polymers show no glass or melting transition[6,14] and often exhibit higher thermal stability when compared to bulk polymers due to the polymer confinement in the two-dimensional host galleries.[12,13,15]

Most previous studies involving intercalative polymerization have been limited, however, to nanocomposites containing conjugated polymers. We have extended the technique to other polymer systems such as polyesters. Of particular interest to us are nanocomposites based on biodegradable polymers such as poly(ε-caprolactone). Although there are previous reports on ε-caprolactone polymerization initiated by graphite intercalation compounds, there is neither strong evidence for polymer intercalation nor is there any description of the properties of such a hybrid.[16,17] Our work has been motivated by a recent study involving polymerization of ε-caprolactam in the presence of layered silicates,[18] which suggested to us that ring-opening polymerization of lactone monomers can be catalyzed by layered silicates. This paper describes our initial work on the intercalation and polymerization of ε-caprolactone within the gallery of fluorohectorite, a mica-type layered silicate.

Experimental Methods

The poly(ε-caprolactone)/layered silicate composite was synthesized by stirring 0.1 g of Cr^{3+}-exchanged fluorohectorite with 1.0 g of ε-caprolactone (Aldrich) at 25 °C for 12 h, followed by heating at 100 °C for an additional 48 h. Upon cooling to room temperature, the reaction mixture solidified. Portions of the solid composite were then examined using differential scanning calorimetry (DSC), X-ray diffraction (XRD), and Fourier-transform infrared spectroscopy (FT-IR).

The unintercalated poly(ε-caprolactone) fraction of the composite (PCL1) was recovered by dissolving portions of the product in acetone followed by centrifugation at 3000 rpm for 2 min. PCL1 was obtained by precipitation of the supernatant into heptane. The resulting white polymer solid was filtered, washed with additional heptane, and dried *in vacuo*. The poly(ε-caprolactone) intercalated silicate was recovered in a similar manner, by suspending the composite in acetone and centrifuging. The process was repeated several times in order to ensure complete removal of the polymer adsorbed on the external surfaces of the silicate particles. The resulting silicate particles were then dried *in vacuo* at 25 °C. For purposes of comparison, pure poly(ε-caprolactone) (PCL2) was synthesized by polymerization of 1.0 g of ε-caprolactone using 0.009 g of aluminum isopropoxide (Aldrich) as catalyst. Bulk polymerization was carried out at 100 °C for 48 h, followed by recrystallization into heptane. Elemental analysis of the purified bulk polymer (PCL2) yielded the following results: calc (wt %) C, 63.16; H, 8.77. Actual: C, 62.80; H, 8.89.

DSC and TGA were performed using a du Pont 9900 thermal analyzer at a heating rate of 10 °C/min under an atmosphere of flowing nitrogen (40 cm^3/min). FT-IR spectra of the products in the form of KBr disks were obtained using a Mattson 2020 Galaxy Series infrared spectrometer. XRD analyses were performed on a Scintag Pad X powder diffractometer using Cu Kα radiation at a scanning rate of 2° 2θ/min. A 200-MHz ^1H nuclear magnetic resonance (NMR) analysis of poly(ε-caprolactone) dissolved in $CDCl_3$ was performed at room temperature using a Varian XL-200 spectrometer. Chemical shifts were determined with respect to an internal standard of 1% TMS. Molecular modeling was accomplished using Alchemy II (Tripos) software.

Results and Discussion

A schematic illustration of the composite synthesis is shown in Figure 1. Intercalation of ε-caprolactone into

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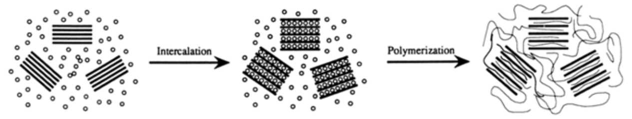

Figure 1. Schematic diagram illustrating the composite synthesis.

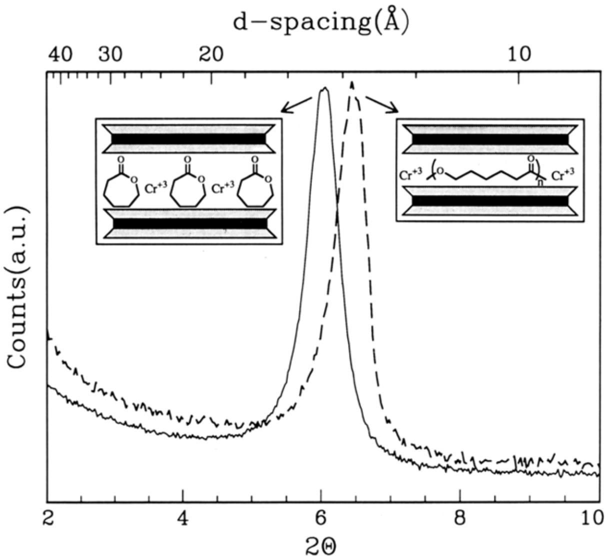

Figure 2. Powder X-ray diffraction of the composite before (solid line) and after (dashed line) polymerization. Insets are schematic illustrations (not drawn to scale) corresponding to the intercalated monomer (left) and intercalated polymer (right).

the silicate galleries is readily accomplished by suspending the silicate powder in the liquid monomer. The monomer intercalated silicate was then heated to 100 °C in the presence of excess ε-caprolactone, upon which polymerization of the monomer occurred. The resulting nanocomposite consists of polymer-intercalated silicate particles embedded in a poly(ε-caprolactone) matrix.

Intercalation of the monomer was revealed by powder XRD, which showed an increase in the silicate *d* spacing from 12.8 to 14.6 Å. Energy minimization of the ε-caprolactone structure provided an approximate measure of monomer dimensions, which were then used along with the known thickness of the silicate layers[19] to predict layer spacings for various intercalation geometries. The (001) *d* spacing observed prior to polymerization was found to be consistent with the orientation of the ε-caprolactone ring perpendicular to the silicate layers. XRD analysis of the composite after polymerization indicates a reduction in the silicate *d* spacing from 14.6 to 13.7 Å as shown in Figure 2. The decrease in the *d* spacing is consistent with the dimensional change accompanying polymerization of ε-caprolactone. Opening of the lactone ring in the monomer (see below) to produce a monolayer of fully collapsed poly(ε-caprolactone) chains is accompanied by a decrease in layer spacing as observed with XRD. The observed layer spacing of 13.7 correlates well with the sum of the thickness of the silicate layer (9.6 Å)[19] and the known interchain distance (4.0 Å) in the crystal structure of poly(ε-caprolactone).[20] Repeated washing with a solvent for poly(ε-caprolactone) did not alter the silicate (001) *d* spacing, indicating that the chemical interaction between the intercalated polymer and the silicate surface is strong and that intercalation of the polymer is irreversible.

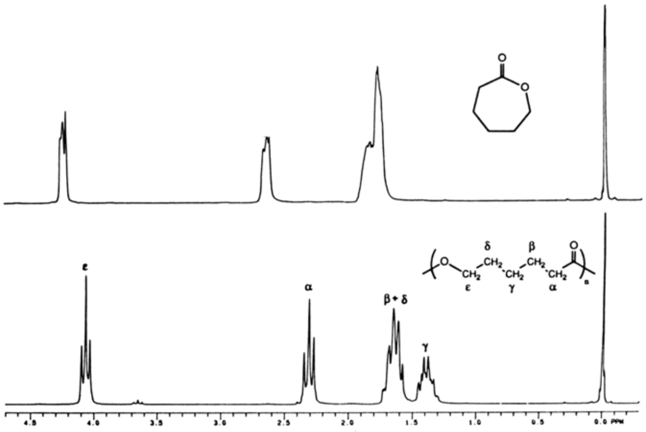

Figure 3. ^{1}H NMR spectra of ε-caprolactone (above) and PCL1 (below).

Table I. ^{1}H NMR Chemical Shifts[a] of Poly(ε-caprolactone) in CDCl$_3$

	α-CH$_2$	β-CH$_2$	γ-CH$_2$	δ-CH$_2$	ε-CH$_2$
PCL1	4.08(t)	1.67(m)	1.39(m)	1.67(m)	2.33(t)
PCL2	4.08(t)	1.66(m)	1.40(m)	1.67(m)	2.33(t)

[a] Ppm from TMS. t = triplet, m = multiplet.

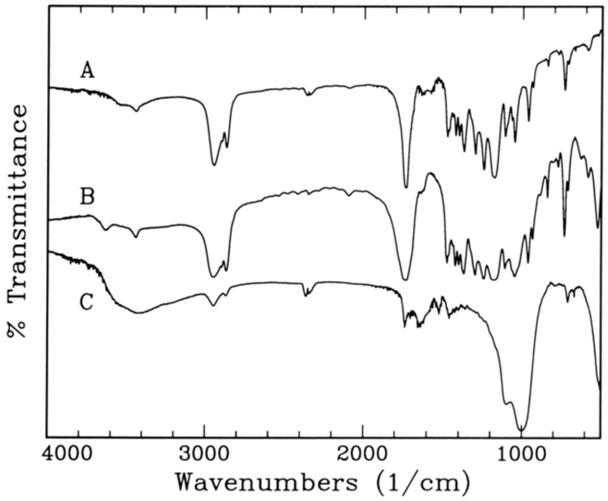

Figure 4. FT-IR spectra of (A) PCL2, (B) nanocomposite, and (C) poly(ε-caprolactone) intercalated fluorohectorite.

^{1}H NMR analysis of the monomer and the polymer extracted from the composite (Figure 3) provides unambiguous evidence of the formation of poly(ε-caprolactone). In addition, comparison of the chemical shifts for the pure poly(ε-caprolactone) (PCL2) and that extracted from the composite (PCL1) shows that the two polymers are nearly identical (Table I).

Additional evidence for poly(ε-caprolactone) formation in the composite is provided by FT-IR spectroscopy. Shown in Figure 4 are infrared spectra of the pure poly(ε-caprolactone) (PCL2), the nanocomposite, and the poly(ε-caprolactone) intercalated fluorohectorite. The latter was obtained from the nanocomposite by successive washings to remove the polymer matrix. The similarity between the PCL2 and the nanocomposite spectra indicates that both samples contain poly(ε-caprolactone). The peaks characteristic of the silicate host are obscured, since the composite contains only 10% silicate by weight. However, removal of the polymer matrix drastically attenuates the polymer absorbances while enhancing those of the silicate. Since the solvent washings are expected to remove nearly all external polymer, the remaining

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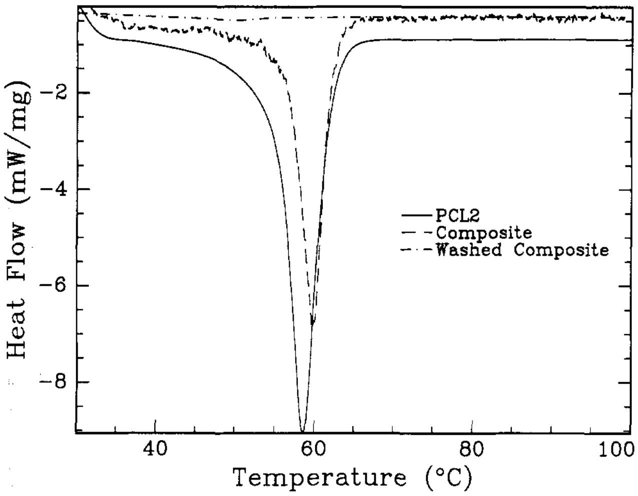

Figure 5. DSC thermograms of PCL2, nanocomposite, and poly(ϵ-caprolactone) intercalated fluorohectorite.

absorbances at 2946 and 2868 cm^{-1} (ν_{sym} and ν_{asym} C–H) and the carbonyl absorbance at 1726 cm^{-1} clearly indicate the presence of intercalated poly(ϵ-caprolactone). The amount of intercalated poly(ϵ-caprolactone) obtained from TGA analysis of the washed silicate particles by heating to 1000 °C is 7.7%.

DSC traces of the nanocomposite, PCL2, and the poly(ϵ-caprolactone) intercalated fluorohectorite are shown in Figure 5. Both the nanocomposite and PCL2 exhibit a large endotherm at approximately 60 °C corresponding to the melting of poly(ϵ-caprolactone) crystallites. The slightly higher melting temperature of the polymer in the composite might be due to the confinement of the polymer chains in the intercrystalline regions between silicate particles. In contrast to the bulk polymer, the intercalated polymer does not show a melting transition. This is attributed to the confinement of the intercalated chains within the silicate galleries (intracrystalline region) that prevents formation of polymer crystallites.

While the exact initiation and propagation mechanisms operating during polymerization in the composite are as yet unknown, experiments involving other cation exchanged silicates suggest that the type of interlayer cation is important in achieving polymerization. For example, Cr^{3+}-exchanged montmorillonite (a related mica-type layered silicate) was also found to initiate polymerization of ϵ-caprolactone when substituted for Cr^{3+}-fluorohectorite, but other forms of montmorillonite and fluorohectorite (e.g., Cu^{2+}, Co^{2+}, Na^{+}) did not catalyze polymerization of ϵ-caprolactone. To further elucidate the polymerization mechanism, spectroscopic end-group analysis of poly(ϵ-caprolactone) was used. The ^{1}H NMR spectrum of the polymer extracted from the composite (PCL1) contains a weak proton resonance centered at 3.65 ppm corresponding to hydroxyl end groups on the poly(ϵ-caprolactone) chain. In contrast, Al isopropoxide initiated polymerization, used in PCL2, is known to proceed via an insertion mechanism[21] and results in isopropoxy end groups. The dissimilar end groups suggest that a different initiation mechanism is responsible for polymerization when Cr^{3+}-fluorohectorite is used. One possibility is that acidic protons from the water associated with the interlayer Cr^{3+} ions may initiate cleavage of the acyl–oxygen bond. To verify this mechanism, ϵ-caprolactone was polymerized using 1,5-pentanediol as initiator. Although the protons in the diol are only weakly acidic, poly(ϵ-caprolactone) was formed. Interestingly, ^{1}H chemical shifts of the hydroxyl end groups of this polymer exactly matched those of the polymer extracted from the composite, supporting our suggestion that proton–catalyzed acyl–oxygen cleavage might be the polymerization mechanism. The acid-catalyzed mechanism is further supported by the failure of the less acidic mono- and divalent cations to form poly(ϵ-caprolactone).

Conclusions

A composite consisting of poly(ϵ-caprolactone) intercalated silicate particles embedded in the same polymer matrix has been synthesized by heating Cr^{3+}–fluorohectorite to 100 °C in the presence of excess ϵ-caprolactone. The matrix poly(ϵ-caprolactone) was isolated and determined to be indistinguishable (except for chain end groups) from the bulk polymer obtained by metal–alkoxide-initiated polymerization. The polymerization reaction appears to proceed through cleavage of the acyl–oxygen bond catalyzed by the interlayer Cr^{3+} ions. The intercalated polymer is strongly adsorbed onto the silicate layers and shows no melting transition.

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