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Clay−Polyvinylpyridine Nanocomposites

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Nanocomposites of montmorillonite mineral with poly-4-vinylpyridinium salts (1,2-form) the quaternized ionene polymer (1,6-form) and poly-4-vinylpyridine (neutral form) have been synthesized and characterized. Only one macromolecular sheet of poly-4-vinylpyridinium polyelectrolyte or the quaternized polyelectrolyte enters the interlayer space, irrespective of the amount of the polyelectrolyte used in the intercalation. Exfoliated hybrids are not therefore generated with polycationic polymers. In contrast, partially protonated poly-4-vinylpyridine is adsorbed at variety of levels and may induce clay exfoliation. Polymerization of monomeric 4-vinylpyridinium salts in the clay galleries is faster than that of the pure 4-vinylpyridinium salt and results in the formation of the quaternized ionene form independently of the polymerization conditions. Adsorption isotherms for the different forms of poly-4-vinylpyridine reveal that surface saturation coverage increases in the following order: partially protonated poly-4-vinylpyridine > quaternized ionene form > completely protonated poly-4-vinylpyridine. Models explaining the different uptake of the three derivatives and the surface selectivity toward quaternized polycations are proposed. The electrochemical results confirm that intercalative polymerization produces only the quaternized form of the polymer and reveal that protonation of poly-4-vinylpyridine occurs because of the acidity of the clay layers.

Introduction

The ability of layered silicates to undergo intercalation by a wide variety of monomers or polymers has been studied for many years, because the resulting intercalates are important in agriculture and industry.[1,2] Recently the development of new generations of polymer−silicate nanocomposites has gained interest, owing to the new techniques available for carrying out structural and property characterization and the improved mechanical, thermal, optical, and other properties, which hold promise for novel technological applications.[3−13]

The interaction of layered silicates with polymers leads to two classes of hybrid materials. In the first class, denoted as intercalated hybrids, one or more polymer chains are inserted between the host layers, generating ordered lamella with a repeat distance of few nanometers. In the second, described as delaminated hybrids, silicate layers of 1 nm thickness are exfoliated and dispersed in the polymer matrix.[14,15] Both classes of clay−polymer nanocomposites can be obtained either by intercalation of monomers followed by interlayer polymerization or by polymer intercalation from solution, providing that a water soluble polymer is available. Recently, a more general approach based on direct intercalation by a molten polymer has been developed, and its advantages in technological applications have been described.[6−8] The melt intercalation method is remarkable in that it can produce both intercalated and delaminated composites with a wide range of polymers from nonpolar polystyrene to weakly polar poly(ethylene terephthalate) to strongly polar nylon.[10]

Polyelectrolytes are a class of important polymers characterized by a large number of ionizable groups.

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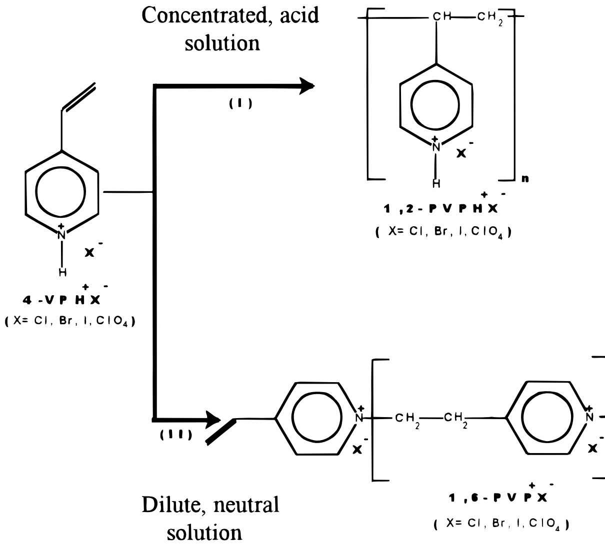
Scheme 1



Clays having negatively charged surfaces are expected to interact electrostatically with cationic polyelectrolytes. A typical class of cationic polyelectrolytes is protonated polyvinylpyridines and the corresponding N-alkylated derivatives. Although polyvinylpyridines find various applications,[16] their interactions with clay surfaces are not well-studied.[17] Protonated poly-4-vinylpyridine is a polyelectrolyte with certain advantages in studies with clays. The first is that the 4-vinylpyridine monomer in the protonated form is expected to easily intercalate into the clay layers by an ion exchange process. The inserted monomer can then undergo polymerization within the spatially constrained interlamellar space of the clay. The bulk polymerization of protonated 4-vinylpyridine (4-VPH$^+$X$^-$) in aqueous solution follows two distinct routes which, according to the monomer concentration and acidity of the medium, yield either the 1,2-polyelectrolyte (**I**) with the pyridinium units in the side chain or the 1,6-polyelectrolyte (quaternary form) (**II**) with the pyridinium units in the main chain, as shown in Scheme 1.[18] The second is that the neutral poly-4-vinylpyridine is easily protonated to form a water soluble, positively charged polyelectrolyte which is expected to insert into the clay lattice. Third, melt intercalation of neutral poly-4-vinylpyridine is feasible if an acidic clay or suitably modified clay is used as the inorganic partner.

These features make polyvinylpyridine an attractive system to study the reactivity of clay surfaces with the monomer or polymer, the latter in solution or in melt. In addition, the intercalative polymerization of the monomer offers the possibility to examine whether the clay surfaces show selectivity for the 1,2- or 1,6-mode of polymerization. In view of these potentialities, we report here the synthesis, characterization, and probable structural models of nanocomposites obtained from the interaction of smectite clays with polyvinylpyridine derivatives and the intercalative polymerization of the 4-vinylpyridinium monomer.

Experimental Section

Materials. The clay used in this study was a montmorillonite from the island of Milos, Greece, with a stoichiometry $\langle Na_{0.63}K_{0.07}Ca_{0.11}\rangle[Si_{7.75}Al_{0.25}]\{Al_{3.21}Mg_{0.69}Fe^{3+}_{0.02}Fe^{2+}_{0.03}Ti^{4+}_{0.05}\}$-$O_{20}(OH)_4$. The mineral was fractionated to $<2\ \mu$m by gravity sedimentation and purified by standard methods. Sodium saturated clay was prepared by immersing the clay in 1 N solution of sodium chloride solution. The sample was washed with distilled−deionized water and transfered into dialysis tubes in order to obtain chloride free clays and then dried at room temperature. The cation exchange capacity (CEC), measured by the Co(II) procedure,[19] was 83 mequiv/100 g of clay. In the ^{1}H NMR measurements the synthetic Laponite clay was used with a CEC of about 100 mequiv/100 g of clay.

4-Vinylpyridine (95%), obtained from Aldrich, was distilled before use. Poly-4-vinylpyridine was prepared as described in the literature.[17] The hydrobromide salt of the 1,2-polymer (1,2-PVPH$^+$Br$^-$) was prepared by treating the neutral P-4-VP with 48% hydrobromic acid, and the bromide salt of the quaternary form of the polymer (1,6-PVP$^+$Br$^-$) was prepared as described before.[20] Finally, the hydrobromide salt of the monomer (4-VPH$^+$Br$^-$) was prepared as described in the literature.[22]

Synthesis of Nanocomposites. To synthesize the [clay-1,2-PVPH$^+$] or [clay-1,6-PVP$^+$] nanocomposites, a quantity from each polyelectrolytic salt, corresponding to 4 × CEC of the clay, was added to a 2 wt % aqueous clay suspension. The products were isolated by centrifugation and washed two times with methanol and then with water. They were air-dried on glass plates.

Intercalative Polymerization. For the intercalative polymerization a quantity of 4-VPH$^+$Br$^-$ corresponding to 5 × CEC of the clay was added to a 2 wt % clay suspension. The concentration of the monomer and the acidity of the medium were adjusted to favor the formation either of the 1,2- or 1,6-polyelectrolyte. Specifically, for the 1,2-form a concentrated solution of the monomer (1.82 M) in an acidic medium, pH 1, was employed. The formation of the 1,6-polyelectrolyte was conducted at pH 7 in a dilute monomer concentration (0.2 M). The duration of polymerization was 6 days, as in the case of bulk polymerization. The products were isolated by centrifugation, washed three times with methanol and then with water, and air-dried on glass plates.

Adsorption Isotherms. The isotherms for the adsorption of 1,2-PVPH$^+$Br$^-$, 1,6-PVP$^+$Br$^-$, and P-4-VP by Na−montmorillonite were obtained by adding the appropriate amount of each adsorbate, in water or in water/methanol (1:1) for P-4-VP, to 100 mg of Na−montmorillonite paste and bringing the suspension volume to 30 mL. The suspension was stirred for 2 h and then centrifuged at 5000 rpm. The amount adsorbed by the clay was calculated from an analysis of the supernatant solution for the remaining polymer. The analysis of the latter was carried out gravimetrically by precipitating the polycations with sodium picrate or picric acid in the case of P-4-VP. Blank experiments showed that the error in determining the polyvinylpyridine derivates was less than 3%.

Characterization. *X-ray Diffraction Measurements.* X-ray diffraction (XRD) data were collected on a D500 Siemens diffractometer using Cu Ka (40 kV, 35 mA) radiation and a secondary beam graphite monochromator. The spectra were recorded in the 2 θ range from 2° to 30°, in steps of 0.03° and a counting time per step of 1 s.

FTIR Spectroscopy. Infrared spectra in the region 400−4000 cm^{-1} were measured with a Nicolet 550 infrared spectrometer equipped with a DTGS detector. Powder of the samples was used for preparation of KBr pellets, containing about 10 wt % material.

^{1}H NMR Spectroscopy. ^{1}H NMR spectra were measured on a Bruker AC250 spectrometer. To avoid broadening of the lines

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due to paramagnetic centers present in the structure of natural montmorillonites, the ^{1}H NMR spectra were obtained using the synthetic clay Laponite. The nanocomposites were powdered and then dispersed by sonication in 0.5 mL of DMSO-d_6. Blank experiments showed that treatment of a nanocomposite with DMSO does not affect its structural characteristics. The suspension was homogeneous long enough to record the ^{1}H NMR spectra.

Cyclic Voltammetry. Cyclic voltammograms (CV) were recorded on a PAR Model 174A polarographic analyzer operated in conjunction with a Model 175 universal programmer. An undivided three-electrode cell was used with a pyrolytic graphite (0.25 cm^2) as working electrode, a saturated calomel electrode as reference, and platinum gauze as the counter electrode. The electrode modification was achieved by allowing 10 μL of an aqueous 1 wt % suspension of the various clay−polyvinylpyridine nanocomposites to dry in air. The CV data were recorded on aqueous 0.1 M Na_2SO_4 solutions containing 1 mM $K_4Fe(CN)_6$ as the redox probing reagent.

Results and Discussion

Intercalation of Poly-4-vinylpyridine and Its Protonated Derivates into Sodium Montmorillonite. Most commercially available poly-4-vinylpyridines are insoluble in water or polar organic solvents, even after treatment with strong acids to convert them to the corresponding protonated salts. For these reasons, we prepared water- or methanol-soluble, well-characterized, neutral poly-4-vinylpyridine following well-established methods.[17] Methanol solutions of the polymer, when treated with concentrated hydrobromic acid, afforded the water-soluble hydrobromide salt of the 1,2-polyelectrolyte. The quaternary bromide salt of the polymer was also readily obtained.[20] These polyvinylpyridinium salts in aqueous solution dissociate to polycationic species, which can enter the clay lamella by an ion-exchange process. Thus, when an aqueous solution of the polycationic 1,2- or 1,6-polymer was added to an aqueous clay suspension, an immediate flocculation of the clay particles was observed. Elemental analysis for sodium in several nanocomposites obtained from the intercalation of the 1,2- or 1,6-polyvinylpyridinium cations showed traces, less than 0.02%, of remaining sodium. This finding shows that each of the polycationic polymers has accessed the charged sites of the clay surfaces by ion exchange and is electrostatically bound to the layers.

Intercalated hybrids were also obtained from water- or water−methanol soluble neutral poly-4-vinylpyridine. This polymer has weak basic properties with the result a small fraction of pyridyl groups to be protonated in aqueous environment. When the polymer is added to a clay suspension the mineral layers will first adsorb the bulky macromolecule, and then, because of the increased acidity of the clay surfaces, the extent of protonation of the pyridyl groups will increase. Both factors shift the equilibrium reaction, shown below, to the right and intercalation proceeds to completion with a concomitant increase in the pH of the medium. Thus, the pH of a 1 wt % solution of poly-4-vinylpyridine in water−methanol (50:50) from an initial value of 6 changed to 9.2 after intercalation. The pronounced acidity of the clay layers is demonstrated by the electrochemical results discussed later. The extent of protonation of the polymer pyridyl groups affects the agglomeration of the clay particles. Thus, while a fully protonated salt of the 1,2-polymer causes immediate flocculation of clay particles, the action of neutral poly-4-vinylpyridine does not induce immediate flocculation. It takes a few hours for the clay particles to agglomerate. Finally, composites with neutral poly-4-vinylpyridine contain, apart from pyridinium groups which are electrostatically bound to the exchange sites of the mineral, a number of pendant pyridyl groups, which are available to bind metal ions from solutions.[21]

$$\overline{\underline{x\mathrm{Na}^{+}(\mathrm{solv})}} + \text{4-PVP} + x\mathrm{H_2O} \longrightarrow \overline{\underline{\text{4-PVPH}^{+x}}} + x\mathrm{NaOH}$$

Characterization of Nanocomposites: X-ray, ^{1}H NMR, and FTIR Analysis. The X-ray diffraction patterns from the two polymeric derivatives, shown in Figure 1, confirm the intercalation reactions. The 1,2-PVPH$^+$/montmorilonite composite shows a d_{001} peak at 15 Å, corresponding to an interlayer separation of 5.4 Å ($\Delta = 15 - 9.6 = 5.4$ Å, 9.6 Å being the layer thickness). The corresponding d_{001} value for the 1,6-quaternary structure is 13.6 Å and therefore $\Delta = 13.6 - 9.6 = 4$ Å. These values represent the mean thickness of a monolayer of uncoiled chain in each polymer. Uncoiling of the polymeric chains is mainly caused by the electrostatic repulsions among the positive pyridinium centers in the macromolecules and is further reinforced during intercalation by the direct contact of the macromolecular units with the silicate layers. The observed different spacings can be explained by taking into consideration the different configuration of the carbon chains in the two polymers. As shown in Figure 1a, the configuration of the 1,2-polyelectrolyte is defined by two parallel planes formed by the pyridyl groups. By contrast, all pyridyl groups in the 1,6-form (Figure 1b) belong to the same plane. Furthermore, in both configurations those pyridyl groups of the macromolecule that interact electrostatically with the negative sites of the silicate surface remain parallel to the sheets because of $\pi-\pi$ interactions with the oxygen plane of the silicate sheet. However, the pyridyl groups that are not engaged in direct electrostatic interactions with the clay ionic sites may adopt different orientations in the interlayer region by rotation about the C−C bond. In the two end cases these pyridyl groups can be parallel or perpendicular to the clay surfaces. The corresponding separations calculated for the 1,2-structure are $\Delta_{\|} = 4.3$ Å and $\Delta_{\perp} = 5.7$ Å, with the observed value of 5.4 Å between these two values implying that the plane of the rotatable pyridyl groups is inclined to an angle of about 71° with respect to the oxygen plane of the mineral layer. Similarly, for the 1,6-polyelectrolyte the calculated separations are $\Delta_{\|} = 3$ Å and $\Delta_{\perp} = 4.3$ Å. Here again the observed value of 4 Å lies between these two limited cases and corresponds to an angle of inclination of about 69°.

The ^{1}H NMR data for the intercalated 1,6-polyelectrolyte support the presence of two types of pyridyl rings. One type (denoted by *) is revealed from broadening and shifting of the pyridyl groups to lower frequencies with respect to the free polymer (Figure 2). Broadening and shifting can be attributed to the electrostatic interactions of the ionically bound pyridyl group and the clay surfaces. The other type, corresponding to the intermediate free pyridyl segments, does not exhibit

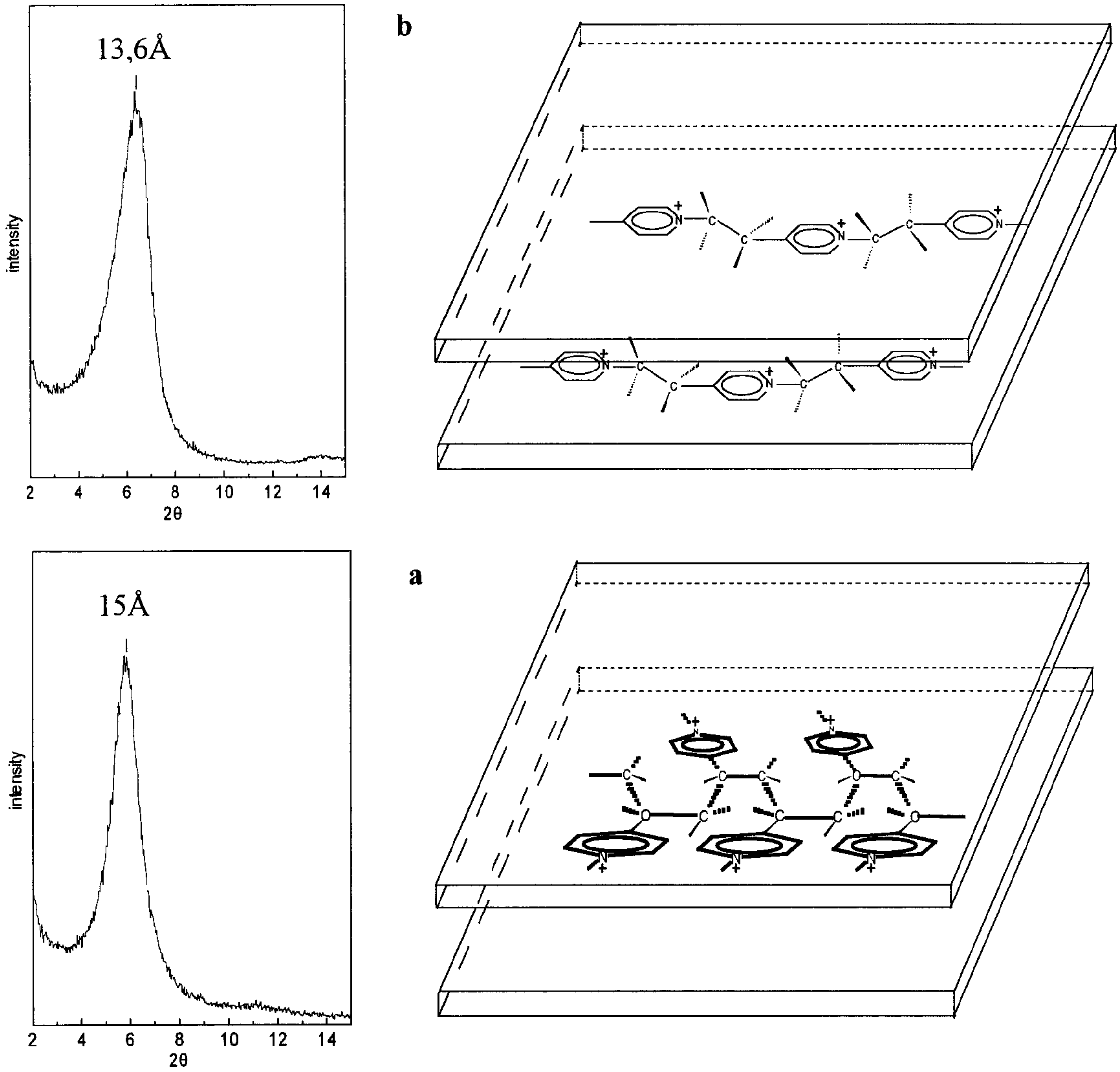

Figure 1. XRD patterns and schematic representation of the geometry of (a) 1,2- polyelectrolyte and (b) 1,6-polyelectrolyte in the interlayer zone of montmorillonite.

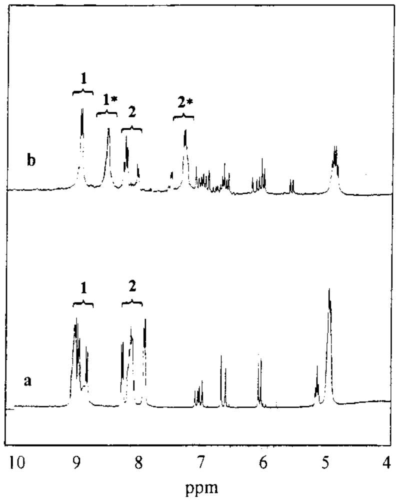

Figure 2. ^{1}H NMR spectra of (a) 1,6-polyelectrolyte and (b) nanocomposite obtained from intercalation of the 1,6-polyelectrolyte into Laponite.

analogous effects and the ^{1}H NMR spectra remain similar (only broadening) to those of the free polymer.

In an attempt to find out whether the silicate mineral could host two or more layers from each polyelectrolyte, we have conducted the intercalation reaction with varying amounts of the 1,2- or 1,6-polymer, ranging from 4 to 90 wt %. The XRD patterns (Figure 3a,b) show clearly that the d_{001} spacing remains unaffected by the amount of added 1,2- or 1,6-polyelectrolyte. The results indicate that the clay surfaces become saturated by adsording only one layer of the 1,2- or 1,6-polyelectrolyte. It is very likely that the strong electrostatic interactions between the polyanionic clay surfaces and the polycationic polymers pin the mineral layers and therefore prevent the penetration of a second polymer layer, even in the presence of manyfold excess of the polyelectrolyte. The conclusion is that the interaction of clay layers with a cationic polyelectrolyte, even in a manyfold excess in an aqueous environment, leads only to intercalated hybrids, either separable or dispersed into the polymer matrix when a large excess of the polyelectrolyte is used in the intercalation.

The behavior of neutral P-4-VP toward intercalation is different. The XRD patterns from several preparations, in which the intercalation was conducted with

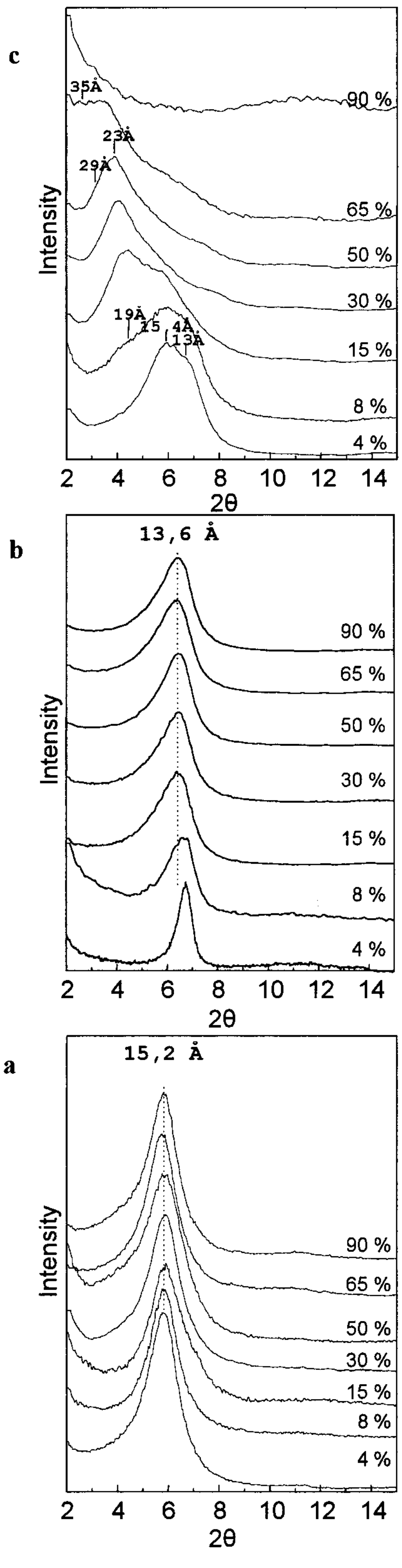

Figure 3. XRD patterns at different polymer loadings for clay−nanocomposites: (a) 1,2-polyelectrolyte, (b) 1,6-polyelectrolyte, and (c) poly-4-vinylpyridine.

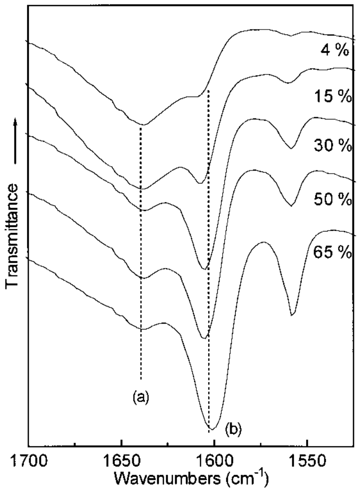

Figure 4. IR spectra between 1700 and 1525 cm^{-1} at different intercalation levels of poly-4-vinylpyridine.

various amounts of neutral P-4-VP, are presented in Figure 3c. The results demonstrate clearly that the d_{001} spacing is influenced by the amount of P-4-VP used in the intercalation reaction. At low polymer loadings, from 4 to 8 wt %, basal reflections at 13 and 15.4 Å were observed. The spacing at 13 Å is interpreted to represent the insertion of only one layer of stretched polymer in direct contact with the silicate surface. However, owing to the segmental protonation of pyridyl groups, it may be possible that the polymer chain enters into the interlamellar space in a coiled configuration, causing broadening of the diffraction pattern and the appearance of the peak at 15.4 Å. Increasing the amount of polymer in the intercalation mixture adds more polymer layers, as evidenced by the peaks at 23 and 29 Å. Finally, at polymers loading higher than 70 wt %, delaminated composites were obtained, as registered by the disappearance of silicate (001) reflections.

The FTIR spectra provide additional evidence for the interaction of the three poly-4-vinylpyridine derivatives with the clay surfaces. The transmittance spectra of the composites show good resemblance to those from the pure polymers, meaning that chemical stability and continuity is maintained in the intercalation reactions. In the composite with poly-4-vinylpyridine, the coexistence of neutral and protonated pyridyl groups in the intercalated phase is indicated by absorptions near 1600 and 1640 cm^{-1}, respectively. Poly-4-vinylpyridine exhibits a strong absorption at 1600 cm^{-1}, due to the stretching of a carbon-substituted pyridyl ring, which is shifted to 1635−1640 cm^{-1} upon protonation.[22−24] The series of spectra, shown in Figure 4, obtained from clay samples treated with varying amounts of P-4-VP, reveal that both neutral and onium pyridyl rings coexist in the laminated polymer. As expected and shown by the infrared results, the intensity at 1600 cm^{-1} for free pyridyl groups increased as the amount of P-4-VP in the intercalation mixture was increased.

The infrared spectra differentiate between the 1,2- or 1,6-intercalated polyelectrolyte, and this information identifies the products from the intercalative polymerization. For this purpose the region between 1700 and 1300 cm^{-1} constitutes a fingerprint region for the respective polymers. Figure 5 displays the infrared absorptions from the 1,2- and 1,6-polyelectrolyte intercalated by ion exchange into montmorillonite. First, the vibration near 1640 cm^{-1}, arising from the protonated

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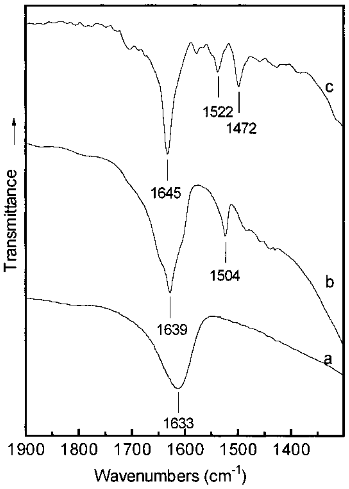

Figure 5. Characteristic IR absorptions from (a) Na−montmorillonite, (b) clay nanocomposite with 1,2-polyelectrolyte, and (c) clay nanocomposite with 1,6-polyelectrolyte.

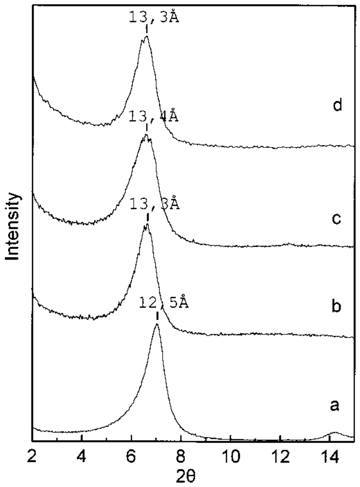

Figure 6. XRD patterns of (a) Na−montmorillonite, (b) montmorillonite−1,6-polyelectrolyte, (c) intercalative polymerization under 1,2-conditions, and (d) intercalative polymerization under 1,6-conditions.

form of a carbon-substituted pyridyl ring or the corresponding quaternary analogue, is sharper in the quaternary composite. The broadening of the peak in the hybrid with the 1,2-polyelectrolyte might arise from the presence of a few neutral pyridyl rings in this polymer chain. Second, the absorption at 1472 cm^{-1}, due to $-CH_2-$ scissoring is strong in the 1,6-quaternized polyelectrolyte and very weak in the 1,2-form. The different number of $-CH_2-$ groups, which is twice in the 1,6-polyelectrolyte, and perhaps different interactions between the two polyelectrolyte and aluminosilicate sheets might be a possible reasons for the discrepancies in intensity observed for the two intercalated phases.

Intercalative Polymerization. As stated in the Introduction, the polymerization of 4-vinylpyridinium salts in aqueous solutions yields two types of macromolecules depending on the monomer concentration and the acidity of the medium. The question that we pose is whether the clay surfaces can selectively lead to the formation of one type of polyelectrolyte. Polymerization of 4-vinylpyridinium bromide was performed in the presence of a clay dispersion and under conditions which in bulk afford solely the 1,2- or the 1,6-polyelectrolyte.[18] In these experiments the amount of 4-vinylpyridinium bromide was equivalent to 5 × CEC of the mineral. Polymerization was completed in less than 24 h.

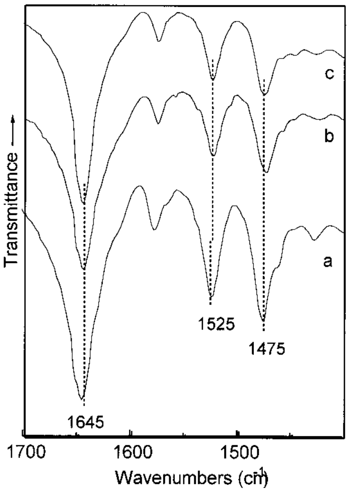

Figure 7. IR spectra from (a) clay−1,6-polyelectrolyte, (b) intercalative polymerization under 1,2-conditions, and (c) intercalative polymerization under 1,6-conditions.

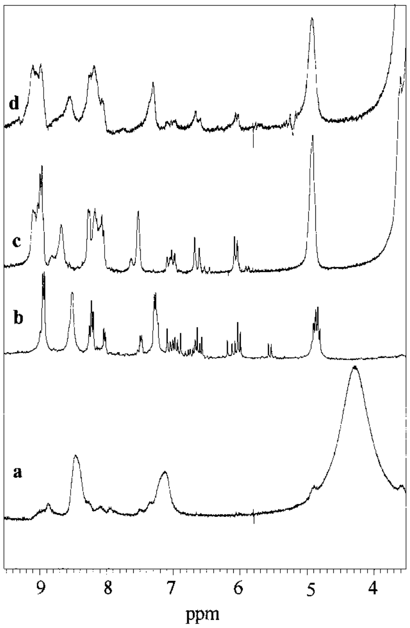

Figure 8. ^1H NMR spectra from (a) montmorillonite−1,2-polyelectrolyte, (b) montmorillonite−1,6-polyelectrolyte, (c) intercalative polymerization under 1,2-conditions, and (d) intercalative polymerization under 1,6-conditions.

Characterization of Intercalative Polymerization: X-ray, ^{1}H NMR, and FTIR Analysis. The XRD patterns (Figure 6) were similar for both polymerization procedures with a d_{001} = 13.3 Å, suggesting that the 1,6- polyelectrolyte was the only product of the interlayer polymerization. The FTIR spectra between 1700 and 1300 cm^{-1} are shown in Figure 7. Spectrum b of the composite, obtained under conditions for 1,2-polymerization, is very similar to spectrum c, which was obtained under conditions for 1,6-polymerization. In addition both b and c spectra are very similar to spectrum a, which was recorded from the intercalation product of 1,6-polyvinylpyridinium polyelectrolyte with clay. These similarities reveal that the 1,6-quaternized polyelectrolyte is the only product of the intercalative polymerization.

Finally, the ^{1}H NMR spectra identify the exclusive formation of the 1,6-polyelectrolyte, regardless of polymerization conditions. The ^{1}H NMR spectra in Figure 8 demonstrate this point. Spectra a and b are from clay–polymer hybrids, obtained by the intercalation of preformed 1,2- or 1,6-polyelectrolyte, respectively. Spectra c and d are from the intercalative polymerization of 4-VPH$^+$Br$^-$ under conditions favoring in bulk polymerization the formation of the 1,2- or 1,6-polyelectrolyte. To avoid interference from unreacted monomer or polymers formed outside of the clay framework, the nanocomposites were thoroughly washed with water. As an indication of polymerization we regard primarily the broad peak near 5 ppm, assigned to the backbone methylene groups. This peak is present in all spectra but missing in spectrum a. Spectra c and d show good similarity to each other and also to spectrum b. We consider these similarities as evidence that the intercalative polymerization of the monomer yields only the 1,6-quaternized polyelectrolyte.

Another issue is whether and to what extent the intercalative polymerization depends on the amount of monomer intercalated into the clay. To study this, FTIR and ^{1}H NMR spectroscopies were used to determine the extent of polymerization as a function of the monomer added to a clay suspension. The amount of monomer in these experiments is expressed in terms of the cation exchange capacity of the mineral. The results from the FTIR and ^{1}H NMR spectra indicate that intercalative polymerization is critically influenced by the amount of monomer. A series of FTIR spectra are shown in Figure 9. The top spectrum f is from a composite obtained from the intercalation of a very small quantity of 4-VPH$^+$Br (1 mg/100 mg of clay) in order to avoid possible polymerization. For the same reason the product was immediately centrifuged, washed, and air-dried. The bottom spectrum a is from the intercalation of preformed 1,6-PVP$^+$X$^-$. The peaks at 1645, 1525, and 1475 cm^{-1}, indicated by dotted lines, and in particular the last two which are not present in the monomer, are used as markers for the polymerization. Spectra b–e were recorded from products that were received when 4-VPH$^+$-Br$^-$ in amounts equivalent to 4, 3, 2, 1 × CEC of clay were added to an aqueous clay suspension and left for 24 h under stirring for polymerization. We observe that the peaks at 1645, 1525, and 1475 cm^{-1} develop upon increasing the amount of 4-VPH$^+$Br$^-$ added. On the other hand, the characteristic peak at 1510 cm^{-1} of the monomer loses intensity on passing from e to b. That this peak has diminished intensity in spectrum b, indicates that some monomer was not probably polymerized. The presence of the weak shoulder at 1525 cm^{-1} in the spectrum e indicates limited intergallery polymerization. Polymerization is clear when the amount of monomer correspond to 3 or better 4 times the CEC of the mineral, as evidenced by the similarity of spectra c and b to spectrum a. Accordingly, the infrared results imply that intercalative polymerization is prominent when the amount of 4-PVPH$^+$Br$^-$ exceeds the threshold of 2 × CEC of the mineral.

Furthermore the ^{1}H NMR spectra of the composites, generated from the intercalative polymerization of 4-vinylpyridinium cation in quantities corresponding to 1, 1.3, 2, 3, and 4 × CEC of the mineral, are shown in Figure 10. Juxtaposing the spectra of the intercalated hybrids (b–f) to those of the pure monomer (a) and of the intercalated 1,6-polyelectrolyte (g) shows that spectra b and c, apart from their broadening and shifting of the lines to lower frequencies, are similar to the spectrum of the pure monomer. This means that at these loadings polymerization had scarcely started in the clay galleries. In contrast, when the loading was increased to 2, 3, or 4 × CEC the corresponding spectra were similar to spectrum g, i.e., the spectrum from the direct intercalation of the 1,6-polyelectrolyte to Laponite. These data reflect the effect of the added monomer upon the intercalative polymerization.

Figure 11 presents an illustration of the events which we propose to take place in the clay sheets. The calculated distance between two negatively charged sites in the clay and the dimensions of the 4-vinylpyridinium ion are also shown. Monomeric units at 1 × CEC are expected to be initially fixed at the exchange sites of the mineral. In these positions, indicated by 1, the interval between two units is large enough to allow self-interaction. Additional monomeric units (2) will be probably positioned for steric reasons at the center of the square of four 1-units. Again, because of large intermolecular separations, interactions between units 1 and 2 are not likely. However, when the monomer amounts to 3 × CEC, clear signs of polymerization are registered in the infrared and ^{1}H NMR spectra, as discussed before. In this instance the monomer is likely to occupy positions 3 and polymerization between units 1 and 3 becomes feasible. Finally, the IR and ^{1}H NMR criteria become more pronounced in the spectra which were obtained from the intercalation of monomer corresponding to 4 × CEC of the mineral. In this case, the additional units take up positions 4 and by bridging the gaps between the monomeric units allow their mutual interactions leading to the realization of an intercalated polymer.

Another important factor for the intercalative polymerization is the proper distance either between two neighboring vinyl units for the formation of the 1,2-polyelectrolyte or between one vinyl group and a protonated pyridyl group for the formation of the 1,6-polyelectrolyte. In the proposed model the distance between two reactive units is estimated to be near 3–4 Å for the former case and near 1 Å for the latter. Furthermore, the formation of the 1,2-polyelectrolyte requires that all vinyl segments have a fixed orientation, i.e., face right or left along the *x*-axis. Clearly this prerequisite constitutes a hindrance for the formation of the 1,2-polyelectrolyte. On the other hand, in the case of the 1,6-polyelectrolyte, electrostatics prevent the placement of two pyridinium groups next to each other along the *y*-axis and therefore the pyridinium–vinyl group configuration is preferred. For these reasons the model offers a plausible explanation for the preferred intercalative formation of the 1,6-polyelectrolyte and for the effect of the extent of monomer intercalation upon the interlamellar polymerization.

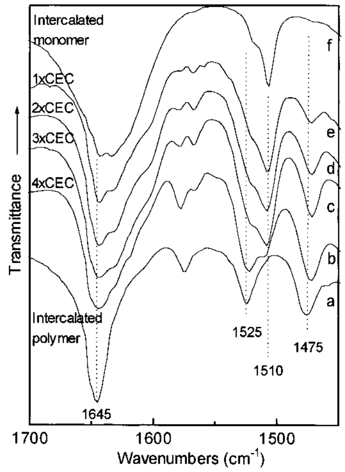

Figure 9. IR spectra from (f) intercalation of 1 mg of 4-vinylpyridinium bromide into 100 mg clay, (e−b) intercalation of different quantities of 4-vinylpyridinium bromide, and (a) intercalation of authentic 1,6-polyelectrolyte into clay.

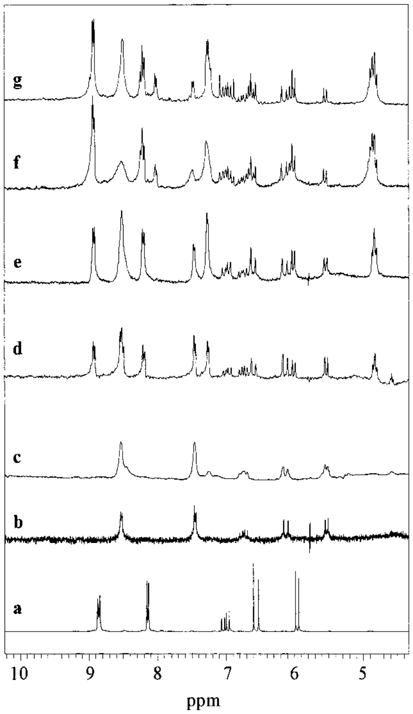

Figure 10. ^{1}H NMR spectra from (a) monomer, (b−f) intercalation of monomer in quantities 1, 1.3, 2, 3, 4 × CEC into clay, and (g) intercalation of authentic 1,6-polyelectrolyte into clay.

Adsorption Isotherms. Figure 12 shows the adsorption isotherms for the uptake of the 1,2-polyelectrolyte (a), 1,6-polyelectrolyte (b), and neutral poly-4-vinylpyridine (c), by Na−montmorillonite. Adsorption increases steeply at low bulk polymer concentration and then levels off for the 1,2- and 1,6-polyelectrolytes, while for the neutral poly-4-vinylpyridine, after a limited plateau, there is a tendency for further adsorption upon increasing the amount of added polymer. This Langmuir-type adsorption for all derivatives, which is observed usually in the adsorption on solid surfaces, reflects the high affinity of the clay surfaces for all types of poly-4-vinylpyridine. The results show that the surface saturation coverage (mg of polymer/g of clay) increases in the order poly-4-vinylpyridine > 1,6-polyelectrolyte > 1,2-polyelectrolyte. The data (dotted line) show that at a bulk polymer concentration of 7 × 10^{-3} mol, 1 g of clay can adsorb 1.75 × 10^{-3} mol (326 mg) of 1,2-PVPH$^+$Br$^-$, 2.6 × 10^{-3} mol (484 mg) of 1,6-PVP$^+$Br$^-$, and 2.85 × 10^{-3} mol (299 mg) of P-4-VP. We first note that neutral P-4-VP is adsorbed in amounts almost twice those of the structurally similar protonated 1,2-polyelectrolyte. Given that the two polymers have similar dimensions, the data suggest that the aluminosilicate layers are laminated by a bimolecular layer of the P-4-VP macromolecule (Figure 12c). This finding, which is in agreement with the XRD results, implicates that the silicate layers are only weakly pinned by the partially protonated P-4-VP, and therefore the penetration of a second polymer layer of P-4-VP becomes feasible. The rise of

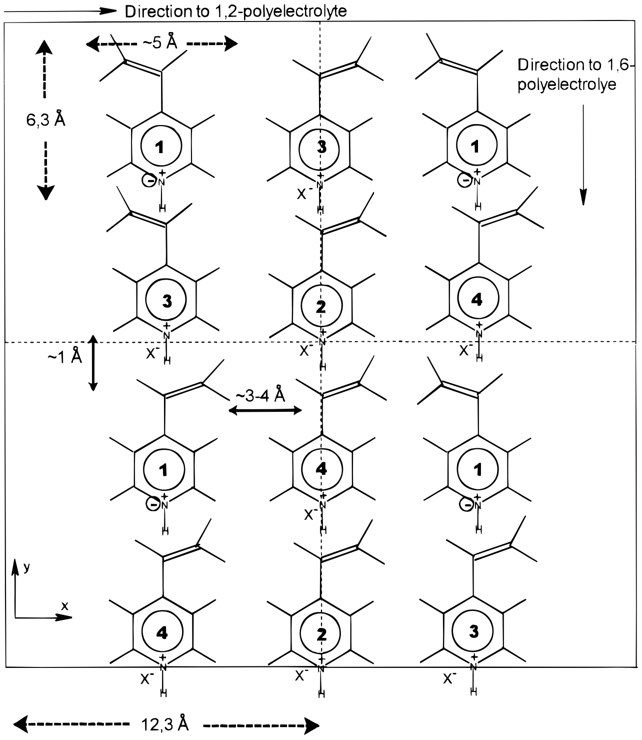

Figure 11. Schematic illustration of intercalative polymerization emphasizing the occupation of the interlayer positions by the monomeric units.

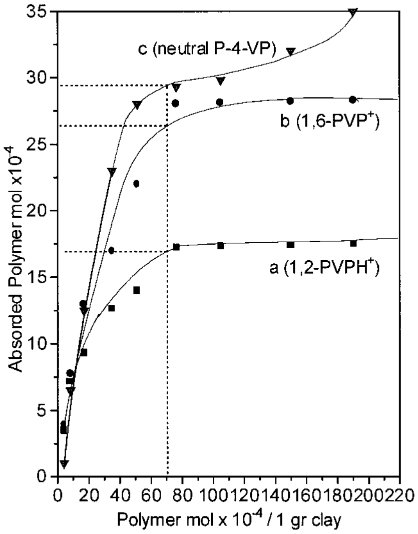

Figure 12. Adsorption isotherms of (a) 1,2-polyelectrolyte, (b) 1,6-polyelectrolyte, and (c) poly-4-vinylpyridine.

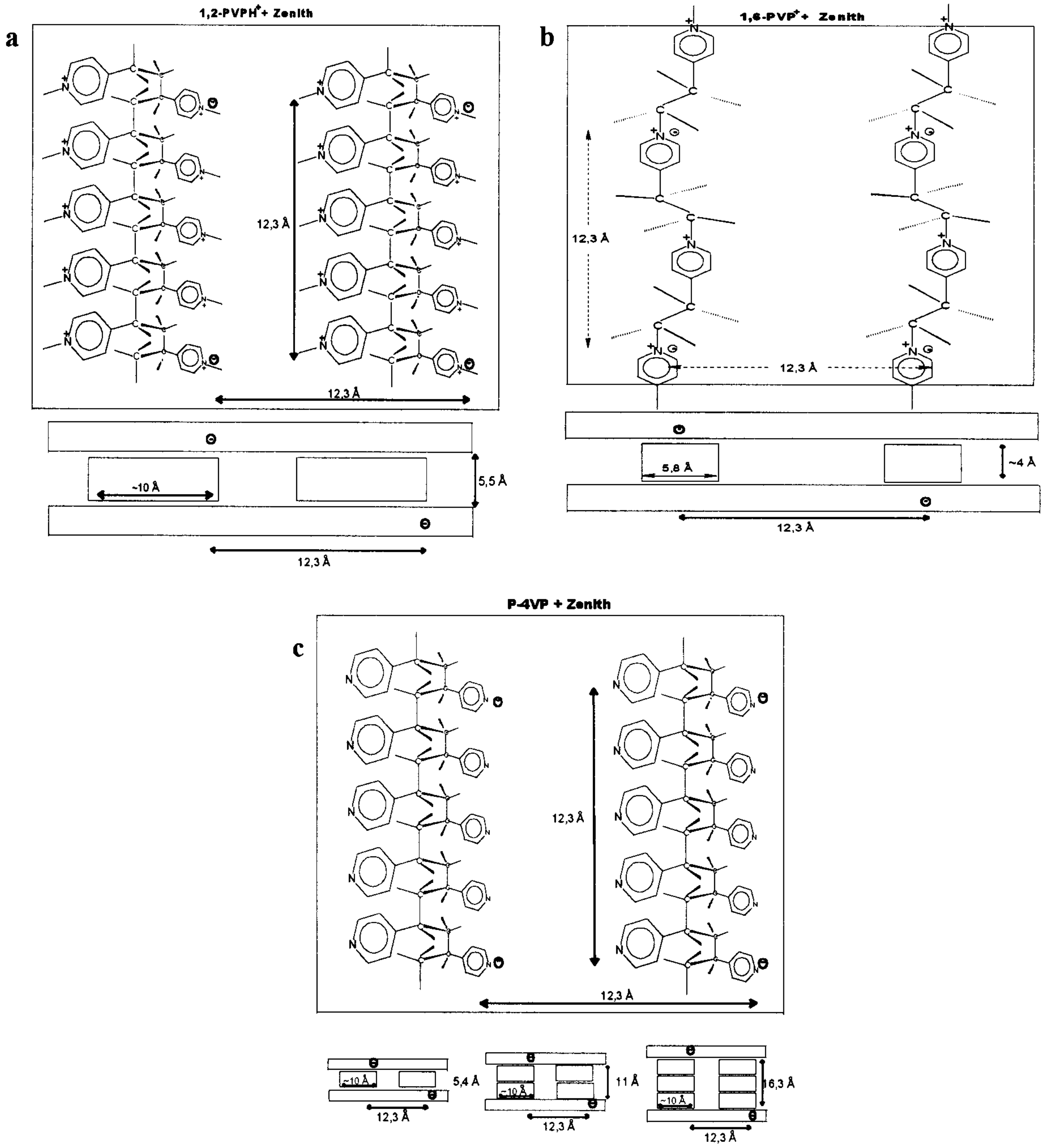

Figure 13. Schematic representation of the placement of (a) 1,2-polyelectrolyte, (b) 1,6-polyelectrolyte, and (c) poly-4-vinylpyridine into montmorillonite.

the adsorption curve at higher bulk polymer concentrations indicates that more polymer layers can be embedded into the lamellar region.

Turning to the different adsorptions observed for the 1,2- and 1,6-polyelectrolytic derivatives we attribute this result to the different chain width of the two polymers. The narrow size of the 1,6-polyelectrolyte, estimated near 5 Å, allows the intergallery accommodation of one more polymer with their counteranions, while the large width of about 10 Å for the 1,2-form inhibits an analogous adjustment. A view illustrating the probable placement of the various polyvinylpyridine derivatives in the clay layers is shown in Figure 13. The sketch based on XRD measurements, adsorption isotherms, and size of the polymers satisfactorily explains the experimental results.

Electrochemistry. Poly-4-vinylpyridine and its alkylated derivatives have played an important role in the development of modified electrodes.[25] Anson and coworkers have reported the use of protonated P-4-VP or quaternized PVP for the electrostatic binding of anionic redox active solute and discussed the advantages and limitations of these polyelectrolytic coatings.[26] The use of clay−polyvinylpyridine nanocmposites in the modification of electrode surfaces is expected to combine the advantages of both the organic and inorganic partners. We discuss briefly the voltammetric response of electrodes modified with a film from clay−polyvinylpyridine hybrids (Figure 14) with the aim to demonstrate certain basic properties of the nanocomposites.

Electrode Modification with a Clay−1,2-PVPH$^+$ Hybrid. The uptake of anionic electroactive solutes from solution will depend on the extent of protonation

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[25] Oyama, N.; Anson, F. C. *J. Electrochem. Soc.* **1980**, *127*, 247.
[26] Oyama, N.; Anson, F. C. *J. Electrochem. Soc.* **1980**, *127*, 640.

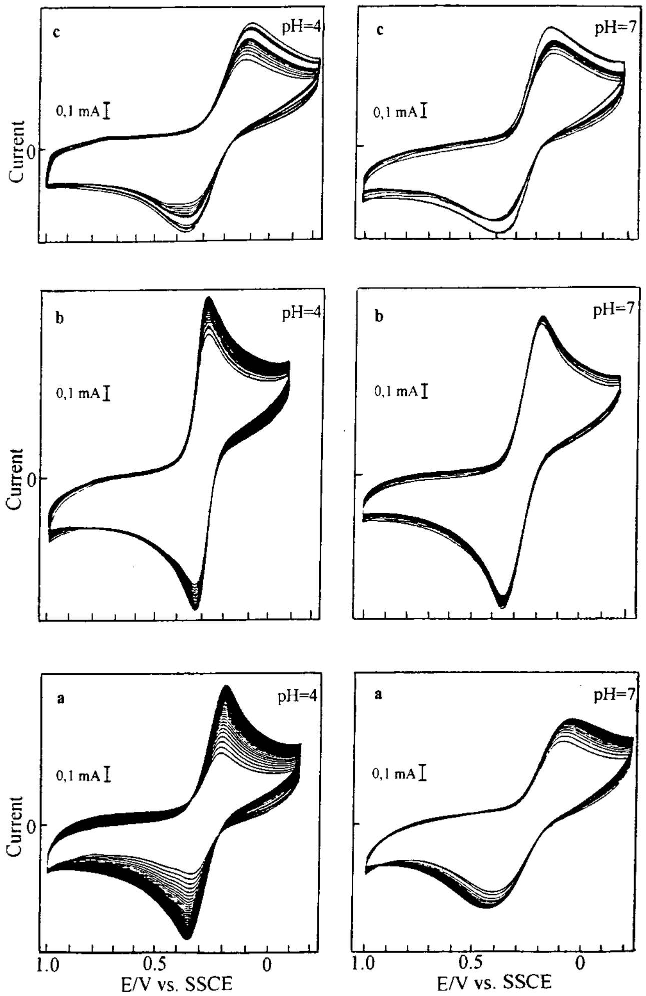

Figure 14. Cyclic voltammograms (u = 100 mV s^{-1}) for Fe(CN)$^{3-/4-}$ recorded at pyrolytic graphite electrodes coated with (a) clay−1,2-PVPH$^+$Br$^-$, (b) clay−1,6-PVP$^+$Br$^-$, and (c) clay−4-vinylpyridine monomer. Experiments were conducted at pH 4 (left) (0.1 M acetate buffer) and pH 7 (right) (0.1 M Na_2SO_4).

of the “free” pyridyl groups in the polymeric backbone and therefore upon the pH of the medium. The voltametric results presented in Figure 14a show clearly that the intensities of the oxidation or reduction currents from the $[Fe(CN)_6]^{3-/4-}$ couple depend on the pH of the solution and therefore upon the degree of protonation of the coating. It is important to note that a voltammetric wave of sufficient intensity persists even at pH 7 of the medium, meaning that an adequate number of pyridyl groups in the clay galleries are protonated as a result of the increased acidity of the clay layers. The reduction wave at pH 7 amounts to about 50% of the wave at pH 4. By contrast, a bare graphite electrode exhibits a wave at pH 7 about 1% of the wave at pH 4 (data are not shown).

Electrode Modification with a Clay−1,6-PVP$^+$ClO$_4$ Hybrid and Interlayer Polymerization. Experiments conducted at pH 4 and 7 for the $[Fe(CN)_6]^{3-/4-}$ couple (Figure 14b) show pH independent heights of the waves, as expected for a quaternized form of the polyvinylpyridine. Finally, the electrochemical results offer clear evidence that intergallery polymerization leads to the formation of the 1,6-polyelectrolyte. Figure 14c shows the response for the $[Fe(CN)_6]^{3-/4-}$ couple at pH 4. For this experiment a clay-modified electrode was immersed for 2 days into a 1 mM solution of 4-VPH$^+$Br$^-$ for interlayer polymerization. The corresponding response from a similar experiment conducted at pH 7 is shown in Figure 14c. Again from the pH independence of the two waves we conclude that the polymerization at either pH leads to the quaternized form of the polymer.

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