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ORGANIC/INORGANIC NANOCOMPOSITES PREPARED BY SPONTANEOUS POLYMERIZATION OF ETHYNYLPYRIDINE WITHIN MONTMORILLONITE

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Dedicated to the memory of Professor Sukant K. Tripathy.

ABSTRACT

2-Ethynylpyridine was intercalated and polymerized spontaneously within several montmorillonites with different exchangeable cations. FT-IR and UV/vis absorption spectroscopy showed the formation of extensively conjugated polymers within the galleries of montmorillonite. The poly(2-ethynylpyridine) (P2EPy) liberated from montmorillonite has an absorption peak at 470 nm, while P2EPy from thermal polymerization in bulk absorbs at 370 nm, indicating a more extensively conjugated structure of the former. The rate of polymerization within montmorillonites increases in the following order: sodium montmorillonite < calcium montmorillonite < proton montmorillonite. X-ray data support the model of one layer of P2EPy inserted between the lamellae of the aluminosilicate with pyridine rings of the repeating unit oriented nearly perpendicularly to the surface of the lamellae. The intercalated P2EPy within the galleries of montmorillonite displayed an enhanced thermal stability.

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Key Words: Nanocomposite; Montmorillonite; Spontaneous polymerization; Poly(2-ethynylpyridine)

INTRODUCTION

Organic/inorganic hybrid nanocomposites have recently attracted much attention because of their usefulness in a wide range of applications including next generation optics, optoelectronic nanodevices, chemical or biological sensors, and catalysts [1-2]. Intercalation polymerization of organic monomers within lamellar, expandable aluminosilicates such as montmorillonite has provided a vehicle for the exploration of oriented nanocomposites for more than three decades [3-9]. The main focus of the research was to understand the molecular orientation effects on polymerization within the galleries of the aluminosilicate and to compare the results with solution or bulk polymerization.

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 [10-13]. Lamellar aluminosilicates were also known to trigger spontaneous polymerization of several organic monomers [14-15]. In the previous work, we prepared a novel nanocomposite derived from intercalation and spontaneous polymerization of ethynylpyridine within montmorillonite [16]. The experimental evidence indicated that montmorillonite is not only a host matrix for the intercalation of ethynylpyridine, but also an initiating agent for the formation of a highly conjugated polyacetylene.

In this paper, we describe spontaneous polymerization of 2-ethynylpyridine within several montmorillonites with different exchangeable cations. The conformation of the resulting intercalated polymer was investigated by X-ray diffraction. The thermal properties of the nanocomposites were also studied.

EXPERIMENTAL

Materials

2-Ethynylpyridine (2EPy) was purchased from Farchan Laboratories and vacuum distilled before use. Sodium montmorillonite (SWy-2, abbreviated as Na-MMT) and calcium montmorillonite (SAz-1, abbreviated as Ca-MMT) were supplied by Source Clay Minerals Repository [17]. To determine the amount of exchangeable cations populating the montmorillonites, the clay samples were washed with HCl solution several times. The concentration of sodium and calcium ions was then determined by plasma atomic emission spectrometry (Table 1). This procedure also produced proton montmorillonite (H-MMT).

Table 1. The Concentration of Exchangeable Cations Na⁺ or Ca²⁺ within Montmorillonites

Samples	Na ⁺ (mmol/g) ^a	Ca ²⁺ (mmol/g) ^b
Na-MMT	0.38	0.25
Ca-MMT	— ^c	0.39

^aThe standard deviation of the concentration of Na⁺ is ± 0.03 (mmol/g).

^bThe standard deviation of the concentration of Ca²⁺ is ± 0.01 (mmol/g).

^cEssentially below detection limit.

Spontaneous Polymerization of 2-Ethynylpyridine within Montmorillonite

A typical procedure preparing nanocomposite of montmorillonite and 2EPy is as follows. To 50 ml of 3% solution of 2EPy in benzene was added 5.0 g of montmorillonite (dehydrated at 110°C for 24 hours), and the mixture was stirred at $65 \pm 3^\circ\text{C}$. The suspension turned red and the red color darkened gradually. After the reaction for 24 hours, 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 hours to remove solvent. The adsorption yield of monomer per unit weight of dehydrated montmorillonite was obtained by measuring the concentration of 2EPy remaining in the benzene solution by UV/vis absorption spectroscopy. Adsorption yield is defined as $\text{Adsorption (\%)} = [(\text{weight of adsorbed monomer}) / (\text{weight of dehydrated clay})] \times 100$. The adsorption yield obtained from the above method was corroborated from the weight loss of the montmorillonite-polymer complex by using TGA.

Liberation of Polymer from MMT/P2EPy Complex

Liberation of P2EPy was achieved through dissolution of the clay with hydrofluoric acid as reported previously [18]. The dry powders of MMT/P2EPy complex was added in small portions with vigorous stirring to an excess of 48% aqueous hydrofluoric acid in an ice bath. After two hours, the solid residual was removed through centrifugation. The solution was treated with 0.5 M NaOH aqueous solution until weakly basic. The resulting suspension was centrifuged and the colorless supernatant was discarded. After air-drying, the solid residue was extracted in a soxhlet with acetone for 48 hours. After extraction, the color of residues changed from dark red to light brown. A shiny black solid was obtained on evaporation of acetone. Treatment of clay/polymer complexes with hydrofluoric acid dissolved the clay and also converted the liberated P2EPy into a protonated form soluble in water.

Thermal Polymerization of 2-Ethynylpyridine

2-Ethynylpyridine was also polymerized thermally in bulk at 145°C for 24 hours in nitrogen. The obtained dark brown solid product was purified by dissolution in THF and precipitated into an excess of petroleum ether. The process was repeated twice. The solid was vacuum dried at 60°C for 24 hours until constant weight. The yield of polymerization was 76%. The product readily dissolved in THF, chloroform and methanol.

Measurement

IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer using KBr pellets. UV/vis absorption spectra were taken on GBC UV/vis 916 spectrometer. Thermal analysis was carried out by a TGA analyzer TA 2950 (Du Pont) with a sweep from 50°C to 800°C at a heating rate of 10°C/min. XRD measurements were run on a Philips 3 KW X-ray generator and vertical diffractometer utilizing Cu K_a radiation. The diffractometer is in the Bragg Brentano type affiliated with a spinner attachment, scintillation detector and graphite monochromator. Samples were scanned at 1 degree/min with counting rates of 500 to 1000 counts per second.

RESULTS AND DISCUSSION

Spontaneous Polymerization of 2-Ethynylpyridine within Montmorillonite

Polar 2-ethynylpyridine molecules are expected to form complexes with montmorillonite through ion-dipole interactions while the very weakly polar benzene molecules are not adsorbed well on montmorillonite. After contact with the solution of 2-ethynylpyridine in benzene, the mineral changed in color from grayish white to red darkening gradually. Figure 1 shows the IR spectra of the monomer 2EPy and the P2EPy liberated from Ca-MMT/P2EPy complex. The absorption peaks at 3290 and 2110 cm⁻¹ present in 2EPy are due to the °C–H and –C°C– stretching bands, respectively. They are absent from the spectrum of the polymer liberated from the mineral host. A new peak at 1630 cm⁻¹ appears in the polymer and is assigned to the conjugated –C=C– bond. Figure 2 shows the UV/vis absorption spectra of the polymer and monomer in chloroform. The I_{max} of 2EPy monomer is 277 nm (curve a). The peak centered at 470 nm of the liberated polymer (curve b) indicates an extensively conjugated structure. This peak can be compared with the absorption at 370 nm for P2EPy obtained by thermal polymerization in bulk (curve c, see Experimental section). It suggests an extensive conjugation for the polymer obtained within the galleries of montmorillonite

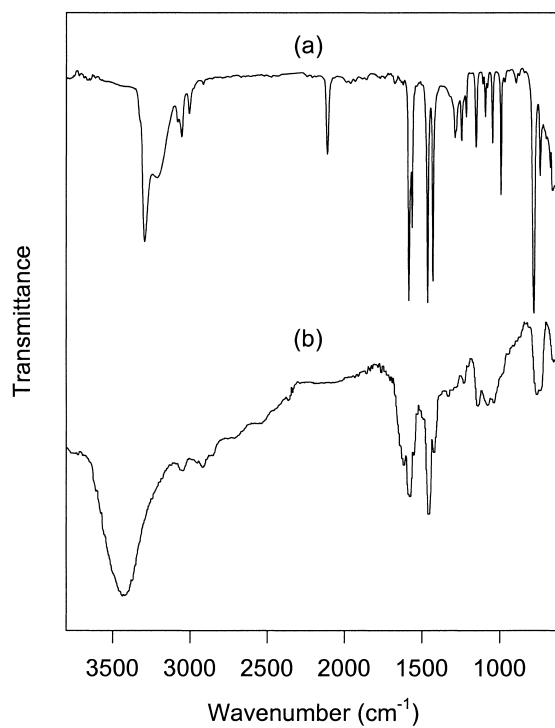


Figure 1. FT-IR spectra of (a) 2-ethynylpyridine and (b) polymer liberated from the Ca-MMT/P2EPy complex.

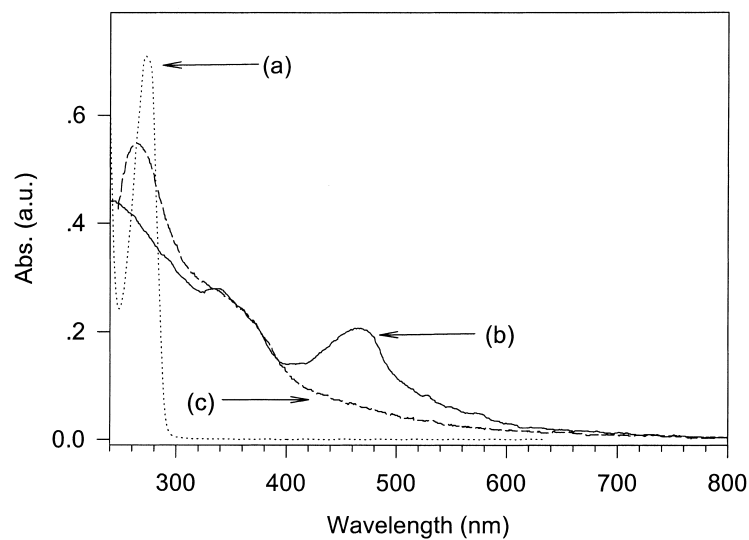


Figure 2. UV/vis spectra of (a) 2-ethynylpyridine; (b) polymer liberated from the Ca-MMT/P2EPy complex, and (c) polymer prepared by thermal polymerization.

[19]. It should be noted that the spectral characteristics of the polymers liberated from H-MMT and Na-MMT are similar.

2-Ethynylpyridine was reported to undergo spontaneous polymerization wherein the acetylenic triple bond is activated via quaternization of the pyridine nitrogen by alkyl halides or methanesulfonates, by formation of donor-acceptor complexes with bromine, and by protonation in a strong acid [20-22]. One of the most important properties of the aluminosilicates is the surface acidity, which can develop on the removal of their adsorbed or intercalated water [10]. The sources of protons can be polarized water molecules on the surface of aluminosilicates, particularly water molecules associated with compensating cations. Thus, it is likely that the acetylenic monomer is quaternized by protons populating the surface of montmorillonite.

When the 2EPy solution in benzene was shaken with montmorillonites, H-MMT turned dark red in five minutes, Ca-MMT in 30 minutes and Na-MMT in 60 minutes at room temperature. Such preliminary observation suggests that the rate of polymerization increases in the following order: Na-MMT < Ca-MMT < H-MMT. In the case of H-MMT, protons replaced most of exchangeable metal cations and are responsible for a higher rate of polymerization. In general, multivalent cations have a greater tendency to polarize the residual water within montmorillonite than univalent cations [10]. Therefore, calcium ions are at the origin of higher acidity than sodium ions. As shown in Table 1, the Na-MMT is in reality a mixed ion clay (sodium and calcium ions), in which the number of calcium ions is smaller than in the Ca-MMT. This explains higher rate of polymerization within Ca-MMT.

Conformation of Polymer Chains within Montmorillonite

The orientation and spatial arrangement of polar organic molecules in the interlayer space of montmorillonite can be deduced from X-ray diffraction (XRD) data based on the 001 reflection of the respective complexes. The XRD data of MMT/P2EPy complexes are shown in Figure 3 and Table 2. Given 0.96 nm of the basal spacing of a dehydrated montmorillonite [23], the interlamellar distance of Na-MMT/P2EPy, Ca-MMT/P2EPy and H-MMT/P2EPy complexes are 0.51, 0.67, and 0.59 nm, respectively. In order to investigate the possible conformation of the polymer chains within montmorillonite, several composites of Ca-MMT with varying amounts of the intercalated 2EPy were prepared. In Table 3, the adsorption yields (t) and interlamellar distance (Δd) for the Ca-MMT/P2EPy complexes are summarized. The average Δd at $t = 8\%$ is 0.53 nm. As t increases up to 24%, the Δd increases to 0.67 nm. The van der Waals dimensions of 2-ethynylpyridine are approximately 0.99 nm (longitudinal) and 0.66 nm (transverse). The area occupied by 2EPy oriented "flat" is approximately 0.65 nm². Assuming that the surface available for adsorption in montmorillonite is 780 m²/g [23], one gram of clay adsorbs 0.1 g of 2EPy which corresponds to $t = 10\%$. This

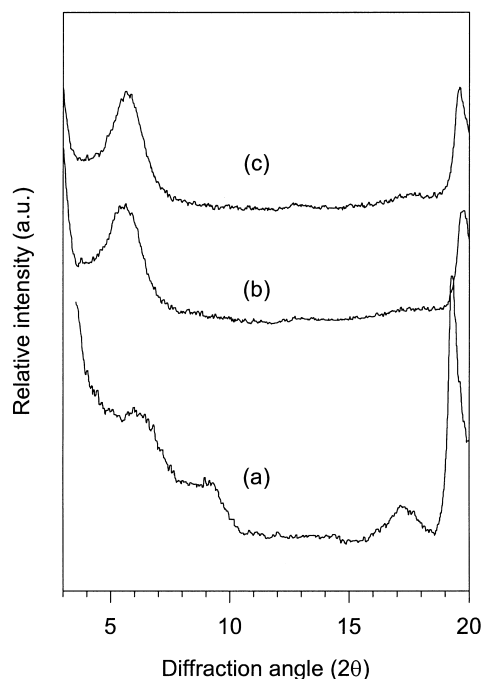


Figure 3. X-ray powder diffraction patterns of (a) Na-MMT/P2EPy; (b) Ca-MMT/P2EPy and, (c) H-MMT/P2EPy complex.

leads to a $\Delta d = 0.25$ nm for the polymer chain adopting a cis-transoidal configuration with pyridine rings oriented “flat” on the lamellar. However, this model is in disagreement with the experimental value of 0.53 nm with a similar adsorption yield (sample 1). Two layered complex with pyridine rings oriented “flat” as shown in Figure 4(a) may lead a Δd of 0.5 nm. But, t in such a case would be substantially higher than the experimental value of $t = 8\%$ (sample 1). The Δd of the Ca-MMT/P2EPy complexes as shown in Table 3 is consistent with the transverse van der Waals dimension of the pyridine ring. In our previous work, we have shown that the trans-transoidal conformation of the polyacetylene chains is preferred [24]. Thus, it is probable that the extended polyacetylene chains on the surface of the lamellae adopt a trans-transoidal conformation with pyridine rings ori-

Table 2. Adsorption Yield and Interlamellar Distance of the MMT/P2EPy Complexes

Samples	Adsorption Yield (%)	Interlamellar Distance ^a (nm)
Na-MMT/P2EPy	10	0.51
Ca-MMT/P2EPY	24	0.67
H-MMT/P2EPy	20	0.59

^aInterlamellar distance $\Delta d = d\text{-spacing} - 0.96$ (nm). The error range of the Δd is ± 0.05 nm.

Table 3. Adsorption Yield and Interlamellar Distance of the Several Ca-MMT/P2EPy Complexes

Samples	Adsorption Yield (%)	Interlamellar Distance (nm)
1	8	0.53
2	14	0.63
3	15	0.62
4	17	0.71
5	21	0.68
6	24	0.67

ented nearly perpendicular with respect to the lamellar surface as illustrated in Figure 4(b). This would also explain the moderate increase of Δd due to an increased tilt of the pyridine rings with the increase in molecular packing (increase in t). Such a model also appears to be consistent with the experimental data for the H-MMT/P2EPy and Na-MMT/P2EPy complexes.

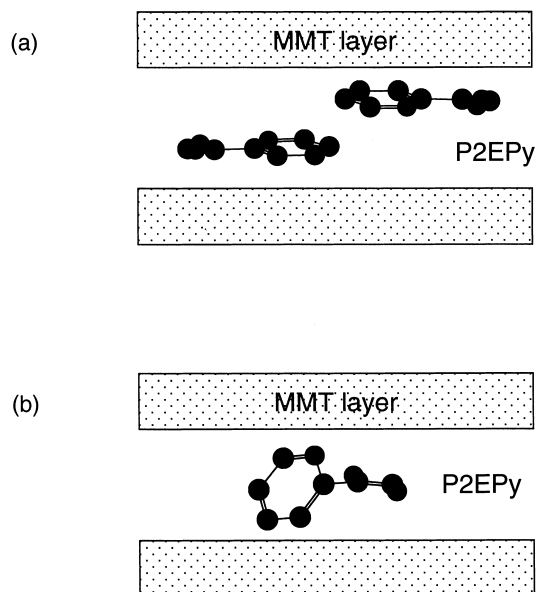


Figure 4. Schematic illustration of possible geometrical arrangement of the polymer chains within montmorillonite: (a) Two layered complex with pyridine rings oriented “flat” on the lamellar surface; (b) the extended polyacetylene chains, flat on the surface of the lamellae, with pyridine rings oriented nearly perpendicular with respect to the lamellar surface.

Thermal Behavior of Complexes

TGA thermograms of the Ca-MMT/P2EPy composite (Sample 5, see Table 3) are shown in Figure 5. For pristine Ca-MMT, there is a 5.8% weight loss at 800°C (in air). This weight loss is attributed to residual sorption water and structural hydroxyl water. In the case of the liberated P2EPy, the polymer shows a sharp weight loss between 400 and 500°C in air and degraded almost completely. As shown in curve (c), the weight of the complex remains constant above 750°C. The total weight loss of 22.8% includes the residual adsorbed water, the structural water, and the intercalated P2EPy. From the weight loss, the content of intercalated P2EPy is calculated to be 0.22 g of polymer/g of dehydrated clay, a result in good agreement with the determination of absorption yields by UV/vis absorption spectroscopy (0.21 g of polymer/g of dehydrated clay, see Experimental section).

The liberated P2EPy (curve b) degrades almost completely at 540°C in air, while approximately 30% of the polymer intercalated within montmorillonite still remains at this temperature. This indicates that the P2EPy intercalated within the montmorillonite has a higher thermal stability. This enhancement of thermal stability is attributed to restricted mobility and spatial confinement of the intercalated polymer in the galleries of layered aluminosilicate [3, 12].

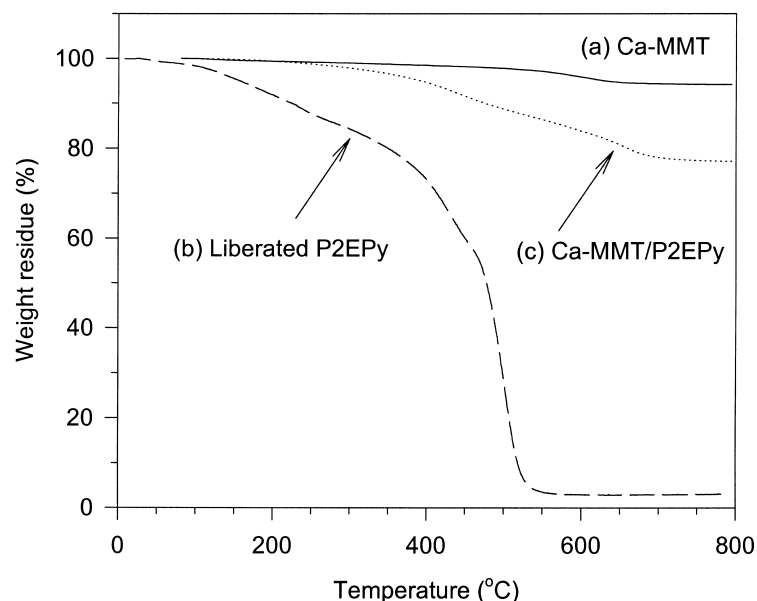


Figure 5. TGA thermograms of (a) pristine Ca-MMT (solid line); (b) liberated P2EPy (dashed line), and (c) Ca-MMT/P2EPy complex (sample 5, dotted line). The samples were heated to 800°C at 10°C/min in air flow.

CONCLUSION

Spontaneous intercalation polymerization of 2EPy 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 highly conjugated polyacetylene. The polymerization rate of 2-ethynylpyridine increases with acidity of the montmorillonite. The extended polyacetylene chains, flat on the surface of the lamellae may adopt a trans-transoidal conformation with pyridine rings oriented nearly perpendicular with respect to the lamellar surface. The polymer confined to the galleries of montmorillonite has a higher thermal stability than the liberated polymer.

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