

Polymer Communication

Liquid crystal polymer nanocomposites: direct intercalation of thermotropic liquid crystalline polymers into layered silicates

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Abstract

Reversible intercalation between two ordered media such as organically modified layered silicates (OLS) and thermotropic liquid crystalline polymers (LCP) in the nematic state is demonstrated. These results indicate that the decreased diffusivities and intermolecular interactions of an ordered polymeric guest do not preclude intercalation, potentially enabling fabrication of ultra-high performance polymer nanocomposites. Fundamentally, the polymer–polymer interactions that lead to a preferred orientation director in the bulk LCP nematic state are suppressed when the chains are confined to the pseudo two-dimensional environment of the OLS interlayer, resulting in a loss of liquid crystallinity. This demonstrates a finite-size effect on the nematic state of thermotropic liquid crystalline polymers. © 2000 Published by Elsevier Science Ltd.

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Polymer-layered silicate nanocomposites have been the subject of recent intense research, motivated by the potential of realizing a combination of mechanical, barrier and non-flammability enhancements relative to the neat resin with only 1–5 wt% addition of a nanoscale filler [1–3]. Additionally, these nanocomposites have been proposed as model systems to examine polymer structure and dynamics in confined environments [4].

Intercalation from a polymer melt is an effective approach to synthesize these nanocomposites [5–7]. The technique involves annealing, statically or under shear, a mixture of polymer and the inorganic host above the softening point of the polymer. The driving force [8–10] has been rationalized in terms of a three-way competition among: (1) the decrease in conformational entropy of the flexible polymer coil when confined within the layered silicate; (2) an increase in the conformational entropy of the organic modifiers as the system expands to accommodate the polymer; and (3) a net energetic gain associated with the establishment of more favorable secondary interactions between the polymer and the OLS than originally present in the unintercalated OLS. Previous melt intercalation reports have exclusively concentrated on the formation of

nanocomposites from semicrystalline or amorphous thermoplastic polymers [5–7,11–13]. These efforts have followed the traditional practice that the guest be solubilized or neat and in a disordered isotropic state (gas, liquid or melt) with complete transitional and orientational freedom.

In this paper, we report the reversible intercalation between organically modified layered silicates (OLS) [14,15] and liquid crystalline polymers (LCP) in the nematic state. The decreased diffusivities and intermolecular interactions of an ordered, non-isotropic macromolecular guest do not preclude intercalation and thus demonstrates the potential to fabricate ultra-high performance polymer nanocomposites. Furthermore, the ultra-confined environment between the aluminosilicate layers (1–3 nm) affords the opportunity to examine finite-size effects on the ordered phases of thermotropic LCP.

Melt intercalation of a model main chain liquid crystalline co-polyether based on 4,4'-dihydroxy-*a*-methylstilbene and a 50:50 mole ratio mixture of heptyl/nonyl alkyl dibromide [16–18] (Fig. 1a; DHMS7,9) was accomplished by annealing a powder mixture of the polymer and OLS (Fig. 1b; OLS) within the nematic region of the polymer. Specifically 0.25 g of DHMS7,9 ($M_n = 14,100$, PDI = 1.9, $T_g = 20^\circ\text{C}$; $T_m = 90^\circ\text{C}$; $T_{xn} = 115^\circ\text{C}$; $T_{ni} = 190^\circ\text{C}$) and 0.75 g of OLS in a powder form were thoroughly mixed in an agate mortar, formed into a

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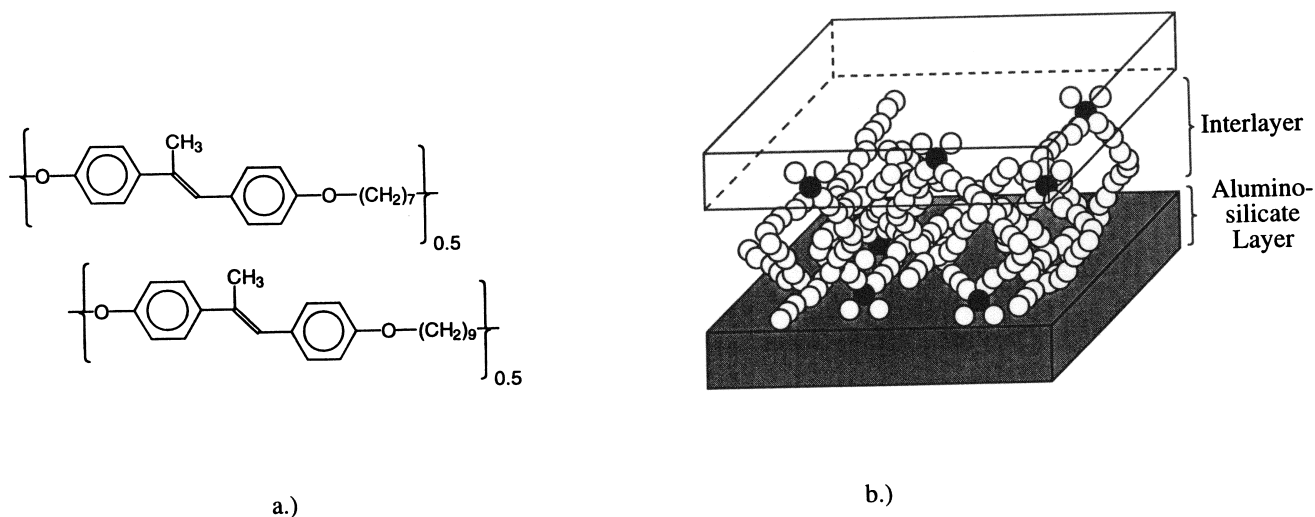


Fig. 1. (a) Chemical structure of DHMS7,9. (b) Schematic structure of OLS. The 2D, aluminosilicate layers (thickness = 0.95 nm) consist of two silica tetrahedral sheets fused to an edge-shared octahedral sheet of either alumina or magnesia. Charge generation associated with isomorphous substitution within the layers (e.g. Al for Si or Mg for Al) is balanced by exchangeable cations within the interlayer, in this instance quaternary alkyl ammonium cations (●-ammonium; ○-CH₂CH₃).

pellet using a hydraulic press and a pressure of 70 MPa. The mixture was subsequently heated at 160°C under vacuum and quenched in air to room temperature. At this anneal temperature, DHMS7,9 is in the nematic state and an intercalated structure resulted. Similar processing conditions (thermal anneal of OLS–LCP blends in the LCP's nematic state) produce intercalated OLS–LCP nanocomposites using a range of modified layered silicates (octadecyl

ammonium fluorohectorite [12,15], dimethyl ditallow ammonium montmorillonite (Rheox, Inc.), dimethyl benzyl tallow ammonium montmorillonite (Rheox, Inc.) and bis (2-hydroxyethyl) methyl tallow ammonium montmorillonite (S30A, Southern Clay Products, Inc.) and LCP (copolyester of 4-hydroxyacetophenone azine and 50:50 mole ratio mixture of sebacoyl/dodecane dioyl dichloride [19] and Vectra RD501 ($T_m = 210^\circ\text{C}$), (Hoechst)). To examine the

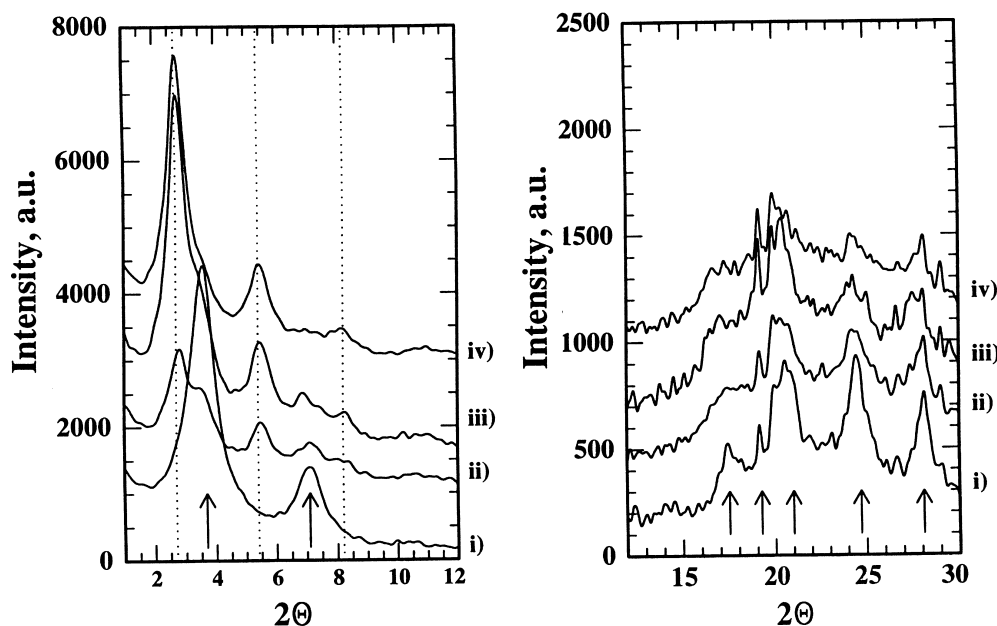


Fig. 2. X-ray diffraction patterns of the 25 wt% DHMS7,9–75 wt% M2C18 mixture (i) before annealing and after (ii) 100, (iii) 280, and (iv) 620 min anneal at 160°C. Dotted lines indicate (00*l*) reflections of DHMS7,9 intercalated M2C18 whereas arrows indicate original reflections of unintercalated M2C18 and DHMS7,9. Data vertically offset for clarity.

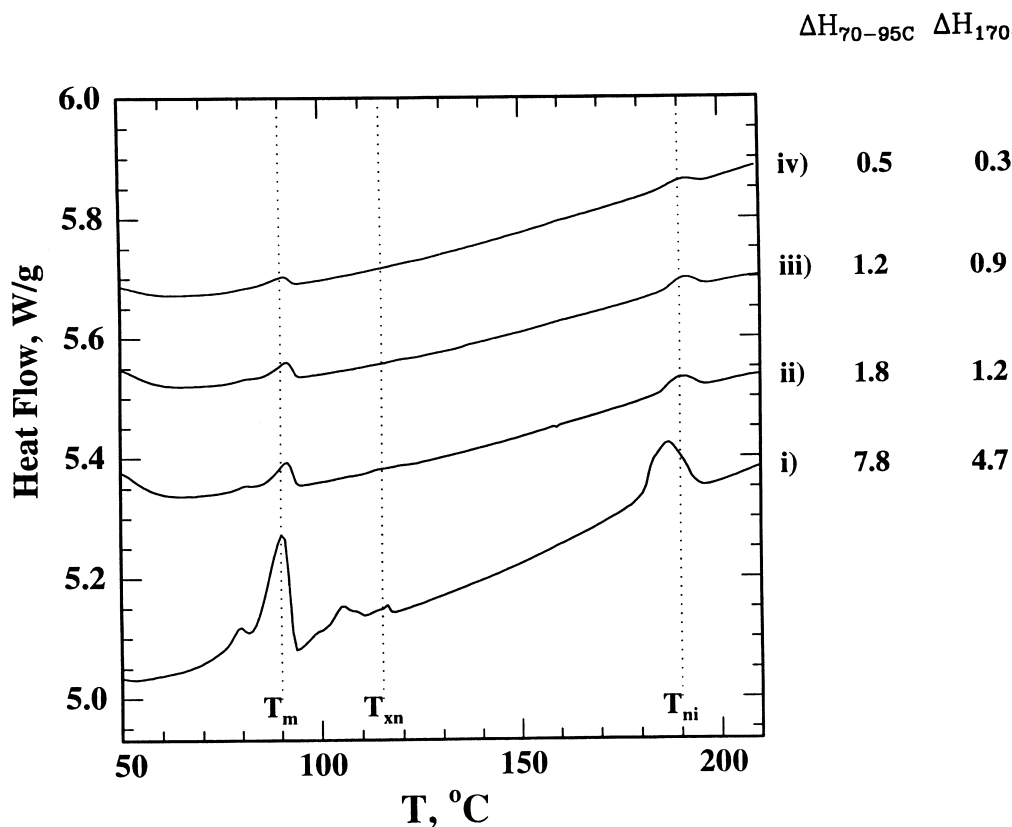


Fig. 3. Differential scanning calorimetry (2nd thermal cycle at 10°C/min up to 235°C under flowing N₂) for: (i) DHMS7,9; (ii) mixture of 25 wt% DHMS7,9–75 wt% M2C18 before annealing and after (iii) 100 and (iv) 620 min anneal at 160°C. The melt transition (T_m), intermediate to nematic transition (T_{xn}) and nematic to isotropic transition (T_{ni}) are indicated. The breadth of T_m is associated with multiple crystalline forms of DHMS7,9 [18]. The latent heat associated with the melt ($\Delta H_{70-95^\circ\text{C}}$) and nematic to isotropic ($\Delta H_{170-195^\circ\text{C}}$) transitions for the various samples are in J/g. Data vertically offset for clarity.

details of the process, we will discuss intercalation of DHMS7,9 in dioctadecyl dimethyl ammonium modified montmorillonite (M2C18).¹

Fig. 2 shows X-ray diffraction patterns at room temperature of the 25 wt% DHMS7,9–75 wt% M2C18 mixture before annealing and after 100, 280, 620 min anneal at 160°C. The XRD pattern before heating contains peaks characteristic of both pristine M2C18 ($d_{00l}^{\text{prist}} = 24.7, 12.4 \text{ \AA}$) and crystalline DHMS7,9 ($d = 5.12, 4.63, 4.03, 3.67, 3.15 \text{ \AA}$). After annealing at 160°C for as little as 100 min, a new series of basal reflections corresponding to an intercalated structure dominate the spectrum ($d_{00l}^{\text{int}} = 32.7, 16.3, 10.6 \text{ \AA}$) while the original basal reflections corresponding to the unintercalated silicate are substantially reduced. In concert, the relative intensity of the crystalline DHMS7,9 reflections decrease with prolonged annealing reflecting the decreased concentration of polymer outside of the OLS interlayer and the influence of the OLS on polymer crystallization. The development of the intercalated phase from 25 wt% DHMS7,9 to 75 wt%

M2C18 mixture continues at a substantially reduced rate for anneals longer than 620 min. This qualitatively agrees with previous kinetic measurements of amorphous polymer melt intercalation, which showed the reaction approaches equilibrium asymptotically [20]. Mixtures containing a larger fraction of DHMS7,9 result in enhanced intercalation rates reflecting the interfacial nature of the intercalation reaction. For example, a 75 wt% DHMS7,9–25 wt% M2C18 mixture annealed at 160°C in vacuum exhibits fully intercalated M2C18 in less than 100 min. Furthermore, complete intercalation of Vectra RD501 in S30A (5% S30A, $d_{00l}^{\text{int}} = 30.7, 14.7 \text{ \AA}$) occurs in less than 5 min at 220°C (300 r.p.m) in a twin screw compounder (DACA Instruments Microcompounder), indicating that dynamic shear mixing even further reduces the time necessary for formation of intercalated structures.

The intercalated DHMS7,9 is confined between two ‘rigid’ silicate layers, which contain short alkyl chains, in this instance octadecyl. This environment is substantially different than that of the bulk polymer and is expected to considerably influence the thermal phase behavior of the intercalated polymer [4,5,13,21–24]. Fig. 3 shows differential scanning calorimetry (2nd thermal cycle at 10°C/min up to 235°C under flowing N₂) for a portion of the temporal series of 25 wt% DHMS7,9–75 wt% M2C18 samples

¹ Dioctadecyl dimethyl ammonium montmorillonite (M2C18) was synthesized from dioctadecyl dimethyl ammonium bromide (Kodak) and Na + montmorillonite (Southern Clay Products, Inc., 100 meq/100 g) by the previous described procedures (Refs. [11,14]).

annealed at 160°C shown in Fig. 2. As the annealing time increases and more intercalated phase is present, the latent heat associated with the bulk endothermic phase transitions of DHMS7,9 (T_m and T_{ni}) decreases. The intermediate to nematic transition (T_{xn}) is difficult to discern in the DHMS7,9-M2C18 mixture because of its relatively weak nature. After 620 min at 160°C, the latent heat associated with the melting (T_m) and the nematic–isotropic transition (T_{ni}) are substantially reduced. The observed transitions correspond to a minor amount of DHMS7,9 outside the M2C18 interlayer which is also seen in the X-ray diffraction pattern (Fig. 1).

The pseudo two-dimensional (2D) environment in the interlayer suppresses polymer–polymer interactions that manifest in a preferred orientation director in the bulk. The absence of a common director for the polymer is apparent when optically examining a fully intercalated hybrid between cross-polarizers. In contrast to the neat LCP, the hybrid films do not show any birefringence at any temperatures up to decomposition. Additionally, the bulk phase transitions of the LCP are suppressed. Similar observations have been made with DSC for melting and glass transitions of other intercalated polymers [4,5,13,21–24]. This behavior contrasts that of oligomeric molecules which still exhibit bulk-like phase transitions, such as melting and preferred orientational ordering, when confined between the silicate layers [15,25]. Recent molecular dynamic simulations [26], NMR relaxation studies [27] and dielectric spectroscopy [28] suggest that the intercalated chains adopt a disordered, multi-layered conformation with a relaxation spectrum that is dependent on distance from the aluminosilicate surface.

For many systems, intercalation of the polymer from solution results in the incorporation of solvent instead of polymer between the silicate layers [5,29]. Thus melt intercalation enhances the specificity of the polymer by eliminating competing host–solvent and polymer–solvent interactions. The preference for solvent intercalation facilitates retrieval of the intercalated DHMS7,9 and subsequent characterization of the recovered polymer and deintercalated OLS. For example, DHMS7,9 was recovered by suspending the 25 wt% DHMS7,9–75 wt% M2C18 annealed for 1820 min in THF at ca. 55°C for 12 h. The deintercalated M2C18 and dissolved DHMS7,9 were separated via centrifugation. The solids were washed two times with hot THF and dried at room temperature. The polymer was recovered from the supernatant by allowing the solvent to evaporate at room temperature. Fourier transform infrared spectroscopy of the original DHMS7,9 and recovered DHMS7,9 and of the original M2C18 and the deintercalated M2C18 were identical. Additionally, size exclusion chromatography (THF, 30°C) indicates that the molecular weight and polydispersity of the displaced DHMS7,9 is similar to that of neat DHMS7,9 annealed under the same conditions used to fully intercalate DHMS7,9. This indicates that chemical reactions or substantial molecular weight degradation does not occur during intercalation.

Intercalation from the nematic liquid crystalline phase of a polymer differs from conventional polymer melt intercalation in that the guest species as well as the host possess long-range order. In general as the nematic to isotropic transition is approached, entropic disorder overcomes the favorable topological interactions in the melt, effectively varying the initial thermodynamic state of the guest phase. Additionally, the dynamics of the chains in the nematic state are anisotropic and depend on the orientation of the local director, which will be modified by the presence of the dispersed layered silicate phase. Thus, it is expected that the driving force and kinetics of intercalation and the ultimate intercalated structure should depend on the distribution and order parameter of the nematic phase and thus the processing temperature of the guest phase. The influence of these factors on the direct intercalation between two ordered macromolecular phases is not well understood experimentally or theoretically.

In conclusion, the ability to perform direct intercalation between two ordered macromolecular phases expands the range of possible intercalation compounds and offers a new approach to examine the structure and dynamics of confined LCPs. The decreased diffusivities and intermolecular interactions of an ordered guest do not preclude intercalation and nanocomposites can be formed using conventional melt compounding equipment, raising the potential to fabricate ultra-high performance polymer nanocomposites. Fundamentally, the polymer–polymer interactions that lead to a preferred orientation director in the bulk LCP nematic state are suppressed when the chains are confined to the pseudo 2D environment of the OLS interlayer resulting in a loss of liquid crystallinity. This demonstrates a finite-size effect on the nematic state of thermotropic LCP.

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