Synthesis and characterization of PAn/clay nanocomposite with extended chain conformation of polyaniline

Q. Wu, Z. Xue, Z. Qi[*], F. Wang

State Key Laboratory of Engineering Plastics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

Abstract

The synthesis and characterization of high conductive polyaniline/clay hybrid nanocomposite with extended chain conformation are presented in this paper. The conductive emeraldine salt form of polyaniline is inserted into the layers of montmorillonite clay to produce the hybrid with high conductivity. The properties of the hybrid are characterized by X-ray diffraction, FT-IR, conductivity measurement, qualitative and quantitative analysis of electron absorption spectra; the results show that what we obtain is really a nanocomposite and over 90% of the polyaniline chain is inserted between the layers. Owing to the confined environment in the nanometer size layers of the nanocomposite polyaniline is a single chain with extended-chain conformation. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyaniline; Extended chain; Intercalation polymerization

1. Introduction

Intercalation polymerization is a promising strategy to study the confining polymer chains in the nanometer size inorganic galleries. As conjugated polymers usually have high electric conductivity with many of potential applications, the insertion of conjugated polymers in the layered (two-dimensional) or microporous (three-dimensional) inorganic hosts has received extensive attention over the past few years and many conjugated polymer/inorganic host hybrid composites have been synthesized and studied, such as polyaniline/MoO_3 [1], polyaniline/HUO_2PO_4 [2], polyaniline/V_2O_5 [3], polypyrrol/mordenites, polythiophene/mordenites [4]. In intercalation polymerization the inorganic host serves as a template within which a guest molecule of nanometer dimension is assembled. The constrained environment is expected to lead to a high degree of polymer ordering and to useful properties [5] such as high anisotropy of electric conductivity even more than 10^3 and the increasing capacity and reversibility when PAn/MoO_3 nanocomposite serves as the cathode of lithium rechargeable battery [1]. But because of the complex of the heterogeneous systems, some key problems still remain ambiguous and the problems related with the structure and properties of the nanocomposite still need to be resolved.

In this paper we select montmorillonite (MMT) as the

host because of its important advantages: (a) MMT is a natural mineral and its layer structure consists of two silica tetrahedral sheets, stacking of the layers of ca. 1 nm thickness by weak dipolar force leads to interlayers or galleries between the layers [6]. The galleries normally occupied by hydrated cations that balance the charge deficiency is generated by the isomorphous substitution in the tetrahedral sheets. The monomer (aniline) can be introduced into the galleries easily by ion exchange and are hardly separated from the galleries any more [7]; (b) it is an inactive inorganic host without redox character, so the polymerization can be controlled; (c) it is a well-ordered host in two dimensions, after the intercalation of monomer, extrinsic initiator can enter and initiate the polymerization in the interlayers, and this is important to probe the polymerization mechanism by various experiment tools. While in the three-dimensional ordered host a similar method is unrealistic due to the blocking traffic channel. These favorable characters can assist us to avoid interference, which often occurs in other intercalate systems.

On the contrary, intercalation polymerization also can afford a promising strategy to study the chain structure of PAn and polymerization mechanism. As we know our understanding of the PAn structure is still fragmentary due to the amorphous or poor crystalline nature and insolubility in common organic solvents, important structural problems associated with single chain and macromolecule aggregation remain to be solved. But when PAn is inserted into the inorganic galleries the strong intermolecular interaction of

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* Corresponding author. Tel.: +86-10-62648834; fax: +86-10-62569564.
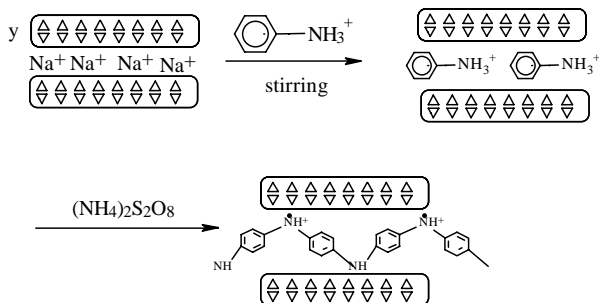*E-mail address:* qizn@infoc3.icas.ac.cn (Z. Qi)

Fig. 1. Schematic structure of the synthesis of PAn/MMT nanocomposite.

polyaniline chains was eliminated by the host barriers and polyaniline single chain can be obtained, while it is impossible in normal chemical polymerization of aniline. In addition the polymerization rate is much slow in the confined environment. Aniline polymerization is a somewhat complicated process and it is a typical precipitation polymerization with a high reaction rate. These features make it difficult to catch and characterize the reaction intermediates and monitor the reaction rate. While in intercalation polymerization the slow kinetic diffusion retards the reaction rate, it possibly affords a novel method to study the polymerization mechanism of the induction period, the formation of dimer, and the propagation of polymer chains.

2. Experimental section

2.1. Reagents

Sodium monmorillonite (Na-MMT) was purchased from Zhangjiakou Clay Mineral Corporation, specific surface is $700 \ m^2/g$ and the cation exchange capacity (CEC) is 80 meq/100 g, prior to use it is washed by saturated NaCl solution many times. HCl, NaCl, $(NH_4)_2S_2O_8$ were of analar grade and used without further purification. Aniline was distilled under vacuum prior to use.
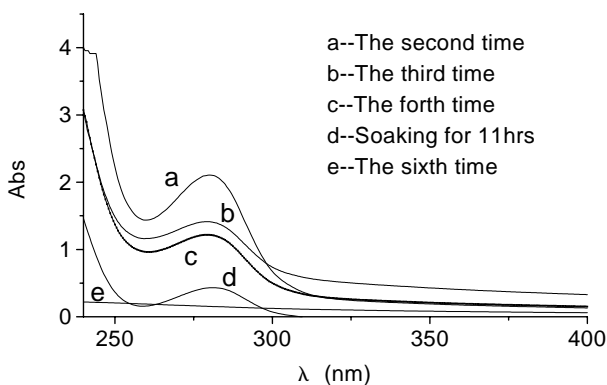

Fig. 2. UV absorption of the samples washed out of An/MMT.

2.2. Synthesis

Five grams of Na-MMT was added into 250 ml deionized water and stirred for 2 h at 80°C, then 1 ml of aniline and 0.02 mol of HCl were added. After stirring for 6 h at 80°C the mixture was washed with a large amount of de-ionized water several times. Cooling down to room temperature and regulating the pH value at 2 with HCl, 0.8 g (0.0035 mol) ammonium persulfate $((NH_4)_2S_2O_8)$ was added and the polymerization lasted for more than 10 h. The dark green precipitate was isolated by filtration, washed with deionized water thoroughly and dried under vacuum.

2.3. Instruments

X-ray diffraction (XRD) patterns were obtained on a Rigaku D/MAX/2400 X-ray diffractometer; FT-IR spectra were recorded on a Perkin–Elmer 2000 spectrometer using KBr pellets. UV–Vis spectra were recorded on a Shimadzu UV/1601PC spectrometer and UV–VIS-NIR spectra were recorded on a Shimadzu UV3100 spectrophotometer. Room temperature conductivity measurements were performed using a four-probe method.

3. Results and discussion

3.1. Structure characterization of PAn/clay hybrid nanocomposite

As shown in Fig. 1 in the first step of the reaction, excess aniline is used to exchange Na^+ completely. After washing with a large amount of de-ionized water only the monomer that has been introduced into the galleries remains in the reaction system. The final wash is tested by UV–Vis spectra and found to be free of residual monomer, indicating that the monomer extricated has been removed completely (Fig. 2, curve c). Collecting all residual liquid from its absorbance at 280 nm (assigned to the $n-\pi^*$ transition of neutralized anilinum) we can calculate the saturation insertion amount to be 6.8 wt.% of MMT according to the UV–Vis absorption working curve of aniline. The calculated insertion amount by cation exchange capacity (CEC) was a little higher than the experimental result. The difference is possibly due to the slow kinetics of diffusion for An^+ and the experimental odds caused by these two measurement methods. It is believed that after An^+ is inserted into the galleries, a coordinate bond is formed between the monomer and inorganic material, so An^+ is hardly exchanged by other cations in theory [7]. To determine if all the An^+ cannot escape from the interlayer, we put the washed An/MMT into de-ionized water, and regulated the pH value to 2 with HCl, and kept stirring for 18 h (except for the initiator, the conditions were the same as with the polymeization), and then detected the aniline content of the centrifugal residual liquid by UV–Vis spectrometer (Fig. 2, curve d). We have found that a small amount of monomer (8% of the total) escapes from the
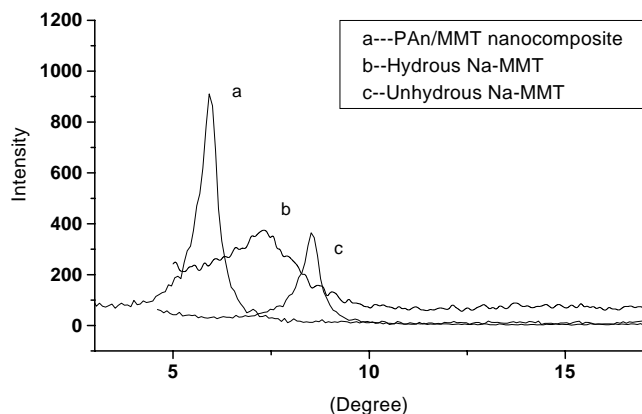
Fig. 3. XRD patterns: (a) PAn/MMT $d_{001} = 14.82$ Å; (b) hydrous Na-MMT $d_{001} = 12.00$ Å; (c) Na-MMT $d_{001} = 9.6$ Å.

Fig. 5. FT-IR spectra: PAn/MMT nanocomposite blends of PAn and NaMont (the content of PAn is 7.2 wt%).

galleries, becoming free monomer. Thus in the PAn/MMT hybrid the content of PAn is 7.2%, and by a conservative prediction 90% polymer is inserted into the MMT galleries.

XRD pattern (Fig. 3) of PAn/MMT nanocomposite powder shows the interlayer distance is 14.82 Å and a difference of 5.22 Å from the corresponding 9.6 Å for anhydrous silicate framework. The expansion of interlayer distance is very close to that reported for polyaniline in V_2O_5 (5.23 Å) [3], and less than polyaniline in FeOCl (5.94 Å) [8]. The expansion is in agreement with the intercalation of single chains with extended chain conformation rather than coiled conformation of polyaniline in the galleries of the host. From these, the structure of PAn/clay hybrid is proposed as shown in Fig. 1.

3.2. Polyaniline chain conformation in PAn/clay hybrid nanocomposite

From the XRD results we can presume that in the PAn/clay hybrid nanocomposite the polyaniline is an extended chain conformation and we obtain the direct proof from UV–Vis-NIR and FT-IR spectra.
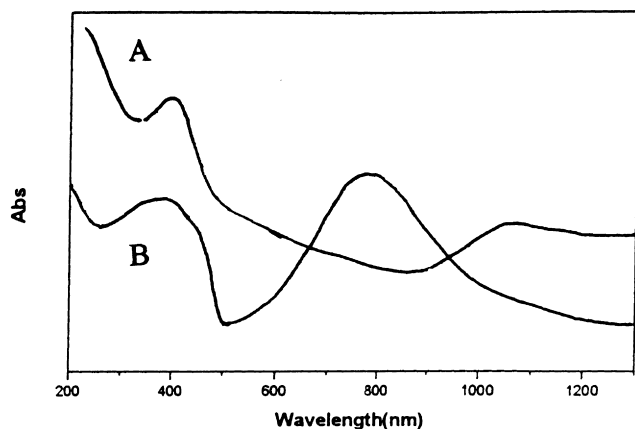

Fig. 4. UV–Vis–NIR spectra of: A, PAn/MMT nanocomposite; B, bulk PAn.
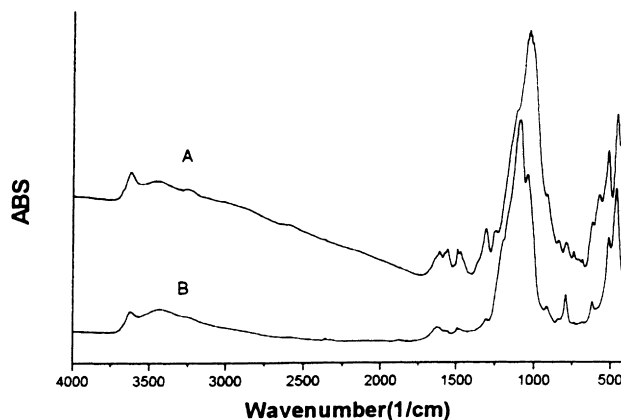
The UV–Vis–NIR spectra show the obvious difference between PAn/clay hybrid nanocomposite and bulk PAn (Fig. 4). In bulk PAn a strong absorption peak usually emerges in 700–800 nm (n–π). But in the PAn/clay hybrid nanocomposite this peak disappears, displaced by a broad absorption band (called "free-carrier tail" by other authors [9]) in the near infrared region. It is consistent with the delocalization of electrons in the polaron band promoted by an extended conformation of the polymer chains. In bulk PAn the strong interaction of chains make π-conjugation defects, and always lead to "compact coil" conformation. While in the MMT galleries, the nanometer template not only eliminates the interaction of different PAn chains, but also limits the contraction of the chains. The interaction between the adjacent isolated polarons, therefore, becomes stronger, and the polaron band becomes more dispersed in energy. As a result the absorption peak disappears and the "free-carrier tail" appears. A similar tail can usually be found in large-size organic acid doped PAn, i.e. dodecyl-benzene-sulfonic acid(DBSA), D,L-camphor sulfonic acid (CSA) as dopant [10], caused by an "expanded coil" conformation and accompanied by a large increase in conductivity. Hence it is believed that in this PAn/clay hybrid nanocomposite the extended chain conformation can give rise to conductivity.

FT-IR spectra (Fig. 5) also confirm the formation of "free-carrier tail" in the intercalated polyaniline. In the FT-IR spectra of PAn/MMT, 917.7 and 840.6 cm^{-1} are the characteristic vibrations of clay, 1489.1, 1562.9 and 1311.5 cm^{-1} are the characteristic vibrations of emerldine salt [11,12]. In comparison with polyaniline and Na-MMT blends (the content of PAn is 7.2 wt.%, same with the nanocomposite), the nanocomposite has an obvious higher absorption in the high frequency region and it is also caused by the perfect delocalization of electrons [1].

3.3. Conductivity of the nanocomposite

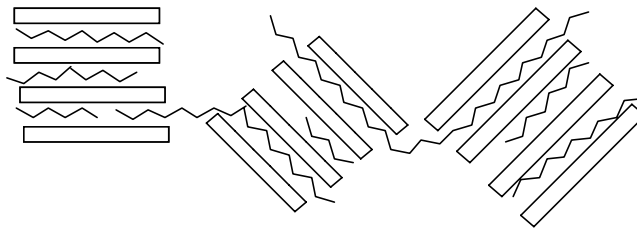The room temperature conductivity of the hybrid

Fig. 6. Schematic model of the PAn/MMT nanocomposite.

nanocomposite is 10^{-3} s/cm. It has a relatively high conductivity in comparison with other PAn/inorganic host hybrids. The conductivity is controlled by two contradictory reasons and the model is shown in Fig. 6. On one hand, the content of polymer is very low and the confinement of conducting polymers in the interlayer space disrupts the three-dimensional organization of the polymer chains. On the other hand, the extended PAn chains with high conjugation and small amount polymer bridges can enhance the conductivity of the hybrid nanocomposite. The polyaniline bridges are likely to be formed by free monomers that we talked about earlier and the bridges can facilitate the electron transformation between different layers.

4. Conclusion

We have successfully synthesized PAn/clay hybrid nanocomposite with relatively high conductivity by the method of intercalation polymerization. In the hybrid nanocomposite over 90% polyaniline is inserted between the layers and it is a single chain with an extended-chain conformation owing to the confined environment in the nanometer size gallery.

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