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# Synthesis, characterization, and gas permeabilities of cellulose derivatives containing adamantane groups



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## ABSTRACT

Cellulose derivatives containing adamantane groups are homogeneously synthesized by a simple, rapid and environmentally friendly way using 1-allyl-3-methylimidazolium chloride (AmimCl) ionic liquid as reaction media. Without any catalysts, cellulose adamantates (CA<sub>d</sub>) with degree of substitution (DS) in a range from 0.71 to 2.25 are prepared just in one-step. In addition, a series of mixed esters, cellulose adamantate acetate (CA<sub>d</sub>Ac), are also synthesized via the “one-pot” process. The obtained CA<sub>d</sub> and CA<sub>d</sub>Ac are characterized by means of FT-IR, NMR, XRD, DSC and TGA. Meanwhile, their gas permeabilities of these materials for O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, CO and CO<sub>2</sub> are studied. CA<sub>d</sub> exhibits improved solubility in organic solvents, low glass transition temperature and good thermostability. In particular, the free-volume topology of CA<sub>d</sub> membranes has been tailored by controlling the DS of adamantane, thus CA<sub>d</sub> membranes display a significant enhancement for gas permeability with good ideal permselectivity for several gas pairs, such as O<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/CO. For CA<sub>d</sub>Ac, introducing only a small amount of adamantane groups in cellulose acetate could achieve better gas permeability and similar or slightly lower ideal permselectivity.

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## 1. Introduction

Gas separation with membrane process is a relatively recent technology but very promising, owing to low cost, high energy efficiency, ease of processing and excellent reliability [1,2]. Nearly all imaginable gas mixtures can be separated by gas separation membranes, and large industrial applications such as air separation (obtaining of technical grade nitrogen or oxygen enriched air), hydrogen separation, and separation of CO<sub>2</sub>/CH<sub>4</sub> mixtures and CO<sub>2</sub>/N<sub>2</sub> (treatment of flue gas), have already been realized for more than 30 years [1,2]. Polymeric membranes have several advantages over inorganic membrane materials, making them more economical, and thus dominate the membrane gas separation market. Although hundreds of polymers have been investigated as potential membrane materials, only several ones such as polysulfone, polyimide and perfluorinated polymer, have been actually applied in industrial gas separating plants [1–4]. Most of these applied polymers are petroleum chemicals, which are obtained by environmentally-unfriendly methods, have a relatively high cost and exhibit a trade-off behavior between permeability

and selectivity [2,5]. Thus, looking for novel polymers with environmentally-friendly property, low cost and a good proportional permeability/selectivity behavior is a major step towards the development of better membrane materials.

Cellulose as the most abundant biopolymer available from the natural world has drawn great attention from researchers, because it has many attractive properties such as biodegradability, biocompatibility and inexhaustible renewability [6]. More importantly, cellulose as a homopolymer composed of D-anhydroglucopyranose units (AGUs) possesses a large amount of hydroxyls groups at the C2, C3, and C6 positions of each AGU. Thus, it is susceptible to chemical modifications of esterification and etherification. By simple reactions between active substituents and hydroxyls on the cellulose backbone, a wide variety of cellulose derivatives has been developed [6–9]. They derive interesting properties from both cellulose and modified groups, including moderately rigid chains, good flexibility, mechanical strength, good solubility in organic solvents, and excellent membrane-forming ability. So the cellulose derivatives are suitable for separation membrane materials [10,11]. For example, cellulose acetate (CA), one of the most common cellulose derivatives, has been widely exploited in commercial application for gas separation, and found to be the most suitable commercial membrane for biogas separation and enrichment [1]. However, the existence of numerous hydroxyls in cellulose also generates a well-developed intra- and inter-molecular hydrogen bonding network, so cellulose is insoluble in water or conventional

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organic solvents. Thus, some harsh conditions are required usually for the homogeneous modification of cellulose [12–14]. Recently, this dilemma has been perfectly solved when certain ionic liquids (ILs) are found to have outstanding dissolving capability for cellulose, which provides a new and versatile platform for cellulose processing and derivatization [15–19]. A series of cellulose derivatives such as cellulose acetate, benzoate, sulfonate, dendrimer derivative and hydroxyalkyl cellulose, have been successfully prepared in ILs [20–23].

Adamantane, a highly symmetrical tricyclic hydrocarbon, is known as a new generation of fine chemical raw materials. It is named after the structure of carbon atoms which is equivalent with diamond lattice. It performs many outstanding properties such as high thermal stability, good antioxidant ability, antibacterial activity and hydrophobicity [24,25]. Besides, its stiff structure and large free volume are also very attractive in polymer fields [26–29]. Pixton and Paul have introduced bulky adamantane groups into the backbone of polysulfone to reduce chain mobility and prevent tight chain packing. As a result, polysulfone copolymers containing adamantane groups exhibit superior gas permeation properties [29].

Combining excellent membrane-forming ability and good mechanical strength of cellulose derivatives and large free volume feature of adamantane, novel cellulose derivatives containing adamantane groups could be applied in gas separation. Although the cellulose derivatives containing adamantane groups have been synthesized in N,N-dimethylacetamide (DMAc)/LiCl, dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride (TBAF) and ILs, there remain some drawbacks, such as complex dissolution process of cellulose, time consuming and multi-step reactions, and difficult recycling of solvents, which limit their applications in industrial production [30–33]. More importantly, the gas permeability of adamantane-containing cellulose has not been investigated yet.

In this article, using 1-allyl-3-methylimidazolium chloride (AmimCl) ionic liquid as a reaction medium, we synthesize CAD by homogeneous acylation of cellulose with adamantoyl chloride in the absence of any catalysts. Via a “one-pot” process, both adamantyl and acetyl groups have been successfully introduced into cellulose chains. The permeation performances of cellulose derivatives containing adamantane groups for O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, CO and CO<sub>2</sub> are also thoroughly studied.

## 2. Experiment section

### 2.1. Materials

Cotton pulp (degree of polymerization  $\approx$  730) was dried at 70 °C for 3 h under vacuum before use. AmimCl was synthesized according to our previous work [17]. Adamantoyl chloride was purchased from Chongqing Voton Chemical Co., Ltd. Pyridine, acetic anhydride and ethanol were analytical grade and used as received.

### 2.2. Preparation of cellulose/AmimCl solution

For a typical preparation of cellulose solution in AmimCl, 2.5 g cotton pulp was dispersed into 60 g AmimCl. Then, the mixture was stirred at 80 °C for 3 h to guarantee complete dissolution. Finally, a clear cellulose solution with 4 wt% of polymer concentration was obtained.

### 2.3. Synthesis of cellulose adamantate (CAD)

Cellulose adamantates were synthesized according to Scheme 1. With the presence of pyridine (3.5 mol/mol AGU),

adamantoyl chloride was added into cellulose/AmimCl solution. The solution was mechanically stirred for a certain period at given temperatures (Table 1). Then the resultant mixture was precipitated in a 5-fold amount of ethanol. The insoluble fraction was filtrated and washed with ethanol three times. Then it was re-dissolved in DMSO or chloroform (CHCl<sub>3</sub>), precipitated again in ethanol and thoroughly washed until the IL was removed completely. Finally, the product was dried under vacuum at 60 °C for 24 h.

*FT-IR (KBr):* 2902 cm<sup>-1</sup>  $\nu$  (CH), and 1732 cm<sup>-1</sup>  $\nu$  (C=O).

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm)=2.7–5.4 (cellulose backbone) and 1.3–2.3 (adamantate).

<sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm)=175.7–177.6 (C=O), 41.3–101.3 (cellulose backbone), and 28.3–39.1 (methene and methyne of adamantate).

### 2.4. Synthesis of cellulose adamantate acetate (CAAdAc)

*Method A:* By using pyridine (3.5 mol/mol AGU) as the cosolvent, adamantoyl chloride (3 mol/mol AGU) and acetic anhydride (3 mol/mol AGU) were simultaneously added into the cellulose/AmimCl solution at 80 °C for 2 h (sample E).

*Method B:* By using pyridine (3.5 mol/mol AGU) as the cosolvent, acetic anhydride (3 mol/mol AGU) was added into the cellulose/AmimCl solution first at 80 °C for 2 h. Then, adamantoyl chloride (3 mol/mol AGU) was added under vigorous stirring and reacted for 1 h (sample F).

*Method C:* By using pyridine (3.5 mol/mol AGU) as the cosolvent, adamantoyl chloride (3 mol/mol AGU) was added into the cellulose/AmimCl solution first at 80 °C for 1 h. Then, acetic anhydride (3 mol/mol AGU) was added under vigorous stirring and reacted for 2 h (sample G).

Each resultant CAAdAc obtained from Methods A, B, and C was precipitated in a 5-fold amount of ethanol and filtered to separate the precipitate. The solid was washed 3 times with ethanol and dried under vacuum at 80 °C for 24 h.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm)=2.7–5.4 (cellulose backbone) and 1.3–2.3 (adamantate and acetate).

<sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm)=169.2–176.4 (C=O), 62.0–101.3 (cellulose backbone), 28.3–41.3 (methene and methyne of adamantate), and 22.1 (methene of acetate).

### 2.5. Membrane fabrication

Nonporous planar membranes of two series of CAD and CAAdAc cellulose esters were fabricated by casting their pyridine solutions (concentration 4–5 wt%) on a clean glass plate and evaporating solvent at 45 °C. Finally, the obtained transparent membranes (thickness: 30–50  $\mu$ m) were dried under vacuum at 60 °C for 24 h.

### 2.6. Measurements

*FTIR spectrometry:* The IR spectra of samples were recorded with a Fourier Transform IR spectrometer (FTIR PE-2000, the United States) by using the KBr pellet technique.

*<sup>1</sup>H NMR spectroscopy:* Samples (10 mg) were dissolved in DMSO-d<sub>6</sub> or CDCl<sub>3</sub> (0.5 ml). <sup>1</sup>H NMR spectra were acquired on a Bruker AV400 spectrometer with 16 scans after adding a drop of deuterated trifluoroacetic acid, which shifted the peaks of active hydrogens to the low field. The <sup>1</sup>H NMR frequency was 400 MHz. By using the following formula (1), the degree of

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