Polym. Bull. (2009) 62:573–580
DOI 10.1007/s00289-009-0038-y

ORIGINAL PAPER

Photo-induced polymerization in ionic liquid medium: 1. Preparation of polyaniline nanoparticles

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Received: 18 September 2008 / Revised: 26 December 2008 / Accepted: 9 January 2009 /

Abstract Photo-induced polymerization is employed to prepare polyaniline (PAN) nanoparticles in ionic liquid for the first time. Photons and photoactive ionic liquid cations replace conventional oxidants and metal complexes to promote the polymerization of aniline monomer. The diameter of the resulted PAN is confirmed in nano-scale by SEM. With increase of protonic acid in medium, the yield of the PAN increased, the UV absorption of the PAN strengthened, and a blue shift of the π-polaron absorption was observed. And the conductivity of the PAN also increased with the acid content in medium. The potential mechanism of photo-induced polymerization of aniline is proposed. Moreover, after the ionic liquid is separated from the reaction mixture and reused for five times, no obvious decrease in catalytic activity could be found in photo-induced polymerization of aniline. The method may open a new pathway to prepare nano-scale conducting polymers with sunlight.

Keywords Photo-induced polymerization · Ionic liquid · Polyaniline · Nanoparticle

Introduction

Ionic liquids (ILs) are a class of organic salts that are liquid at or near room temperature [1]. Typical ILs exhibit unusual properties including

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nonflammability, nonvolatility, higher ionic conductivity, wide electrochemical windows, and excellent thermal and chemical stability. ILs are attracting much interest in many fields of chemistry, due to their potential as a recyclable alternative to traditional organic solvents [2]. Although it has been confirmed that ILs have significant absorption in the entire UV region and part of the visible region and also exhibit fluorescence behavior [3–6], photochemical studies in ILs is still limited. In this regard, the studies on reaction kinetics [7–9], photo-induced electron transfer [10], selective fluorescence quenching [11], energy transfer and hydrogen transfer [12] in ILs are noteworthy. These studies determined the effect of viscosity and polarity on the rate constant, suggested the reaction mechanisms, and accumulated the kinetic parameters. However, most investigations using ILs as media for photochemical reaction are limited in theory. The related application is mostly focused on the photodegradation of toxic organic compounds, for example pentachlorophenol [13]. Moreover, there is no report on the photo-induced polymerization of conducting polymer nanoparticles in ionic liquid thus far.

Conducting polyaniline (PAN) is one of the most promising conducting polymers due to its good environmental stability, ease of preparation, high conductivity, and large variety of applications such as in chromatography, light-emitting diodes, electrochromic devices, electrostatic discharge protection, secondary batteries, and corrosion-protecting paint [14–16]. Traditionally, PAN is prepared by chemical or electrochemical oxidation. A few investigations for photo-induced polymerization of aniline have been published. It was reported that photons and metallic ions replaced conventional oxidants to promote polymerization of aniline monomer [17]. Especially, N. Kobayashi et al. [18–21] have performed multiple investigations on the photopolymerization reaction of aniline derivatives with transition metal complexes, and the application of PAN image formation with photochemistry reaction has also been realized. But all of the works in literatures are processed in aqueous or conventional organic solvent system.

More recently, synthesis of conducting polymers has been advocated by using ILs. The methods of interfacial [22] and electrochemical [23] polymerization for PAN in ILs have been reported. Our research group has successfully prepared PAN in a novel IL/water emulsion system [24, 25]. All of the PAN exhibit excellent physical and chemical properties. Another potential advantage of synthesis in ILs is their unique solvent capabilities, which can avoid organic solvent volatilization. In present investigation, PAN was prepared firstly by photo-induced polymerization in ILs without conventional oxidants and metal complexes. The common incandescent lamp was chosen as light source, which exhibits a similar wavelength region to that of sunlight. The morphology, structure and characteristics of the product were analyzed by SEM, FTIR, and UV–vis, and the reuse performance of IL was also investigated. 1-Butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6) was chosen as medium for this study because it is air and water stable, commercially available, and remains popular in applications development.

Experimental

Materials

1-Butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6) was prepared according to the previous procedure [24]. Aniline, acetone, and methanol were purchased from Sinopharm Chemical Reagent Co., Ltd., and were used as received. Double distilled water was used throughout this study.

Polymerization

Photo-induced polymerization experiments were carried out in quartz vessels. The different amount of nitric acid, in molar ratios of 1:1, 2:1, 3:1 and 4:1 with the aniline, were added to the 0.22 mmol L^{-1} solutions of aniline in [bmim]PF_6. The mixtures were illuminated with a common 35 W incandescent lamp for 6 h. The reaction temperature was kept around 25 °C. For collection of the products, the obtained dispersions were diluted with acetone to decrease the viscosity of the mixtures. Afterward, the precipitates were gathered by centrifugation with 3,000 r min^{-1}, and were washed with water and acetone several times until the remaining solution became clear. The final products were dried in a vacuum oven at 40 °C for further characterization. A blank test was processed to estimate the effect of the photo-degradation of aniline. The experimental condition kept the same with that above, but without nitric acid added.

Characterization

The contents of residual aniline monomer were determined by an Aglient-1100 high performance liquid chromatography (HPLC). The morphologies of the synthesized PAN were observed by a JSM-6700F scanning electron microscope (SEM). Fourier transform infrared (FTIR) analysis was performed using a Perkin–Elmer spectrophotometer. Ultraviolet visible (UV–vis) absorption spectra were recorded on a LabTech UV-240 spectrophotometer. The electrical conductivity of the samples were measured by conductivity meter in the 0.1 g L^{-1} solutions of PAN in methanol after ultrasonic dispersion 10 min, and compared with a commercial grade PAN (in the form of emeraldine base, provided by Hunan China Science Ben'an New Materials Co., Ltd.).

Results and discussion

Figure 1 shows the absorption spectrum of pure [bmim]PF_6. The spectral shape and nature are consistent with those reported by Samanta et al. [3–6]. The absorbance is significant even at 350 nm. The other notable part of the spectra is that the absorption tail is fairly long and it extends even beyond 450 nm.

The color of the fresh reaction system was light yellow. Under the radiation, the color of the system changed from light green to dark green, which indicated the

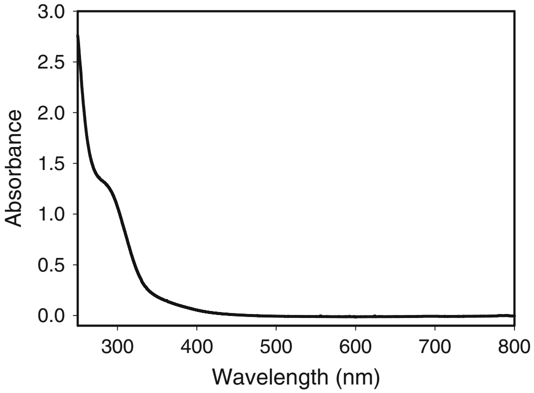


Fig. 1 Absorption spectrum of pure [bmim]PF_6

polymerization of aniline. In order to estimate the conversion rate of the photo-induced polymerization of PAN, the mass of the prepared PAN and the residual aniline monomer were measured and the results are shown in Table 1. At first, it could be found from the blank test (Condition 1) that there are 1% aniline monomers photo-degraded under 6 h radiations. After nitric acid added, namely the Conditions 2–5, the aniline monomers are largely consumed by photo-induced polymerization. Specifically, it could be considered that the aniline monomers are completely consumed under the Conditions 4 and 5. On the other hand, when the molar ratio of nitric acid with aniline is more than 2:1, the prepared PAN could be easily gathered by low speed centrifugation. And the yield of the PAN increases with the content of acid in medium. However, the yield of the PAN increases slowly under the condition with high concentration of nitric acid (Conditions 4, 5). The yields of the PAN are not high. It could be ascribed to the most PAN in form of oligomers, formed by photo-induced polymerization, can not be collected by low speed centrifugation. The resulted yields can be enhanced by improving collection method.

The SEM micrograph of the PAN particles prepared under the Condition 4 is shown in Fig. 2, which clearly shows that the diameter of the PAN nanoparticles is about 50–80 nm. The diameter and morphology of those PAN prepared under the Conditions 3 and 5 have little difference from those of the PAN in Fig. 2.

FTIR spectra of the PAN obtained by photo-induced polymerization under the conditions of different acidic contents are shown in Fig. 3. The peak at 1,384 cm^{-1} is a result of nitrate doped. The C–C vibrations in the benzene rings are observed at 1,494 cm^{-1}. The peaks at 821, 1,143, 1,301 cm^{-1} correspond to out of plane C–H

Table 1 The conversion rate of the photo-induced polymerization of aniline for 6 h

Condition	Nitric acid:aniline	Residual aniline/%	Yield of PAN/%[a]
1	0:1	99.0	–
2	1:1	84.7	–
3	2:1	50.8	7.17
4	3:1	0.487	25.3
5	4:1	0.417	29.3

[a] The yield of PAN equals to the mass of PAN divided by the mass of aniline reagent

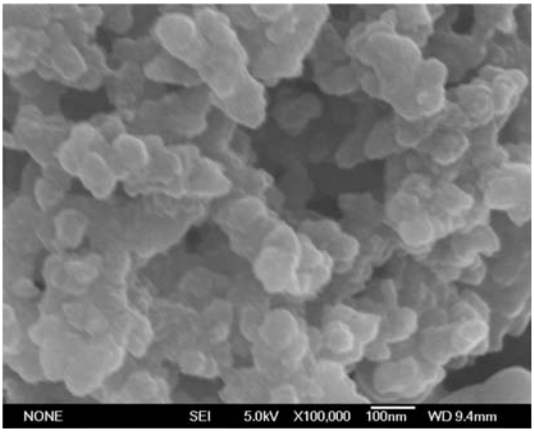


Fig. 2 SEM micrograph of the PAN nanoparticles

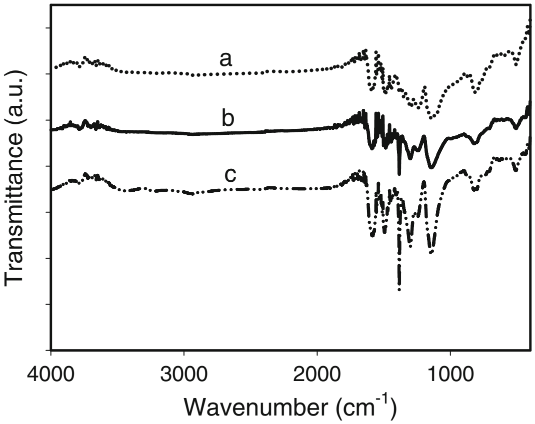


Fig. 3 FTIR spectra of the PAN prepared by photo-induced polymerization under the Condition 3 (**a**), the Condition 4 (**b**), and the Condition 5 (**c**)

vibration at the benzene ring, in plane C–H vibration at the benzene ring, and C–N vibration, respectively. These are in good agreement with previous reports [22]. However, it is noteworthy that the peak of quinine rings is shifted to higher wavenumbers (1,583 cm^{-1}).

Figure 4 shows the UV–vis absorption spectra of the samples prepared by photo-induced polymerization. The characteristic peaks of PAN appear at 325–360, 400–430, and 925–980 nm, which are attributed to π–π*, polaron–π*, and π–polaron transitions [14], respectively. It can be found that the increase of acid content strengthens the UV absorption of PAN and leads to a blue shift of the π–polaron absorption of PAN.

The conductivity of the 0.1 g L^{-1} methanol solutions of three samples prepared under the Conditions 3, 4, and 5 is 15.0, 17.3, and 18.6 μS cm^{-1}, respectively. It is confirmed that the increase of acid content improves the doping level of PAN, and it also can be confirmed from the result of UV–vis absorption spectra. The conductivity of three PAN are excellent, and similar to, even more than that (16.7 μS cm^{-1}) of commercial grade PAN at the same concentration in methanol.

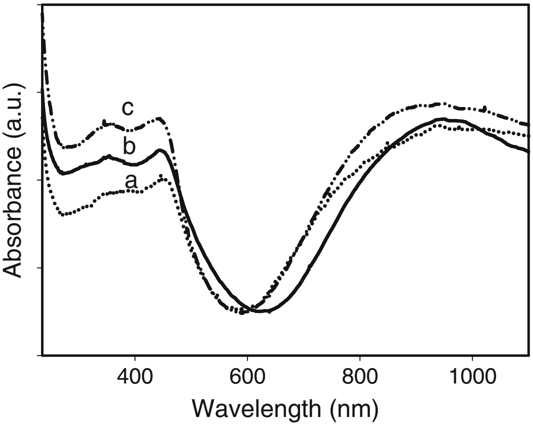
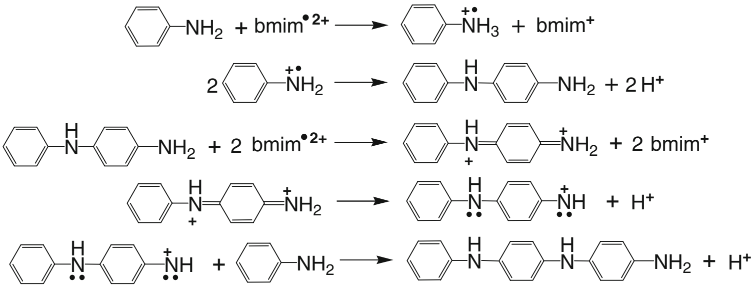


Fig. 4 UV–vis absorption spectra of the samples prepared by photo-induced polymerization under the Condition 3 (**a**), the Condition 4 (**b**), and the Condition 5 (**c**)

On the basis of the mechanism of polymerization of aniline in literatures [26–28] and the fluorescence behaviour [3–6] and photochemical reaction kinetics [8, 9] of ILs, a potential mechanism of photo-induced polymerization of aniline is proposed, as shown in Scheme 1. When photons react with the solution, they promote the $bmim^+$ to the excited state and the $bmim^{\cdot 2+}$ radical cations are produced. Aniline monomers are oxidized by them to the aniline radical cations, which can form the dimers through a head-to-tail coupling. Then, the dimers are sequentially oxidized to quinoid units which could be deprotonated to afford nitrenium ions, and react with an aniline monomer to produce the trimers. This process is repeated, leading to form oligomers, and eventually to the formation of PAN.

The PAN particles could be easily separated by centrifugation after the reaction system was diluted, and the used [bmim]PF_6 could be recycled by distillation in vacuum to remove the solvent. In order to examine the reuse performance of [bmim]PF_6, the medium was reused five times under the Condition 4 without further purification. The yields of the PAN prepared in fresh and reused [bmim]PF_6 are shown in Fig. 5. It can be found that the yields of six times exhibit slight difference, and the catalytic activity of [bmim]PF_6 basically remains unchanged under our experimental condition. But, the yields in reused [bmim]PF_6 is more than that in fresh [bmim]PF_6. The yield of the 6th time is 26.2%, which is 104% of that



Scheme 1 The potential mechanism of photo-induced polymerization of aniline in [bmim]PF_6

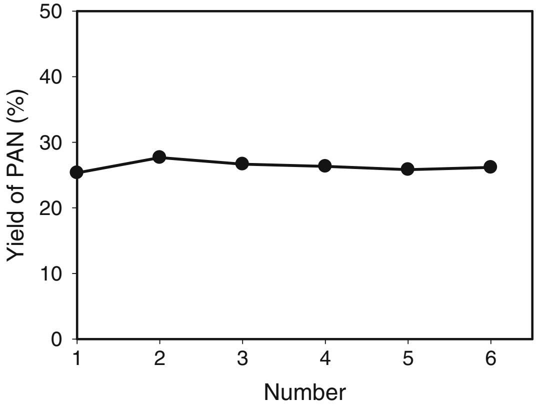


Fig. 5 The effect of the reused [bmim]PF_6 on PAN yields (the first time polymerization was processed in fresh [bmim]PF_6)

of the first time. This is because the remaining oligomers are present in reused [bmim]PF_6 after centrifugation and distillation, and can react with aniline monomer further in the next polymerization. Under the same conditions of the oligomers presented, namely the later five times, there is only a slight decrease (27.7–26.2%) in the yield of PAN.

Conclusions

A novel approach, i.e., photo-induced polymerization, was successfully employed to prepare PAN nanoparticles in ILs for the first time. Polymerization of aniline in [bmim]PF_6 proceeded under illumination without conventional oxidants and metal complexes. In contrast with the polymerization of aniline by the electrochemical and chemical oxidation, the photo-induced polymerization is simple and green, and can be easily generalized to sunlight. The diameter of the resulted PAN was about 50–80 nm. The yield of the PAN was near 30% with simple centrifugation. The structure and doping level of the PAN is affected by the content of protonic acid in medium, and the conductivity of the PAN increases with the acid content. The potential mechanism of photo-induced polymerization of aniline is proposed. Moreover, it is confirmed that [bmim]PF_6 as the medium of photo-induced polymerization can be used repeatedly.

Acknowledgments This project is supported by the Research Project of Changsha Science and Technology (K0802123-11) and the Foundation of State Key Laboratory of Chemo/Biosensing and Chemometrics of Hunan University (200706). Thanks for the help of Professor Zhong Xie (Center of Physics Experiment, Hunan University).

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