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Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP) of MMA from PANI Powders

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Summary

The macro-initiator for atom transfer radical polymerization (ATRP), bromoacetyl modified polyaniline (BrA-PANI) with a bromoacetyl group content of 0.27 m mol/g, was successfully prepared by the bromoacetylation of the amine groups of the undoped PANI with bromoacetylbromide. Then the poly(methyl methacrylate) (PMMA) brushes were grafted from the BrA-PANI surface via a surface-initiated atom transfer radical polymerization (SI-ATRP) of MMA with the catalysts of 1,10-phenanthroline and Cu(I)Br. The percentage of grafting (PG%) was found to increase linearly with the increasing of the polymerizing time and that of 27.18% was achieved after the SI-ATRP in toluene solution at 80°C for 6 h. The product, the shell-core poly(methyl methacrylate)-polyaniline (PMMA-PANI) powders were also characterized by FT-IR, XPS and SEM.

Introduction

Poly(aniline) (PANI) has attracted much attention due to its growing applications such as in rechargeable batteries [1,2], EMI shielding [3,4], and sensors [5,6]. PANI is a particularly attractive material owing to its good stability, easy synthesis, and desirable conductivity. On the other hand, PANI is mechanically weak and its processability is poor. It degrades before melting, is insoluble in common organic solvents, soluble only in concentrated sulfuric acid [7] under specific conditions, and also has only limited solubility in organic solvents like methylpyrrolidinone and tetrahydrofuran [8]. In order to improve on these problems, the composites and copolymers are prepared [9].

The polymer-modified PANI had been achieved by the “grafting to” method in which the polymers with functional end groups were chemically bonded onto PANI [10-12] or by the “grafting from” method in which the monomers were polymerized from the pre-treated PANI surfaces [13,14].

The surface-initiated atom transfer radical polymerization (SI-ATRP) processes had been successfully used for the preparation of well defined structural polymers grafted nanoparticles [15] and films [16] because of its controlled/”living” mechanism [17]. It could also provide much higher grafting efficiency.

In the present work, the poly(methyl methacrylate) (PMMA) brushes were grafted from the BrA-PANI surface via a surface-initiated atom transfer radical polymerization (SI-ATRP) of MMA from the macro-initiator, bromoacetyl polyaniline (BrA-PANI) prepared by the bromoacetylation of the amine groups of the undoped PANI with bromoacetylbromide, with the catalysts of 1,10-phenanthroline and Cu(I)Br.

Experimental

Reagents

MMA (AR) was from Tianjin Chemical Co., China and purified by vacuum distillation before use. Bromoacetylbromide is analytical reagent grade from ACROS ORGANICS. Both 1, 10-phenanthroline and Cu(I)Br are analytical reagent grade and re-crystallization from ethanol before using. Aniline and ammonium peroxodisulfate (APS) were all analytical grade reagents purchased from Tianjin Chemicals Co. Ltd., China. THF and other solvents used are all analytical reagent grade from Tianjin Chemical Co., China and used without further purification. The distilled water was used throughout.

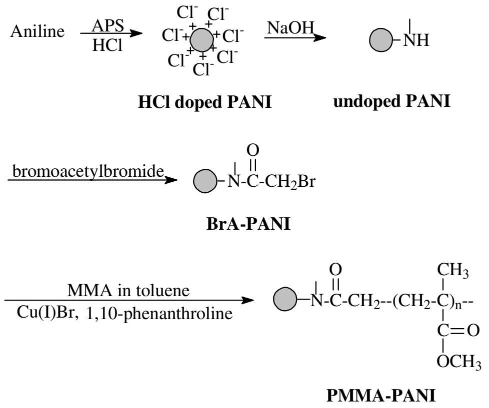
Preparation of the macro-initiator

The PANI powders were prepared by the followed procedure: 50 mL 1.0 mol/L aqueous solutions of APS was drop-added into the 100 mL 1.0 mol/L HCl aqueous solution of aniline (0.50 mol/L) within 30 min under stirring at the room temperature. The mixture was stirred for another 4 h. The product was filtered and washed with water and acetone each for three times with ultrasonic vibrations in turn. Then the PANI powders were extracted with ethanol for 20h to remove the oligoaniline. It was converted to emeraldine (EM) base by treatment with excess 0.5M NaOH for 24 h, followed by washing with deionized water until the filtrate was neutral. The base powder was dried under reduced pressure for 24 h [18].

The amino groups on the surface were then reacted by immersing 4.0 g of the undoped PANI powders in a solution containing bromoacetylbromide (400 mg, 2.0 mmol) in THF (20 mL). The reaction proceeded at room temperature for 12 h. The bromoacetamide modified polyaniline (BrA-PANI) was thereafter thoroughly washed with dichloromethane and ethanol. The BrA-PANI was also ultrasonicated for three minutes each time in both solvents. The BrA-PANI was dried in vacuum at 40°C. The preparation process could be schematically shown as Scheme 1.

SI-ATRP

The grafting was accomplished by immersing the BrA-PANI (3 g) into the reaction mixture containing methyl methacrylate (MMA) 20 mL, Cu(I)Br 143.4 mg (1.0 mmol), 1,10-phenanthroline 360 mg (2.0 mmol) and toluene 20 mL. The SI-ATRP proceeded at 70°C for a certain time with electromagnetic stirring. N_2 was bubbled throughout the polymerizing period. The products were subjected to intense washing: toluene, ethanol and diluted HCl solution. Ultrasonication was used in combination with all three solvents. The PMMA-PANI obtained was then dried in vacuum at 40°C.



Scheme 1. Preparation of BrA-PANI and PMMA-PANI.

Analyses and characterizations

Elemental analysis (EA) of C and N was performed on Elementar vario EL instrument. Bruker IFS 66 v/s infrared spectrometer was used for the Fourier transform infrared (FT-IR) spectroscopy analysis. X-ray photoelectron spectroscopy (XPS) was accomplished using a PHI-5702 multi-functional X-ray photoelectron spectrometer with pass energy of 29.35 eV and an Mg Kα line excitation source. The binding energy of C 1s (284.6 eV) was used as a reference. The surface morphologies of the PMMA-PANI powders were characterized with a Philiphs XL-20 scanning electron microscope (SEM) (Philiphs Co., the Netherland).

The percentage of grafting (PG%) and the conversion of MMA (C%) were calculated according to the following relationships from the results of carbon elemental analyses:

$$\text{PG}\ (\%) = \text{Grafted PMMA (g)} / \text{PANI charged (g)} \times 100\%$$

$$\text{C}\ \% = \text{Total PMMA (g)} / \text{Monomer charged (g)} \times 100\%$$

Results and discussion

In the FT-IR spectrum of PANI, the main characteristic peaks are assigned as follows: the band at 3410 cm^{-1} is attributable to N-H stretching mode, C=N and C=C stretching mode for the quinonoid and benzenoid units occur at 1568 and 1492 cm^{-1}, the band at 1289 and 1234 cm^{-1} have been attributed to C-N stretching mode for benzenoid unit.

As in that of the macro-initiator for ATRP, BrA-PANI, the characteristic band at 1637 cm^{-1} of amide groups was found. It testified the bromoacetylation of the amine groups of the undoped PANI with bromoacetylbromide. The elemental analysis of the BrA-PANI showed that the content of the bromoacetyl groups was 5.4 mmol g^{-1}.

Table 1. The surface compositional data from XPS.

Samples	XPS analysis (at.%)					
	C	N	O	Br	Cl	Cu
BrA-PANI	58.46	27.84	4.82	8.69	0.19	0
PMMA-g-PANI	42.78	12.25	27.05	16.35	0.42	1.24

After the SI-ATRP of MMA, the products were washed with toluene and found no non-grafted PMMA in the solution by precipitation with ethanol. However, the peak at 1740 cm^{-1} originated from the carbonyl peak of PMMA was found in the FT-IR spectrum of the PMMA-PANI. It showed that the PMMA brushes had been successfully grafted from the macro-initiator, BrA-PANI, via a SI-ATRP technique as Scheme 1. The kinetics of SI-ATRP of MMA was studied by monitoring the changes in the carbon element content of the PMMA-PANI by elemental analyses (EA) as a function of time. To prove the controlled nature of the polymerization initiated from the surface by the BrA-PANI macroinitiator, the effects of the polymerizing time on the PG% and the C% were investigated (Figure 1). They increased linear with the increasing of the polymerizing time, and reached 27.08% and 9.06%, respectively, after a polymerizing time of 6 h, calculated from the EA results. It indicated that the proposed method showed the characteristics of the controlled/”living” radical polymerization.

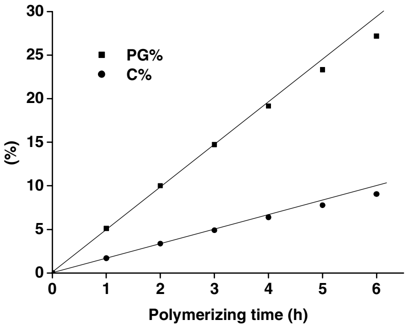
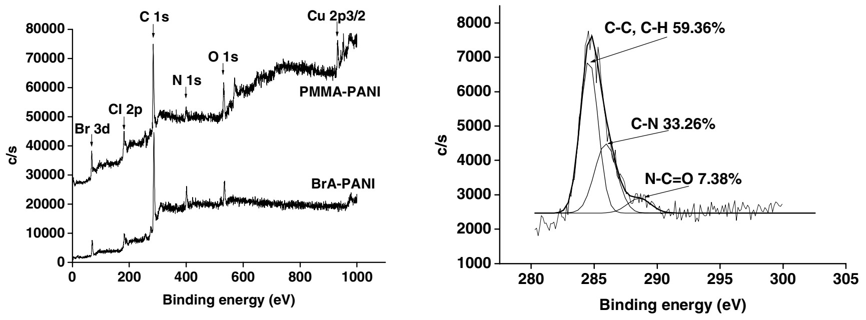


Figure 1. Effect of the polymerizing time on the PG% and C%.

XPS was used to determine the surface composition of the PMMA obtained by the SI-ATRP from the functionalized PANI powders. In the survey scan spectra of the BrA-PANI, C 1s (285 eV), N 1s (399 eV), O 1s (533 eV), Br 3d (70 eV) and Cl 2p (192 eV) were found [19]. It also showed that the amino groups at PANI surfaces had been bromoacetylated. And the present of the Cl 2p maybe resulted from the remained HCl doped PANI segments and the adsorption of HCl in the washing procedure after the SI-ATRP. After the SI-ARTP of MMA, Cu 2p3/2 (593 eV) was also found due to the adsorption of the catalyst, Cu(I)Br, on the PANI surfaces. It could be testified by the increase of the surface element content of Br from 8.69% to 16.35% after the SI-ATRP (Table 1). The decrease of the surface element contents of C and N and the increase of that of O showed that the PMMA brushes had been grafted from the PANI surfaces.

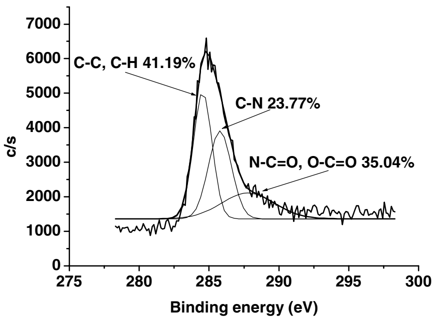
The diluted HCl solution was used for the removal of the Cu(I)Br after the SI-ATRP. It also could be found from the XPS analyses that the Cu(I)Br had not been washed completely because of the adsorption. And the PANI had been re-doped with HCl in the washing procedure.

Figures 2b and 2c present the XPS curve-fitting of C1*s* core-level spectra of the BrA-PANI and PMMA-PANI. The C 1s core-level spectra of all the samples can be deconvoluted into three peaks at 284.6, 286.2, and 288.7 eV, which correspond to C-C and C-H, C–O and C=O moieties, respectively. For the BrA-PANI, the N-C=O peak



(a) XPS survey scan spectra

(b) C(1s) core-level spectrum of BrA-PANI



(c) C(1s) core-level spectrum of PMMA-PANI

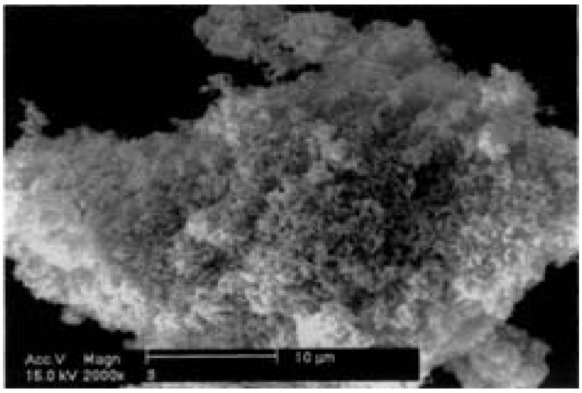
Figure 2. XPS analyses of the BrA-PANI and PMMA-PANI.

can be associated with the bromoacetylation of the amine groups of the undoped PANI with bromoacetylbromide. As for the PMMA-PANI, the positions of the peaks of C 1s core-level spectra did not differ from those of the BrA-PANI. However, the intensity of the peaks of the C-H and C-C and C-N moieties was substantially decreased (Figure 2c) compared to those of the BrA-PANI (Figure 2b). And the peak of the C=O moiety was increased. The increase of the intensity of the C=O peak with respect to the BrA-PANI is obviously due to the PMMA brushes grafted, since the latter contains a large number of O-C=O groups.

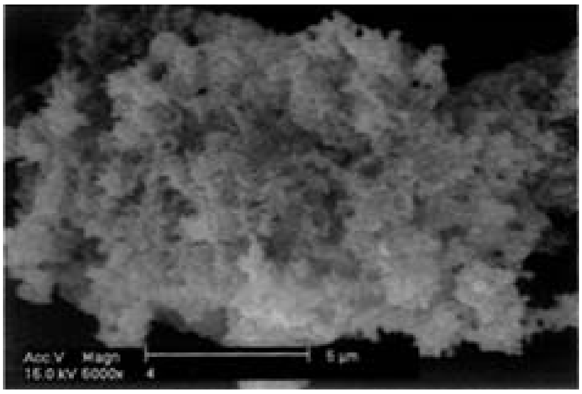
The grafting of PMMA brushes from the surfaces of the PANI powders was additionally confirmed by the change of the surface morphology. The surface of the PMMA-PANI was smoother than that of the BrA-PANI (Figure 3).

Conclusion

The undoped PANI powders had been modified by first bromoacetylating of the surface amine groups of the undoped PANI with bromoacetylbromide and then the bromoacetyl modified PANI (BrA-PANI) was used for the surface-initiated atom transfer radical polymerization (SI-ATRP) of MMA to obtain the core-shell PMMA-PANI with PMMA brushes on the surfaces. Surface analysis by X-ray photoelectron



(a) BrA-PANI



(b) PMMA-PANI

Figure 3. SEM images.

spectroscopy showed the PMMA brushes had been successfully grafted from the PANI surface. The proposed method could be useful to improve the mechanical and processable properties of PANI.

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