Intercalative Redox Polymerization and Characterization of Poly(4-vinylpyridine)–Vermiculite Nanocomposite

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ABSTRACT: A new nanocomposite material consisting of poly(4-vinylpyridine) (PVP) and vermiculite is synthesized by the intercalative redox polymerization of VP in the gallery of copper(II) ion-exchanged vermiculite. The formation of a single filament of the polymer in the gallery is confirmed by the increase in gallery spacing of 4.7 Å as indicated by X-ray diffraction (XRD) analysis. Electron spin resonance studies confirm the presence of Cu(II) upon ion exchange and its absence following redox polymerization. The amount of polymer present in the gallery is found to be ~18–19 mass % by thermogravimetric analysis. Confining the polymer to the gallery spacing in vermiculite results in enhanced thermal stability that is evident from the increase in the initial decomposition temperature by ~300°C. Differential scanning calorimetry of the nanocomposite indicates that the polymer is confined to a restricted geometry because of the absence of a glass-transition temperature, which confirms the XRD finding. The IR absorption peaks corresponding to PVP and the expected PVP UV $\pi-\pi^*$ transition at 275 nm, along with the XRD and thermal data confirms that the gallery expansion is due to the PVP filament. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 555–561, 2001

Key words: intercalation; redox polymerization; nanocomposite; vermiculite; copper(II) ion exchange; 4-vinylpyridine

INTRODUCTION

Nanoporous chemistry is an emerging subdiscipline of chemical and material sciences that deals with the development of methods for synthesizing nanoscopic materials within pores or layers of various micro- and mesoporous materials. The field also investigates the fundamental difference between such materials and the macroscopic sample of the same material.[1] These nanoporous materials take the shape of the pores in which they are synthesized. Thus, conducting polymers such as polyaniline, polypyrrole, polythiophene, and other nonconducting polymers such as poly(acrylonitrile), polystyrene, and poly(methyl methacrylate) are incorporated in host mediums such as zeolites, MCM-41, montmorillonite, ferric oxychlorides, zirconium dioxides, vanadium pentoxide, silica, clays, polycarbonates, and mica-type silicates. Traditional synthetic schemes involve intercalation of the polymer via the polymerization of the intercalated monomer. The other method used for the intercalation is melt–polymer intercalation using organically modified mica-type silicates. Redox polymerization is also reported. Depending on the degree of intercalation of the polymer into the matrix, the hybrids range from exfoliated to intercalated. The polymer penetration results in finite expansion of the silicate matrix by a few angstroms, resulting in

polymer–silicate alternate layers. Extensive polymerization produces exfoliated hybrids consisting of silicates suspended in a polymer matrix. If the silicate and the polymer are immiscible, then macrocomposites are formed instead of nanocomposites. There are several review articles that deal with the detailed developments in this area of research.[1–4]

A literature survey indicated that polymer intercalation in the gallery of vermiculite is of recent origin. The direct intercalation of lightly brominated isobutylene bromomethylstyrene copolymer into a single crystal of organically modified vermiculite was reported in 1999.[5] We also recently reported on the intercalative redox polymerization of poly(N-vinyl-2-pyrrolidone) in the gallery spacing of vermiculite.[6] There are definite advantages in using vermiculite as the host material and these are outlined in the next few paragraphs.

Vermiculite is used in the construction, horticultural, agricultural, and industrial markets. It is often used with binders such as Portland cement, polymeric resins, high alumina cement, sodium silicate gypsum, clay, fertilizers, peat, and bark. The cation exchange properties enable it to hold onto ammonium, potassium, calcium, and magnesium cations and release them when required. Particularly the surface of vermiculite is known to adsorb specific metal ions such as Cu^{2+} and Zn^{2+}. Poly(vinylpyridine)s (PVPs) are useful polymers and in the crosslinked form they have many demonstrated applications including metal recovery; promotion of base catalyzed reactions; as acid scavengers; and form coordination complexes with Cu^{2+}, Co^{2+}, and Pd^{2+}. Thus, a nanocomposite of vermiculite and PVP offers the advantage of both constituents. For example, modified vermiculite can be used in place of vermiculite as a soil substitute for plant growth and transplantation, because minor quantities of metal ion nutrients can be bound to the PVP phase of the nanocomposite and delivered selectively. A composite of vermiculite and PVP in contrast to the nanocomposite does not enable direct access to the vermiculite phase. In addition, the polymer phase is trapped in the gallery in the nanocomposite and offers better mechanical stability following a reaction with a hazardous waste such as radioactive iodine and phenol.

In view of the known advantages offered by vermiculite and PVPs and the scope for broader applications of a nanocomposite of vermiculite and PVP, the synthesis of a vermiculite–polymer hybrid material was undertaken. The objective of the work presented in this article was to intercalate PVP in the gallery spacing of vermiculite and characterize it. The motivation for this study was the scope of the use of the nanocomposite in a wide variety of applications including the removal of hazardous substances such as radioactive iodine and phenols at affordable costs when compared to carbon black.

EXPERIMENTAL

Materials

Calcined vermiculite was a generous gift from Femnor Minerals (Chennai, India) and was heat treated at 100°C for 24 h before use. The VP (4-vinylpyridine, Acros Organics, Belgium) was vacuum distilled over calcium hydride before use. p-Xylene (S. D. Fine Chemicals, Chennai) was dried over anhydrous calcium chloride, distilled, and stored over 4-Å molecular sieves. Copper(II) chloride (S. D. Fine Chemicals) was used without further purification. All other solvents were purchased from Vindhya Chemicals (Chennai) and were used after purification following standard procedures.

Methods

Powder X-ray diffraction (XRD) results were recorded on a Shimadzu XD-D1 diffractometer using Cu Kα radiation over a 2θ range of 5–60. Thermal analyses [thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)] were performed using DuPont's 2950 Thermal Analysis System between ambient and 700°C at a heating rate of 10°C/min under a nitrogen atmosphere. Electron spin resonance (ESR) measurements were performed using a Varian E-112 X/Q band spectrometer operating at 9 GHz with a 100-kHz modulation and phase sensitive detection. All the experiments were performed at the X-band frequency. IR spectra were recorded using a Shimadzu IR-470 spectrometer (KBr pellet). UV measurements were performed using a Shimadzu UV-240 spectrophotometer. In this analysis the nanocomposite containing PVP was treated with concentrated sulfuric acid to destroy the silicate matrix and then the excess acid was neutralized using aqueous sodium hydroxide. Benzene was added to this mixture to extract the polymer into the organic layer. The organic layer was then separated, dried, and placed in a UV cuvette for spectral measurement.

A Mate ARL 3410 inductively coupled plasma (ICP) analyzer with a minitorch was used for the Cu^{2+} analysis.

Redox Polymerization of VP with Copper(II)–Vermiculite

The Cu(II)–vermiculite was prepared and characterized as reported previously.[6] The redox polymerization was carried in xylene medium. Two milliliters of VP were added to 0.1 g of Cu(II)–vermiculite, and the mixture was heated at 60°C for 24 h with continuous stirring. After this the reaction mixture was allowed to cool and the residue was filtered, followed by numerous methanol rinses to remove any physically attached PVP. The residue was finally rinsed with acetone and dried at 75°C for a few hours.

RESULTS AND DISCUSSION

The basis for the work reported in this study is an earlier research article illustrating that cupric acetate brings about the redox polymerization of VP in solution.[7] This implied that if we replaced the exchangeable Mg^{2+} cations present in the gallery of vermiculite with Cu(II), we could bring about the intercalative redox polymerization of VP. Toward this end, the divalent cations in the gallery were replaced by Cu(II) and characterized by ICP, ESR, and TGA analysis.[6]

Following the introduction of Cu(II) into the gallery of vermiculite, redox polymerization was carried out as reported in the Experimental section. XRD analysis was performed to confirm the formation of the nanocomposite. The XRD pattern of the nanocomposite is compared with that of vermiculite and Cu(II)–vermiculite in Figure 1. Following intercalation a new peak corresponding to a d spacing value of 14.7 Å ($2\theta = 6.02$) was seen while the peak corresponding to a d spacing value of 10.0 Å ($2\theta = 8.82$) in the calcined vermiculite (due to d [002]) disappeared almost completely. The observed expanded dimension along the stacking direction ($\Delta d = 4.7$ Å) suggested the presence of a polymer monolayer between the layers of the vermiculite (nanocomposite) with the polymer main chain oriented parallel to the silicate layers. We attributed this to the fact that smectites (montmorillonite, vermiculite, and hectorite) have lower charge density compared to the fluorohectorites and, when the monolayer of the PVP is placed parallel to the layers, the interac-
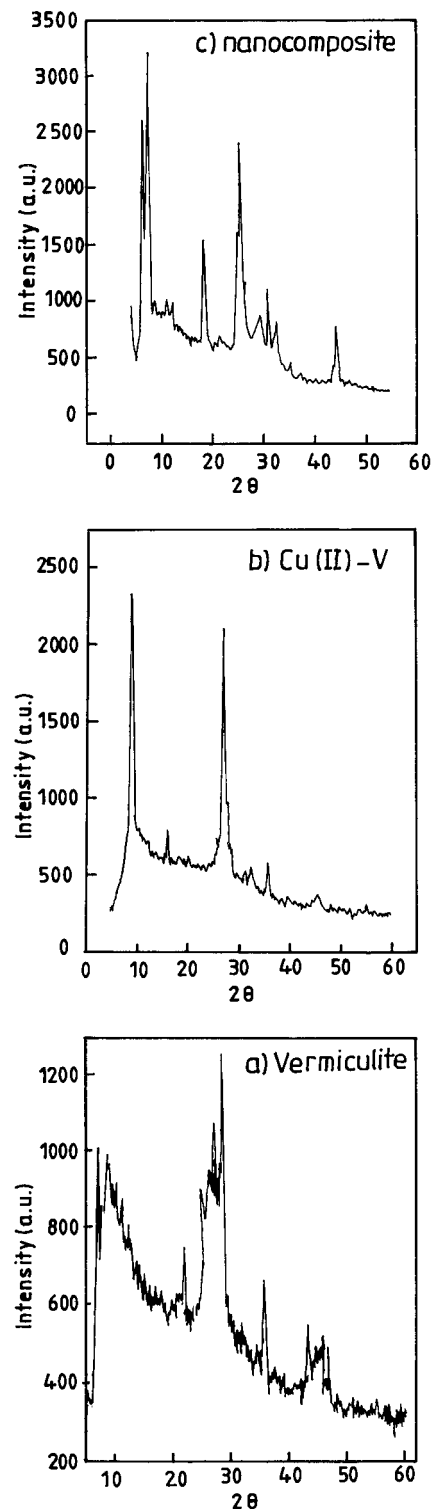

Figure 1 The XRD patterns of (a) calcined vermiculite, (b) Cu(II)–vermiculite, and (c) the nanocomposite.

tion between the layers and the π electrons of the aromatic ring is maximized.[8]

The TGA of the nanocomposite [Fig. 2(c)] was carried out to establish the presence of the inter-
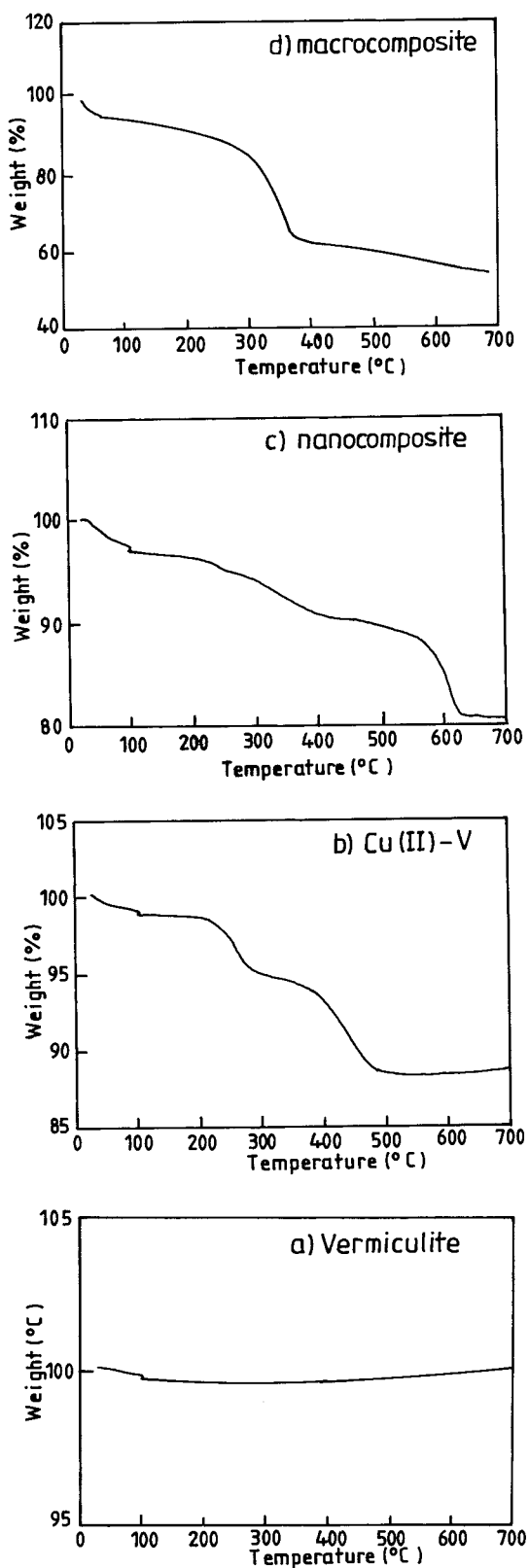
Figure 2 The TGA results of (a) calcined vermiculite, (b) Cu (II)-vermiculite, (c) the nanocomposite, and (d) the macrocomposite prepared by atom transfer radical polymerization.
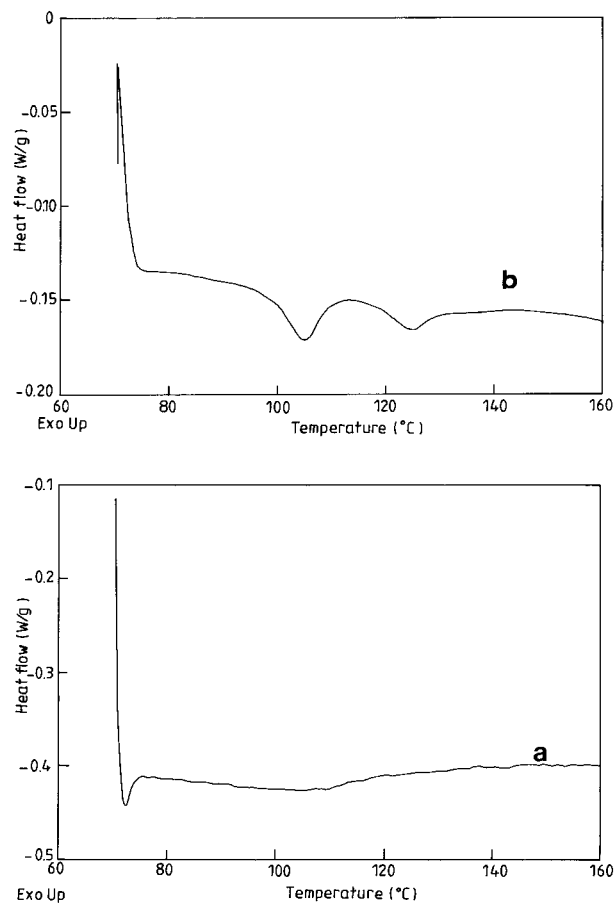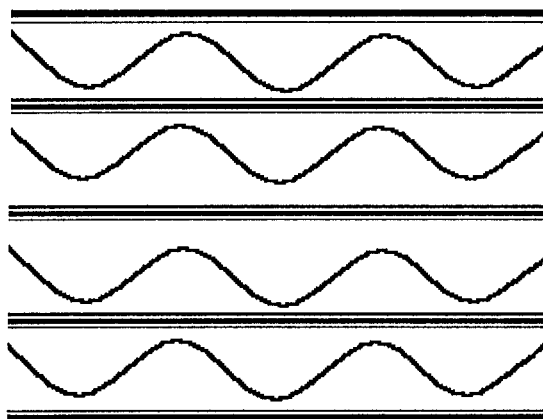

Figure 3 The DSC results of (a) the nanocomposite and (b) a copolymer of styrene and 4-vinylpyridine.

calated polymer, quantitate the amount of polymer present in the gallery, and study any change in the thermal degradation behavior upon intercalation. The nanocomposite showed increased

Scheme 1 A pictorial representation of a polymer molecule confined to the restricted geometry of the intergallery spacing in vermiculite.
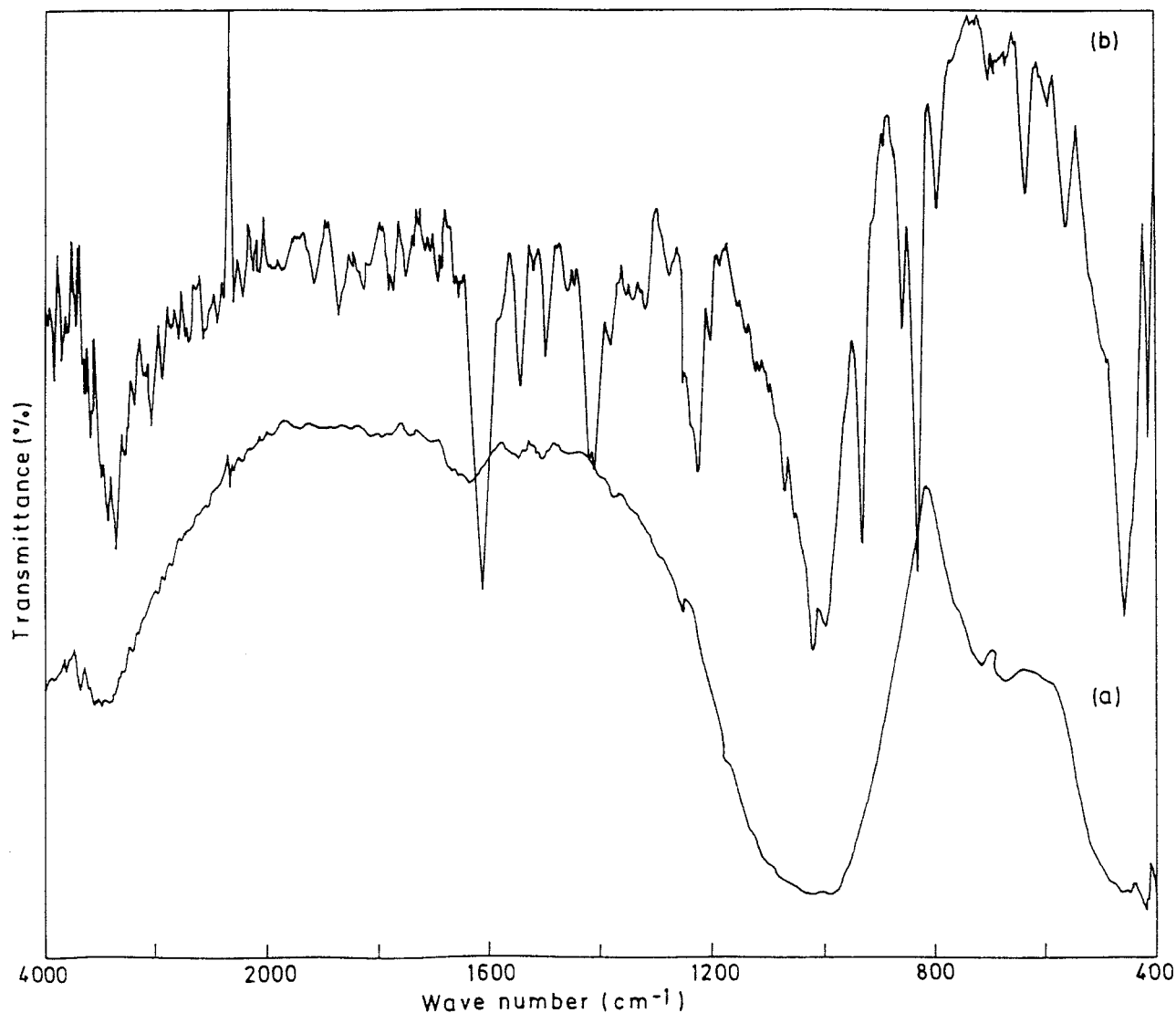
Figure 4   IR spectra of vermiculite (trace a) and the nanocomposite (trace b).

thermal stability that was evident from the increase in the initial decomposition temperature from 350 to 600°C. The macrocomposite of PVP and vermiculite prepared by the atom transfer radical polymerization of VP in the presence of vermiculite did not show any change in the thermal stability when compared to the homopolymer [Fig. 2(d)]. This result was surprising, particularly in the context of the behavior of the macrocomposite. We were not sure of the cause of this behavior but believed that the vermiculite matrix must have acted to "kill" the free radicals formed as a result of thermal activation at a higher rate compared to thermal breakdown, thus enhancing the stability. The fact that there was a small but finite mass loss in the anticipated region between 300 and 400°C in the case of the nanocomposite

indicated that the above reasoning was not entirely unjustifiable. It must be mentioned at this point that we reported earlier that partially intercalated poly(N-vinyl-2-pyrrolidone) undergoes much slower degradation compared to the nonintercalated polymer.[6] The TGA analysis further indicated the amount of PVP intercalated to be about 18 to 19 mass % of the total mass of the nanocomposite taken.

The DSC analysis of the nanocomposite is shown in Figure 3(a) and this suggests some interesting behavior. The endothermic glass transition observed between 125 and 130°C for the homopolymer and the macrocomposite was not observed in this case. This was not particularly surprising because the intercalated polymer was geometrically constrained from indulging in any

long-range motion as shown in Scheme 1. Because long-range motion of segments is one of the principal criterions of the glass transition, the polymer molecule present in the gallery space did not exhibit a glass transition. This was probably the first experimental evidence confirming one of the theoretically expected behaviors of geometrically confined polymers (such as an individual polymer chain restricted to gallery spacing in an inorganic matrix or an adsorbed homopolymer). A DSC scan run under an identical set of conditions for a copolymer of styrene and VP prepared by atom transfer radical polymerization in our lab is given in Figure 3(b) as a reference. This clearly shows the glass transition due to the styrene block at around 105°C and that due to the VP block at around 125°C.

The IR spectra of vermiculite and the nanocomposite are presented in Figure 4. The principal peaks observed for vermiculite were 3700 (Si—OH) and 1014 cm^{-1} (broad Si—O). In the nanocomposite peaks characteristic of PVP such as 3040 (aromatic C—H), 2923 (aliphatic C—H), 1607 (aromatic C=C), 1500 (aromatic C=N), and 750 and 700 cm^{-1} (out of plane deformation of C—H) were observed in addition to the peaks corresponding to vermiculite. The UV spectrum of the intercalated polymer was recorded using benzene as the solvent and this is shown in Figure 5. The $\pi-\pi^*$ transition observed at 274 nm as expected for PVP gave additional confirmation for the intercalative polymerization of VP. (The absorption maximum for the VP monomer was found to be 256 nm.)

CONCLUSION

Exchangeable divalent cations (particularly magnesium) present in the gallery of vermiculite are successfully ion exchanged with Cu(II) ions. The Cu(II) present in the gallery is used to polymerize VP. Essentially complete intercalation is achieved as confirmed by XRD studies. The TGA of the nanocomposite suggests remarkably improved thermal stability upon intercalation. The DSC of the nanocomposite suggests that the polymer chain is confined to the gallery as evident from the lack of exhibition of a glass transition. This study leads us to another important conclusion that although solid-state chemists can infer gallery expansion by the XRD pattern, polymer chemists can infer the same result from the absence of the glass transition in intercalated polymers if the intercalation is essen-
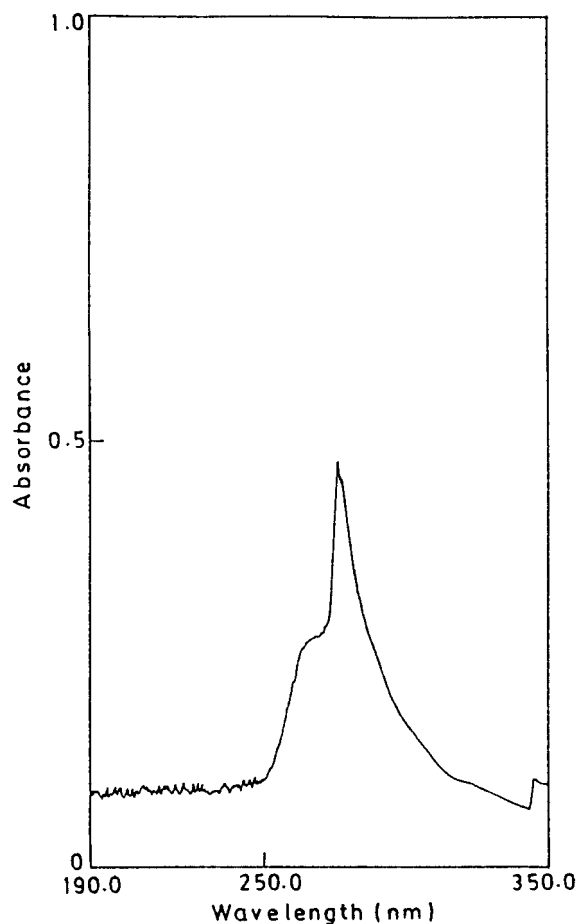

Figure 5 The UV spectrum of poly(4-vinylpyridine) prepared by intercalative redox polymerization.

tially complete (i.e., if significant mass of the polymer is intercalated).

The utility of the new material that was synthesized is promising. For example, the removal of color from dye wastewater using vermiculite was reported.[9] Thus, it was shown that vermiculite is an excellent adsorbent for basic blue dye wastewater, requiring moderately short contact times. It is well known that phenols form a molecular complex with pyridine, as well as with PVPs. This is also the case with molecular iodine. Thus, common impurities from the industrial wastestream such as iodine, weak acids, and phenol can be removed using the new material. It can also be used as a reusable mild acid scavenger, which can be easily removed from the reaction medium by filtration. For example, the present material could function as a catalyst in the formation of cyclohexanone ketal from a mixture of cyclohexanone and ethylene glycol. The cost of vermiculite is ~10% of activated carbon and it is possible to regenerate it by simple heating, so it

offers an attractive alternative for waste removal and recovery.

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