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Synthesis and characterization of poly(ionic liquid)-grafted silica hybrid materials through surface-radical chain-transfer polymerization and aqueous anion-exchange

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Abstract

Poly(ionic liquid)-grafted silica materials were firstly synthesized by polymerization of 1-vinyl-3-butylimidazolium bromide as a new ionic liquid monomer on mercaptopropylated silica by surface radical chain-transfer polymerization. The bromide counterion was exchanged to be three other inorganic anions including tetrafluoroborate, hexafluorophosphate, and trifluoromethanesulfonate through simple aqueous anon-exchange reaction. The obtained poly(ionic liquid)-grafted silica materials were characterized by elemental analysis, infrared spectra, thermogravimetric analysis, and X-ray fluorescence. The wettabilities of the materials with different counterions were verified by static water contact angle measurement. This kind of new materials may have some potential applied fields such as used as the catalyst, the extractant, and the chromatographic stationary phase and etc.

Keywords: Inorganic-polymer hybrid, Polymers, Surfaces, Ionic liquids, Silica

1. Introduction

Ionic liquids are molten salts near room temperature. In recent years, ionic liquids have been used in polymer science, mostly as polymerization media [1-3]. These days, however, the application of ionic liquids in polymer science is not limited to polymerization media alone. A novel class of materials called poly(ionic liquid)s have been developed. These materials have properties of both ionic liquids and polymers, and thus poly(ionic liquid)s have found a number of innovative applications [4-7]. Ionic liquids were also supported onto different materials such as silica gel [8], carbon nanotubes [6], Au surface [7], and polymers [9]. Carrier-supported ionic liquids are not real ionic liquids, but they may combine some of the advantages between ionic liquid media and the supported matrices [10]. Ionic liquid monomers were polymerized onto various substrates in several different types of polymerization processes, including controlled/living radical polymerization [11] and reversible addition-fragmentation transfer polymerization [12].

Recently, 1-allylimidazolium ionic liquid was used as a monomer for modification of silica through a surface radical chain-transfer reaction by us [13]. However, the grafting density on the modified surface was very low in this reaction. Since the activity of the monomer was not sufficiently high, the polymerization reaction was thought to proceed via addition instead of radical polymerization. In order to increase the grafting density which would be an important factor as a functional material and get a new class of poly(ionic liquid)-grafted silica materials, 1-vinylimidazolium ionic liquid was synthesized and used for the surface radical chain-transfer polymerization onto the silica, which followed by aqueous anion-exchange reaction in this study.

2. Materials and methods
1-Vinyl-3-butylimidazolium bromide ([VyBIm]Br) was synthesized according to the reported procedure [14]. Silica particles (5 μm, 120 Å, 300 m$^2$ g$^{-1}$) were used for the preparation of 3-mercaptopropyltrimethoxysilane-modified silica (Si-MPS) [15]. The preparation procedure of poly(ionic liquid)-grafted silica is schematically shown in Fig. 1. To a 100 mL round-bottomed container with a magnetic stirrer, 3.0 g Si-MPS was mixed with 4.9 g [VyBIm]Br dissolved in 30 mL acetonitrile. After adding 1% AIBN, the mixture was stirred at 60 °C for 6 h. The precipitates were filtered and washed with the following solvents: acetonitrile, methanol and diethyl ether. Poly(ionic liquid)-grafted silica with bromide as a counterion, represented as Si-VBIm/Br, was dried in vacuum for several hours.

Fig. 1. Schematic representation of polymerization and anion-exchange reactions.

The counterions of poly(ionic liquid)-grafted silica were changed readily via a general anion-exchange method. For example, a solution of 0.2 g Si-VBIm/Br in 3 mL of pure water and a solution of 0.5 g NaBF$_4$ in 2 mL pure water were mixed in a 10 mL test tube. The mixture was stirred for 1 h at room temperature; the resulting solid was filtered and washed with pure water. The obtained Si-VBIm/BF$_4$ was dried under vacuum. The similar procedure was repeated with other salts including NaPF$_6$ and CF$_3$SO$_3$Li, and satisfactory results were obtained in each case. The corresponding modified silica materials were termed Si-VBIm/PF$_6$ and Si-VBIm/TfO, respectively.

3. Results and discussion

[VyBIm]Br was synthesized and then polymerized on Si-MPS through a surface radical chain-transfer reaction. The concentration of mercaptopropyl groups attached to the silica surface was 3.18 μmol m$^{-2}$ for Si-MPS, as calculated from the carbon content (%C) determined by elemental analysis. The polymerization would be started on mercapto groups derived from MPS. As a result, that significant increase of the nitrogen content (%N) was observed in the polymerization process with Si-MPS, the amount of imidazolium groups that bonded to Si-MPS was 10.5 μmol m$^{-2}$ for Si-VBIm/Br, as calculated from the nitrogen content (%N). In our previous work [13], 1-allylimidazolium ionic liquid was used to modify silica with the similar reaction condition, but the amount of imidazolium groups bonded was only 1.68 μmol m$^{-2}$ which was less than the initial amount of a mercapto group. So we conclude that this surface radical chain-transfer reaction is a 1-to-1 addition reaction when 1-allylimidazolium ionic liquid is used as the monomer. On the contrary, the high nitrogen content with 1-vinylimidazolium ionic liquid indicates that polymerization was satisfactorily proceeded. According to the nitrogen contents, the estimated grafting amounts were determined to be 6.85 wt%, 12.6 wt%, 37.1 wt% and 41.8 wt% in Si-VBIm/Br-1, Si-VBIm/Br-2, Si-VBIm/Br-3 and Si-VBIm/Br-4 in the initial molar ratios of ionic liquid monomer to Si-MPS, respectively (shown in supporting information). The average degree of polymerization (DP) prepared in the molar ratio of Si-VBIm/Br-4 used in the current study was calculated to be 3.3. This value is not so high, but the grafted amounts of ionic liquid can be readily adjusted through the change of the initial molar ratio, and it is estimated that DP can be increased by decrease of the grafted amount of MPS.
Obvious differences in wavenumbers and intensities of the absorption bands can be observed between the spectra of Si-MPS and those of poly(ionic liquid)-grafted silica as shown in Fig. 2a. In the spectra of the poly(ionic liquid)-grafted silica surfaces, the absorption bands at 2875 and 2963 cm$^{-1}$ are assigned to the C–H stretching of the alkyl chain, and the band at 3135 cm$^{-1}$ is assigned to the C–H stretching of aromatics. The band at 1570 cm$^{-1}$ is attributed to the imidazolium groups, which confirms the anchoring of the organic molecule onto the silica surface. Another clear band at 838 cm$^{-1}$ is attributed to the P–F bond; this confirms the formation of Si-VBIm/PF$_6$ after the anion-exchange reaction.

Fig. 2. FT-IR spectra (a) and thermogravimetric curves (b) of Si-MPS and poly(ionic liquid)-grafted silica.

A mass loss of about 40.6% was observed in the case of Si-VBIm/Br with an increase in temperature from 200 °C to 800 °C as shown in Fig. 2b. In comparison with Si-MPS, the organic content of Si-VBIm/Br increased considerably after polymerization. On the other hand, in terms of the molecular weight, the order of the counterions was Br$^{-}$ < BF$_4^{-}$ < PF$_6^{-}$ < CF$_3$SO$_3^{-}$. However, the order of mass loss for poly(ionic liquid)-grafted silica was Si-VBIm/Br < Si-VBIm/BF$_4$ < Si-VBIm/TfO < Si-VBIm/PF$_6$, as shown in the figure. Si-VBIm/PF$_6$ undergoes the highest mass loss as it decomposes at about 180 °C, and the resultant hydrofluoric acid corrodes the silica substrate. The possible reaction may be as follows: SiO$_2$ + 4HF = SiF$_4$↑ + 2H$_2$O.

It is important to evaluate the feasibility of the reaction by determining the residual original counterions. The bromide content for poly(ionic liquid)-grafted silica was detected by XRF (as shown in the supporting information). Compared with Si-VBIm/Br, the residual bromide in other poly(ionic liquid)-grafted silica are little but still existed. Considering that the aqueous anion-exchange reaction is a simple and facile step, the results are still impressive and very useful for the preparation of this kind of materials.

The success of the polymerization and anion-exchange reactions also could be confirmed through the varied wettabilities of Si-MPS and poly(ionic liquid)-grafted silica materials with different counterions determined by static water contact angle measurement. As shown in Fig. 3, the contact angle of Si-MPS was measured as 100°. After polymerization of ionic liquids, the hydrophobicity of Si-VBIm/Br decreased and its contact angle was 84°. After anion-exchange, replacement of Br$^{-}$ with BF$_4^{-}$ clearly led to a hydrophobic change in the contact angle from 84° to 115°. Si-VBIm/PF$_6$ and Si-VBIm/TfO are more hydrophobic, and their contact angles were 131° and 129°, respectively.
Fig. 3. Wettabilities determined from contact angle for (a) Si-MPS, (b) Si-VBIm/Br, (c) Si-VBIm/BF₄, (d) Si-VBIm/PF₆, and (e) Si-VBIm/TFO.

4. Conclusions

The results of this study have demonstrated that (i) vinylimidazolium ionic liquids can be readily polymerized on silica particles through a surface radical chain-transfer reaction, (ii) that the counterions can be exchanged by a simple aqueous anion-exchange reaction, and (iii) that the wettabilities could be tuned accordingly with different counterions. This research has opened a new possibility of using poly(ionic liquid)-grafted silica materials as chromatographic stationary phases or as an extractant etc.; research on these topics is currently under way.

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References