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Short communication

Synthesis of room temperature ionic liquids from carboxymethylated chitosan

Ling Huang, Maolin Zhai *, Jing Peng, Ling Xu, Jiuqiang Li, Genshuan Wei

Beijing National Laboratory for Molecular Sciences, Department of Applied Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

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Abstract

Natural oligosaccharide-derived room temperature ionic liquids (RTILs) were prepared from 1-ethyl-3-methylimidazolium hydroxide (EMIM·OH) and carboxymethylated chitosan (CM-chitosan) by acid–base neutralization reaction. These EMIM·CM-chitosan ionic liquids exhibited good ionic conductivity and thermal stability, as well as low glass transition temperature, implying their potential wide applications in direct electrochemistry, biosensors, and biocatalysis.

Keywords: Ionic liquid; Carboxymethylated chitosan; 1-Ethyl-3-methylimidazolium; Ionic conductivity; Thermal stability

1. Introduction

Room temperature ionic liquids (RTILs) have attracted considerable attention in recent years due to their special physical and chemical properties (Welton, 1999). However, it is hard to prepare high purity RTILs by conventional anion exchange reactions because the by-products such as metal salts are difficult to eliminate until recently neutralization reactions of tertiary amines and organic acids were used to prepare pure RTILs (Hirao, Sugimoto, & Ohno, 2000; Ohno & Yoshizawa, 2002; Yoshizawa, Ogihara, & Ohno, 2001). Furthermore, task-specific (Bates, Mayton, Ntai, & Davis, 2002) and biodegradable (Gathergood, Garcia, & Scammells, 2004) ionic liquids have an attractive future in green chemistry because their utilization will greatly reduce the risk of environment. It was reported that 20 natural amino acids can be utilized to synthesize chiral and biodegradable RTILs (Bao, Wang, & Li, 2003). Some characteristics of these RTILs such as good miscibility with organic solvents, high ionic conductivities, and low glass transition temperatures (T_g) were also reported.

Chitosan is a poly-β-(1–4)-D-glucosamine derivative, which is obtained by full or partial deacetylation of chitin. Carboxymethylated chitosan (CM-chitosan) has similar molecular structure with amino acids and can be obtained by carboxymethylated reactions between chitosan and monochloroacetic acid (Zhai et al., 2004). Chitosan and CM-chitosan are attractive nontoxic, biocompatible, biodegradable, and film-forming biomaterials that can be used as biosensors and biocatalysis (Bindhu & Abraham, 2003; Xu, Luo, Du, & Chen, 2004). Despite composite system based on chitosan and RTILs for electrochemistry applications has been presented by Lu et al. (Lu, Hu, Yao, Wang, & Li, 2006), there is no report about the synthesis of ionic liquids composed of natural oligosaccharides yet. Furthermore, it will be helpful to improve the biocompatibility of ionic liquid by introducing CM-chitosan as an anion compound.

In our work, RTIL based on 1-ethyl-3-methylimidazolium hydroxide (EMIM·OH) and CM-chitosan was prepared in neutralization reaction (Scheme 1). The primary ionic conductivity and thermal stability of this RTIL was studied, which might enable it to apply in the electrochemistry field. However, this kind of RTIL may not be used as

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* Corresponding author. Tel./fax: +86 10 62753794.
E-mail address: mlzhai@pku.edu.cn (M.L. Zhai).

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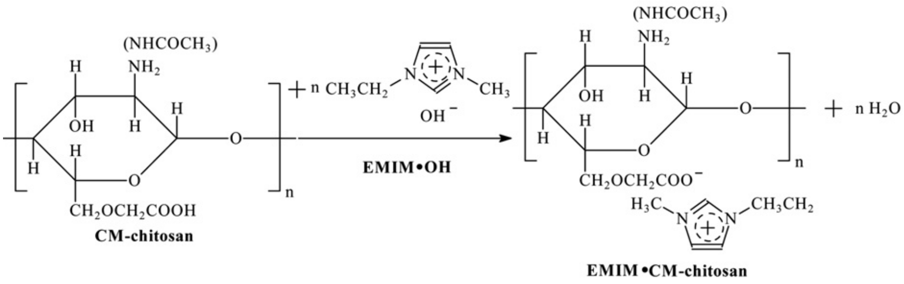

Scheme 1. Synthesis route of EMIM·CM-chitosan ionic liquid.

solvent for certain chemical reactions involved hydroxyl and amino groups because of the presence of free hydroxyl and amino groups in the RTIL.

2. Experimental

2.1. Chemicals

Na-type CM-chitosan (degree of substitution: 91%; degree of deacetylation: 84.0%; M_w: 3.1×10^4 Da) was purchased from Koyou Chemical Industrial Co. Ltd., Japan. Brown CM-chitosan powder with low molecular weight was prepared by γ-ray radiation method described in our previous paper (Huang, Zhai, Peng, Li, & Wei, 2007). 1-Methylimidazole (MIM) was obtained from J&K chemical Ltd. and used as received. Anion exchange resin (711-type) and other reagents were purchased from Beijing Chemical Reagent Company.

2.2. Synthesis of CH_3CH_2Br

In a typical method, 65 ml 98% H_2SO_4 was added dropwise to 281 ml 48% HBr and 145 ml 95% CH_3CH_2OH solution, stirred, and cooled at the same time. Then 109 ml 98% H_2SO_4 was dropped into the mixed solution and steamed out CH_3CH_2Br slowly. ^1H NMR (300 MHz; $CDCl_3$), δ_H: 1.68 (t, CH_3), 3.43 (m, CH_2); ^{13}C NMR δ_C: 19.30 (CH_3), 29.97 (CH_2).

2.3. Synthesis of EMIM·Br

A mixture of 31.08 g (0.38 mol) MIM and 57.75 g (0.53 mol) ethyl bromide (optimal experience ratio: MIM/CH_3CH_2Br = 1/1.4) was stirred and refluxed at 40–60 °C for 48 h, then filtered, washed with ethyl acetate, and dried in vacuum at 50 °C to obtain EMIM·Br. ^1H NMR (300 MHz; $CDCl_3$), δ_H: 1.62 (t, CCH_3), 4.14 (s, NCH_3), 4.44 (m, NCH_2C), 7.68 (s, NCH=CHN), 10.31 (s, NCHN); ^{13}C NMR δ_C: 15.49 (CH_3), 36.46 (NCH_3), 45.03 (NCH_2), 121.81 and 123.51 (NCCN), 136.66 (NCN).

2.4. Synthesis of EMIM·OH

EMIM·Br was transformed to EMIM·OH by anion exchange resin. ^1H NMR (300 MHz; $CDCl_3$), δ_H: 1.59 (t, CCH_3), 4.10 (s, NCH_3), 4.42 (m, NCH_2C), 7.38 (s, NCH=CHN), 7.65 (s, NCHN); ^{13}C NMR δ_C: 15.25 (CH_3), 36.17 (NCH_3), 44.75 (NCH_2), 121.48 and 123.24 (NCCN).

2.5. Synthesis of EMIM·CM-chitosan ionic liquids

Low molecular weight CM-chitosan was prepared in the Na-type CM-chitosan (viscosity average molecular weight: $M_\eta = 2.9 \times 10^4$ Da) aqueous solution by γ-ray radiation. Then the solution was concentrated by the evaporation using rotavapor at 60 °C, and appropriate HCl was added to adjust pH to 1. CM-chitosan was precipitated and washed several times by 95% ethanol to remove NaCl and residual HCl to get H-type CM-chitosan. CM-chitosan was mixed with EMIM·OH solution equimolar between EMIM·OH and carboxyl groups in CM-chitosan. The mixed solution was stirred at 0 °C for 12 h. Water was removed by evaporation and the product was dried in vacuum for 2 days at 60 °C. The water content of ionic liquids determined by TG was about 0.5 wt%.

2.6. Characterization methods

The structure of EMIM·CM-chitosan ionic liquids and intermediates were identified by ultraviolet (UV) spectrophotometer (Hitachi Model 3010), Fourier transform infrared spectrometer (FT-IR, Bruker VECTOR22), and ^1H NMR spectra (Mercury-300, Varian). UV spectra were used to determine the concentration of EMIM·OH, which is necessary in neutralization reaction with equimolar carboxyl groups of CM-chitosan. Thermal analysis was performed by DSC2910 and SDT2960 (thermal analysis, USA).

3. Results and discussion

FT-IR spectra in Fig. 1 manifested the bands at 1737 cm^{-1} (spectrum b) and 1660 cm^{-1} (spectrum c) disappeared because of the neutralization reaction between CM-chitosan and EMIM·OH. Furthermore, the bands at 1576 and 1169 cm^{-1} (spectrum a) increased simultaneously because of introducing cations of $EMIM^+$ to the skeleton of CM-chitosan oligosaccharides. The changes among

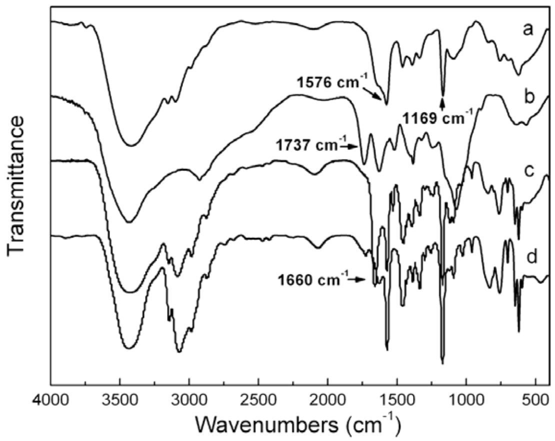

Fig. 1. IR spectra of (a) EMIM·CM-chitosan ionic liquid, (b) H-type CM-chitosan, 1×10^3 Da, (c) EMIM·OH, (d) EMIM·Br.

spectra a, b, and c confirmed the structure of EMIM·CM-chitosan ionic liquids.

The effect of the anion on thermal properties of EMIM·CM-chitosan ionic liquids was investigated with DSC2910 and SDT2960. Thermal analysis results revealed that EMIM·CM-chitosan ionic liquids had no obvious melting point (T_m). However, T_g decreased and decomposing temperature (T_d) increased when the M_η of CM-chitosan decreased (Table 1). It was known that T_g and T_d were related to ionic conductivities and thermal stability, respectively. The low T_g (<−80 °C) and high T_d (>300 °C) of EMIM·CM-chitosan ionic liquids implied that these RTILs can be used as electrolyte materials due to their excellent ionic conductivities and thermal stability. Furthermore, two adjacent peaks were observed in differential thermogravimetric (DTG) curves of composite system based on chitosan and RTILs (Lu et al., 2006), which correspond to the pyrolysis of chitosan and RTILs, respectively. Only a single peak was observed in the DTG curves of EMIM·CM-chitosan ionic liquids, which also proved the completeness of the synthesis reaction. The water content of EMIM·CM-chitosan ionic liquids can be estimated by thermal gravity analysis curves, and the results revealed that the weight loss of EMIM·CM-chitosan ionic liquids prepared from CM-chitosan with M_η of 6×10^2, 8×10^2, and 1×10^3 Da at 100 °C were 0.79%, 0.15%, and 0.38%, respectively. Water in these ionic liquids can not be removed completely due to the good moisture-absorption and moisture-retention abilities of CM-chitosan (Chen, Du, & Zeng, 2003).

Table 1
Thermal properties of EMIM·CM-chitosan ionic liquids with different molecular weight CM-chitosan

	M_η[a]	T_g (°C)	T_d (°C)
1	6×10^2	−89.6	321.5
2	8×10^2	−85.1	316.4
3	1×10^3	−80.2	312.1

[a] Viscosity average molecular weight of CM-chitosan.

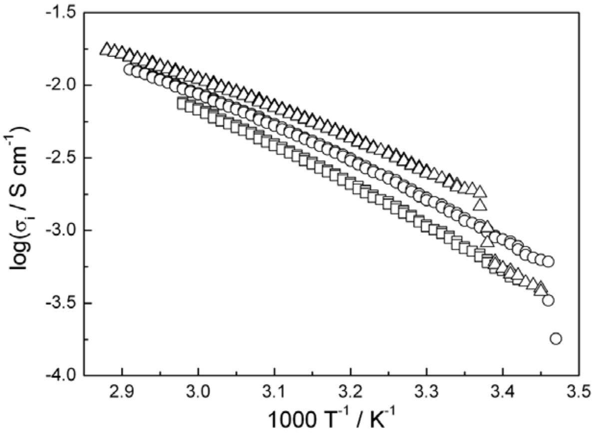

Fig. 2. Temperature dependence of the ionic conductivities of EMIM·CM-chitosan ionic liquids with different molecular weight CM-chitosan: 1×10^3 Da (□), 8×10^2 Da (○), 6×10^2 Da (Δ).

As shown in Fig. 2, temperature dependence of the ionic conductivities (σ) of prepared ionic liquids in the gradual cooling process from 70 to 25 °C was determined by Delta 326 conductivity meter (Mettler-Toledo, Shanghai) with an LE701 conductivity measuring cell. At the same temperature, σ of the ionic liquid prepared from high M_η CM-chitosan was lower than that from low M_η CM-chitosan. For a specific RTIL, σ decreased as the temperature decreased. Furthermore, σ decreased sharply at a critical transition temperature (e.g., 16 °C for ionic liquid b and 23 °C for ionic liquid c) because they were not homogeneous liquid state any longer at this temperature. The change of transition temperature was in consistent with the trend of T_g. All results revealed that M_η of CM-chitosan affect the ionic conductivities of ionic liquids because the ions of high M_η CM-chitosan have poor mobility. For example, the ionic conductivities (25 °C) of EMIM·CM-chitosan ionic liquids prepared from CM-chitosan with M_η of 6×10^2, 8×10^2, and 1×10^3 Da were 1.9×10^{-3}, 1.2×10^{-3}, and 7.5×10^{-4} S cm^{-1}, respectively. Compared to some zwitterionic-type ionic liquids with lithium salts added (Yoshizawa, Hirao, Ito-Akita, & Ohno, 2001; Yoshizawa, Narita, & Ohno, 2004) or ionic liquids from bis(trifluoromethanesulfonyl)imide and bis(perfluoroethylsulfonyl)imide anion (Ohno & Yoshizawa, 2002; Yoshizawa et al., 2001), EMIM·CM-chitosan ionic liquids have much higher ionic conductivities, which is an important property for the electrochemical applications.

4. Conclusions

In summary, a serial of EMIM·CM-chitosan ionic liquids with different molecular weight CM-chitosan were prepared by acid–base neutralization reactions. The T_g and T_d of these ionic liquids were around −80 °C and 300 °C, respectively. Ionic liquids composed of low molecular weight CM-chitosan have good ionic conductivities and thermal stability. At 25 °C, the ionic conductivities of EMIM·CM-chitosan ionic liquids with different molecular weight CM-chitosan (6×10^2, 8×10^2, and 1×10^3 Da) were 1.9×10^{-3}, 1.2×10^{-3}, and 7.5×10^{-4} S cm^{-1}, respectively. Therefore, EMIM·CM-chitosan ionic liquids have potential applications in direct electrochemistry, biosensors, and biocatalysis field.

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