



## Original article

## Application of ionic liquids as a catalyst in the synthesis of polyvinyl butyral (PVB) polymer



Xi-Xi Qin, Zhi-Lin Cheng\*

College of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China

## ARTICLE INFO

## Article history:

Received 27 April 2015

Received in revised form 12 June 2015

Accepted 24 June 2015

Available online 10 July 2015

## Keywords:

Ionic liquids

Catalyst

PVB

Acetalization degree

## ABSTRACT

Polyvinyl butyral (PVB) polymer was successfully synthesized using ionic liquid (IL) catalyst. The synthesis of PVB was achieved by acetalization of polyvinyl alcohol (PVA) and butyraldehyde (BA) in the presence of [HMIM]<sup>+</sup>HSO<sub>4</sub><sup>-</sup> IL catalyst. The FT-IR, <sup>1</sup>H NMR, DSC, GPC and SEM characterizations were used to analyze the structure and properties of PVB. The effects of the concentration of PVA in water and the number of reuse cycles on the acetalization degree were investigated. The results indicated that the maximum acetalization degree of PVB obtained using [HMIM]<sup>+</sup>HSO<sub>4</sub><sup>-</sup> IL catalyst was up to 72%. The comparison of the commercial PVB and the PVB obtained using [HMIM]<sup>+</sup>HSO<sub>4</sub><sup>-</sup> IL catalyst showed that the self-made PVB has a larger molecular weight, higher viscosity, and higher acetalization degree than the commercial PVB.

© 2015 Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences. Published by Elsevier B.V. All rights reserved.

## 1. Introduction

ILs have received much attention in many areas of chemistry and industry due to their potential as “green” recyclable alternatives to traditional organic solvents [1,2]. Prior to the year 2000, ionic liquids had been successfully used in synthesis of polymers. The related reports mainly focused on Ziegler–Natta polymerization of ethylene [3–6] and metathesis polymerization of acyclic dienes [7,8]. Those rather preliminary studies revealed that it is possible to conduct different polymerization processes in ILs. Afterwards, the application of ILs in synthesis of polymer spread to several new types of polymerization processes, including conventional free radical polymerization [9], living/controlling radical polymerizations [10,11], reversible addition-fragmentation transfer (RAFT) [12], as well as in coordination polymerizations [13]. As a result, several advantages of ILs in polymer synthesis were shown [14], including increase of the propagation rate constant and decrease of the termination rate constant, resulting in better control in ATRP [8].

Besides exhibiting many advantages as the solvent, ILs also play an important catalytic role in polymer synthesis. A few reports have found that the polymerization rate using [Bmim][PF<sub>6</sub>] ionic liquid in styrene and methyl methacrylate system was 10 times as fast as in benzene [15].

Poly(vinyl butyral) (PVB) is a member of the class of poly(vinyl acetal) resins. Owing to its several advantages, such as high adhesion to glass, toughness, light stability, clarity as well as excellent mechanical strength and impact resistance, PVB has many desirable applications [16,17]. Synthesis of PVB by the precipitation method is used in industry production for its low cost and simple operation. However, this method is achieved by acetalization of polyvinyl alcohol (PVA) and butyraldehyde (BA) in the presence of the strong inorganic acid, which produces a lot of waste acid water and results in the corrosion of equipment. The synthesis of PVB using ILs instead of inorganic acid has never been developed as of yet.

The present work was to develop an environment-friendly synthesis of PVB by using IL catalyst. The characterizations of structure and properties of PVB were studied.

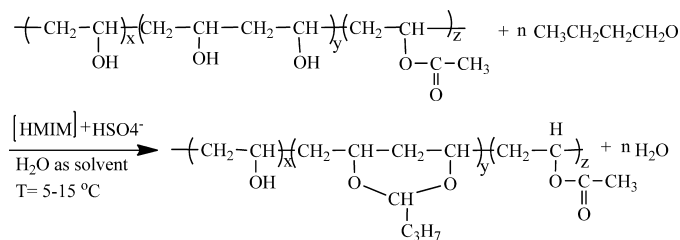
## 2. Experimental

## 2.1. Preparation of ionic liquid

[HMIM]<sup>+</sup>HSO<sub>4</sub><sup>-</sup> ionic liquid was prepared according to literature procedures [18]. *N*-Methylimidazole (Sinopharm Chemical Reagent Co., Ltd.) was used as the starting material for preparation of [HMIM]<sup>+</sup>HSO<sub>4</sub><sup>-</sup>. Firstly, a certain amount of *N*-methylimidazole was added into the flask, and then a few drops of H<sub>2</sub>SO<sub>4</sub> solution was added with vigorous stirring at 0 °C for 4 h. Finally, the resulting product was dried under vacuum at 50 °C for 12 h.

\* Corresponding author.

E-mail address: [zcheng224@126.com](mailto:zcheng224@126.com) (Z.-L. Cheng).



Scheme 1. Synthesis of PVB.

## 2.2. Preparation of PVB

Polyvinyl alcohol (PVA, Sinopharm Chemical Reagent Co., Ltd.) was used as the starting material for preparation of PVB. Firstly, an amount of PVA was dissolved in deionized water with vigorous stirring at 95 °C for 2 h. The flask was immersed in a water bath. At 50 °C, 0.5 g of lauryl sodium sulfate was added into the above solution under stirring for 30 min. Then, *n*-butyraldehyde (98.5%, Sinopharm Chemical Reagent Co., Ltd.) (mBA:mPVA = 0.6) was added into the above solution with vigorous stirring for 30 min at 30 °C. After cooling to below 20 °C, [HMIM]<sup>+</sup>HSO<sub>4</sub><sup>-</sup> ionic liquid was added into the solution with vigorous stirring for 4 h. The resulting mixture was continually stirred at 7–15 °C for 4 h, and then at 4 °C for 4 h. The as-obtained acetal product was washed several times with deionized water and finally dried under the freeze drying machine. The sample was denoted self-made PVB. The synthesis route was shown in Scheme 1.

## 2.3. The recycling procedure of ILs

After the completion of above reaction, the PVB product and the solution containing ILs were successfully separated by vacuum extraction filtration. The separated solution as catalyst and solvent was applied to new PVB synthesis without adding fresh IL. In the recycling process, only an amount of deionized water was supplemented in order to recover the solvent loss.

## 2.4. Characterization

Polymer functional groups were analyzed by infrared spectroscopy (Cary 610/670 Micro infrared spectrometer) in the range of 4000–400 cm<sup>-1</sup> by using KBr pellets. The configuration structure of polymers was detected by NMR spectroscopy (Bruker AV-400 NMR spectrometer). The DSC analysis of polymer was recorded by DSC 8500. The molecular weight of polymer was analyzed by Agilent GPC. The viscosity was measured by SNB-1A Digital Viscometer.

## 2.5. Measurement for the acetalization degree

The measurement of the acetalization degree: firstly, 1 g of PVB was added into 50 mL 95% alcohol under vigorous stirring for 2 h. Then 25 mL 7.5% hydroxylamine was added into the above solution under vigorous stirred for another 2 h and cooled to the room temperature. Finally, bromophenol blue was added, and the solution was titrated to purple with a standard solution of sodium hydroxide. The vacuity contrast group also was done [19].

The calculation formula:

$$B = 0.142 \times (V - V_0 \times c/m)$$

*B* – the acetalization degree;

*V* – the amount of sodium hydroxide solution consumed samples of PVB, mL;

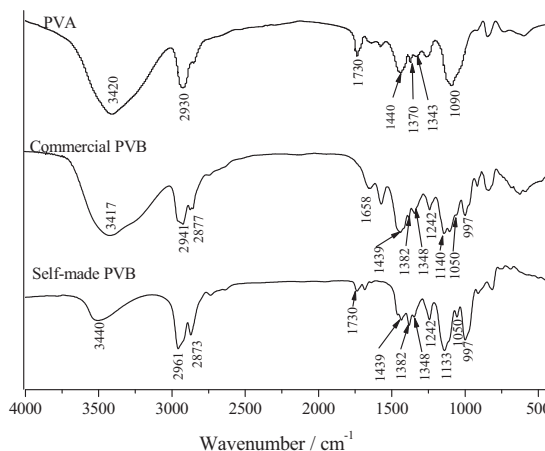


Fig. 1. FT-IR spectra of PVA, commercial PVB and PVB obtained by using [HMIM]<sup>+</sup>HSO<sub>4</sub><sup>-</sup> IL catalyst.

*V*<sub>0</sub> – the amount of sodium hydroxide solution consumed samples of the vacuity contrast group, mL;  
*c* – the concentration of sodium hydroxide, mol/L;  
*m* – the mass of PVB.

## 3. Results and discussion

The self-made PVB and the commercial PVB exhibit similar main peaks in FT-IR spectra as shown in Fig. 1. For the self-made PVB, the peaks at 2873 cm<sup>-1</sup>, 2961 cm<sup>-1</sup> are ascribed to the stretching vibration of saturated –CH, –CH<sub>2</sub> and –CH<sub>3</sub>. The peaks at 1439 cm<sup>-1</sup>, 1382 cm<sup>-1</sup> and 1348 cm<sup>-1</sup> are assigned to C–H bending vibration. The peaks at 1133 cm<sup>-1</sup> and 1050 cm<sup>-1</sup> are assumed to C–O–C–O–C stretching vibrations of five-membered cyclic acetal group and hexatomic cyclic acetal group, which confirms the occurrence of acetalization reaction between polyvinyl alcohol and *n*-butyraldehyde. The peak at 1730 cm<sup>-1</sup> relates to C=O stretching vibration of acetate group. The peaks at 997 cm<sup>-1</sup> and 1242 cm<sup>-1</sup> are ascribed to C–O–C stretching vibration of acetate group [20,21]. The peak at 3440 cm<sup>-1</sup> is assigned to –OH asymmetric stretching of polyvinyl alcohol, which shows a reduction in magnitude compared with the commercial PVB samples.

Fig. 2 gives the <sup>1</sup>H NMR spectra of PVB by obtained using [HMIM]<sup>+</sup>HSO<sub>4</sub><sup>-</sup> IL catalyst and Table 1 lists the NMR data. As can be

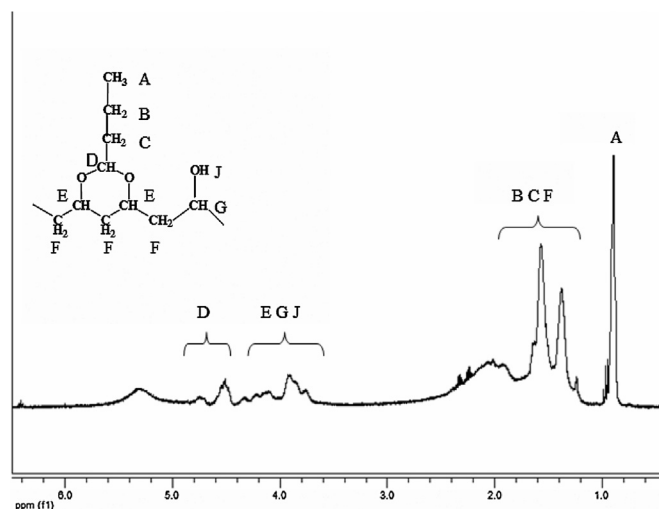


Fig. 2. <sup>1</sup>H NMR spectra of PVB obtained by using [HMIM]<sup>+</sup>HSO<sub>4</sub><sup>-</sup> IL catalyst.

Download English Version:

<https://daneshyari.com/en/article/1254590>

Download Persian Version:

<https://daneshyari.com/article/1254590>

[Daneshyari.com](https://daneshyari.com)