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Nanocomposite Derived from Intercalative Spontaneous Polymerization of 2-Ethynylpyridine within Layered Aluminosilicate: Montmorillonite

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Composites of organic polymers and inorganic layered aluminosilicates such as montmorillonite at the nanometer level have received much attention in recent years.[1−8] The importance of such composites is due to strong synergistic effects between the polymer and substrate. This may result in enhanced electrical, optical, mechanical, and thermal properties when compared to their conventional microcomposite counterparts.

Montmorillonite is composed of layers made up of two silica tetrahedral sheets with a central alumina octahedral sheet. Various ionic or polar organic compounds can be intercalated in the interlayer through ion exchange or through solvation of cations.[9−11] Lamellar aluminosilicates were known not only to provide a nanoscale host for molecular orientation but also to trigger spontaneous polymerization of some organic monomers and influence the structure of polymers formed within their galleries.[12−18] Brønsted acidity and/or transition metal cations populating the surface of lamellar clays have been reported to be responsible for initiating the polymerization.

We have described in a series of papers a method of polymerization of ethynyl derivatives in which a quarternizable atom is attached in alpha or in conjugation with the triple bond such as ethynyl pyridines and alpha haloethynes.[19] These polyacetylenes are characterized by a high degree of conjugation and enhanced thermal and oxidative stability. The acetylenic bond is activated by the presence of a strong electron-withdrawing substituent (such as the pyridinium group) inducing polymerization of the triple bond and the formation of a conjugated, ionic polyacetylene.

In this work, we report a novel nanocomposite prepared by intercalation and spontaneous polymerization of 2-ethynylpyridine within the galleries of montmorillonite. When colorless acetylenic monomer 2-ethynylpyridine (C_7H_5N, 2-EPy) was added into the Ca^{2+}−montmorillonite (Ca−MMT) suspension in benzene, the color of the mixture readily turned reddish brown and darkened gradually, possibly indicating polymerization.[20] Such color change was observed in 30 min at room temperature and in 1−2 min at a temperature of 65 °C. The FT-IR spectrum of the polymer extracted with dimethylforamide (DMF) at 80−85 °C from the complex of Ca−MMT and 2-EPy is shown together with that of the acetylenic monomer in Figure 1.[21] The

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(20) A typical procedure for preparation of the nanocomposite of Ca^{2+}−montmorillonite (Ca−MMT, Source Clay Minerals Repository, cation exchange capacity: 1.20 mequiv/g) and 2-ethynylpyridine (2-EPy, Farchan Lab.) is as follows: 0.395 g of 2-EPy was added to a suspension of 1.00 g of dehydrated Ca−MMT in 25 mL of benzene and then the mixture was stirred at 65 ± 3 °C. The suspension turned red in a few minutes and the red color darkened gradually. After the reaction for 24 h, the dark brown complex was separated from the suspension by centrifugation and washed several times with benzene to exclude the interstitial monomer trapped between the aggregates of clay particles. It was then dried at 110 °C for 24 h to remove solvent, yielding dark brown powder (sample 3, see Table 1). The adsorption yield of monomer per unit weight of dehydrated montmorillonite was obtained by measuring the concentration of 2-EPy remaining in the benzene solution by UV/vis absorption spectroscopy. The adsorption yield is defined as follows: adsorption yield (%) = [(weight of adsorbed monomer)/(weight of dehydrated clay)] × 100.

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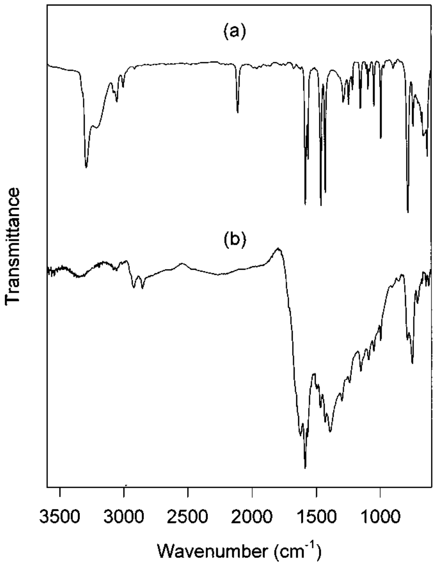

Figure 1. FT-IR spectra of (a) 2-ethynylpyridine and (b) the polymer extracted from the Ca−MMT/2-EPy complex. The polymer was extracted with DMF at 80−85 °C from the Ca−MMT/2-EPy complex. The detailed procedure is described in ref 21.

≡C−H and −C≡C− stretching bands at 3290 and 2110 cm^{-1} present in the monomer are absent in the extracted polymer. A strong new band at 1625 cm^{-1}, due to −C=C− stretching, was observed, indicating formation of a polymer with extensive conjugation. Additional evidence for polymerization is provided by the large bathochromic shift in the UV/vis absorption spectrum of the polymer as illustrated in Figure 2. The absorption maximum occurs between 440 and 500 nm tailing up to 700 nm, indicating extensive conjugation of the polymer backbone.

2-Ethynylpyridine was reported to polymerize spontaneously by alkyl halides[19a] or methanesulfonates[19d] by formation of donor−acceptor complexes with bromine[19e] and by protonation in a strong acid.[19f] It is likely that in the present case the monomer is also quarternized by protons of the surface of montmorillonite as evidenced from the broad peak due to the N−H bond at 3345 cm^{-1} in Figure 1b. Such protons could be generated by residual water molecules strongly polarized by the exchangeable cations.[10, 22−24]

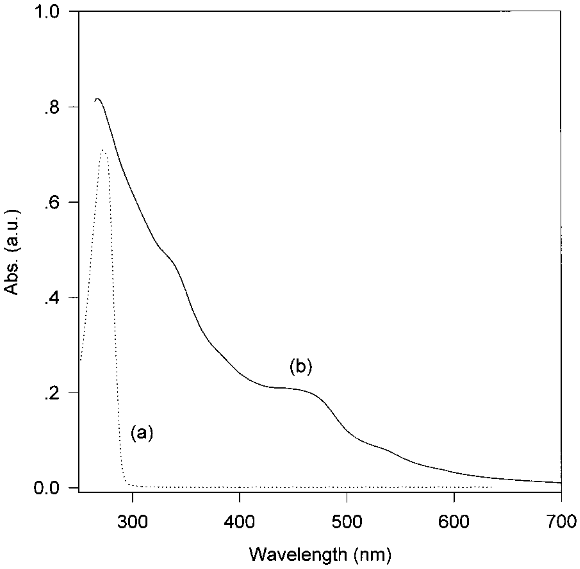

Figure 2. UV/vis spectra of (a) 2-ethynylpyridine (dotted line) and (b) the polymer extracted from the Ca−MMT/2-EPy complex (solid line).

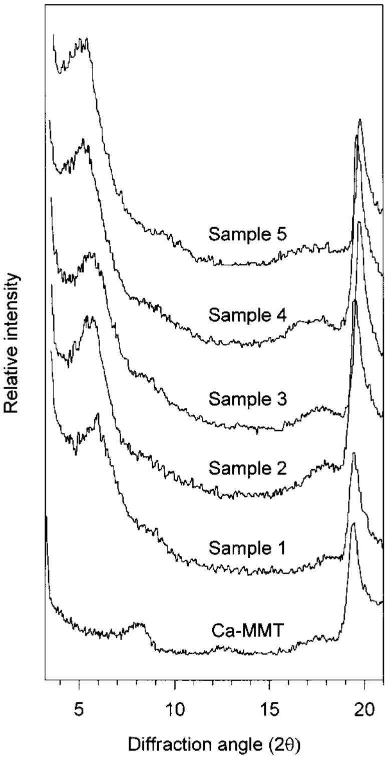

Figure 3. X-ray powder diffraction patterns of Ca^{2+}−montmorillonite and Ca−MMT/2-EPy complexes at different monomer adsorption yields.

Figure 3 shows the X-ray diffraction patterns for pristine Ca^{2+}−montmorillonite and for composites of Ca^{2+}−montmorillonite with varying amounts of intercalated 2-ethynylpyridine. In Table 1, the adsorption yields (τ (%) = [(weight of adsorbed monomer)/(weight of dehydrated clay)] $\times$ 100) and d spacings for various Ca−MMT/2-EPy complexes are summarized. X-ray diffraction (XRD) data of the Ca−MMT/2-EPy complexes with different τ show that the montmorillonite galleries are expanded with respect to the 0.96-nm basal plane spacing of a dried Ca−MMT. Interlamellar distance (Δd) of the composites is estimated from $\Delta d = d$ spacing −

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(21) We extracted the polymer solid from the Ca−MMT/2-EPy complex as follows: 0.5 g of Ca−MMT/2-EPy complex was dispersed into 100 mL of dimethylformamide (DMF). The mixture was stirred at 80−85 °C for 1 h to extract the polymer from the complex. A dark brown supernatant was separated from the solid part by centrifuging and then the solvent (DMF) was removed from the supernatant by vacuum distillation. The resulting dark brown solid mass was dissolved in methanol and the solution was poured into 400 mL of cold ether. The precipitated solid was filtered and dried in the vacuum oven. The solid was dissolved in methanol, and after being filtered through a microfilter (pore size = 0.45 μm), the solution was pasted on the NaCl crystal window. The NaCl window was dried in the vacuum oven and was used for IR measurement. It should be noted that DMF can penetrate into the galleries of montmorillonite, but it seems to be difficult to extract the whole polymers intercalated within galleries. (*Note*: The peaks at 2924 and 2855 cm^{-1} shown in Figure 1b are due to organic impurities within the clay.)

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Table 1. Adsorption Yield (τ) and the *d* Spacing of the Various Complexes of Ca^{2+}–Montmorillonite Intercalated with 2-Ethynylpyridine

samples	adsorption yield[a] (%)	*d* spacing[b] (nm)
1	8.0	1.49
2	13.9	1.59
3	15.3	1.58
4	17.0	1.67
5	21.3	1.64

[a] The adsorption yield of monomer per unit weight of dehydrated Ca^{2+}–montmorillonite was obtained by measuring the concentration of 2-ethynylpyridine remaining in the benzene solution by UV/vis absorption spectroscopy. Adsorption yield (τ) is defined as follows: τ (%) = [(weight of adsorbed monomer)/(weight of dehydrated clay)] × 100. [b] The error range of the *d* spacing is ±0.05 nm.

0.96 (nm).[9] For sample 1, the average Δd is 0.53 nm at $\tau = 8.0\%$. As τ increases to over 20%, the Δd increases to 0.68 nm for sample 5. Our previous work has shown that a trans-transoidal conformation is favored for the pyridinium-substituted polyacetylene.[25] Indeed, the Δd of the Ca–MMT/2-EPy complexes is approximately consistent with the transversal van der Waals dimension (0.66 nm) of the pyridine ring. Thus, it is probable that the extended polyacetylene chain backbone, flat on the surface of the lamellae, are adopting a trans-transoidal conformation with pyridine rings tilted with respect to the surface. This would also explain the moderate increase of Δd as a function of τ due to an increased tilt angle (approaching 90°) of the pyridine rings with the increase in molecular packing.

In this communication, we have described a novel nanocomposite of conjugated substituted polyacetylene and a layered aluminosilicate montmorillonite. The experimental evidence indicates that montmorillonite is not only a host matrix for the intercalation of 2-ethynylpyridine but also an initiating agent for the formation of a conjugated polyacetylene. A more detailed investigation concerning the polymerization mechanism and structural order of the polymer within montmorillonite is in progress. We expect that this study may lead to functional nanocomposites with high anisotropy of electrical conductivity and enhanced thermal stability, among others.

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