Carbohydrate Polymers 172 (2017) 223–229

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Controlled synthesis, immobilization and chiral recognition of carboxylic acid functionalized cellulose tris(3,5-dimethylphenylcarbamate)

Miaomiao Han [a], Xiaosa Jin [a,b], Han Yang [a], Xiao Liu [a,c], Yadong Liu [a], Shengxiang Ji [a,*]

[a] Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, PR China
[b] University of Chinese Academy of Sciences, Beijing 100049, PR China
[c] University of Science and Technology of China, Hefei 230026, Anhui, PR China

ARTICLE INFO

Article history:
Received 26 January 2017
Received in revised form 16 May 2017
Accepted 17 May 2017
Available online 18 May 2017

Keywords:
Polysaccharide derivative
Chiral separation
Chiral stationary phase
HPLC
Immobilization

ABSTRACT

Traditional cellulose-based chiral stationary phases (CSPs) are prepared by physically coating cellulose derivatives onto substrates and only compatible with a very limited range of solvents as the mobile phase. Therefore, chemical immobilization of cellulose derivatives onto silica gel has been efficiently applied to improve the solvent compatibility of cellulose-based CSPs. Here we developed a novel approach to homogeneously modifying cellulose tris(3,5-dimethylphenylcarbamate) (CDMPC). A series of carboxylic acid functionalized CDMPCs (CC-Xs) with controlled amounts and randomly distributed carboxylic acid groups was synthesized. CC-Xs were effectively immobilized onto amine-modified silica gel to afford immobilized CSPs. Compared to coated-type CSPs, immobilized CSPs significantly improved the solvent compatibility while maintaining similar chiral recognition abilities, but the introduction of excessive functional groups led to a deteriorated performance for columns. Moreover, a commercial drug, atenolol, was also sufficiently separated on the immobilized CSPs.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Cellulose is one of the most abundant natural materials and attracts wide interest due to its unique physical and chemical properties. Chemical modification of the hydroxyl groups of the anhydroglucose unit (AGU) in cellulose leads to the production of high value-added advanced materials, such as membranes (Amarasekara, Hasan, & Ha, 2016; Kofler et al., 2016; Tiraferri et al., 2011), biomimetic actuators (Cai, Hou, & Yang, 2012; Kim, Yun, & Ounaies, 2006; Kim, Jeon, Kim, Kee, & Oh, 2015; Li, Vadahanambi, Kee, & Oh, 2011), and chiral stationary phases (CSPs) for HPLC (Ikai & Okamoto, 2009; Okamoto & Yashima, 1998). The chiral recognition ability of cellulose was found in the paper chromatography in the middle 20th century. Dent (1948), Kotake, Sakan, Nakamura, and Senoh (1951)), and Dalgliesh (1952) successively observed the separation of racemic amino acids on paper chromatography. The chiral resolution ability of cellulose is attributed to its inherent chirality.

In 1973, Hesse et al. prepared the first practically useful CSP based on microcrystalline cellulose triacetate (Hesse & Hagel, 1973). Since the mid-1980s, the Okamoto group synthesized a number of cellulose and amylose esters, and cellulose and amylose phenylcarbamates with various substituents on the phenyl group and their chiral recognition abilities were evaluated (Okamoto, Aburatani, & Hatada, 1987; Okamoto, Aburatani, Hatano, & Hatada, 1988; Okamoto, Aburatani, Kaida, & Hatada, 1988; Okamoto, Kawashima, & Hatada, 1984; Okamoto, Kawashima, Yamamoto, & Hatada, 1984; Yamamoto et al., 2006). Among these CSPs, cellulose tris(3,5-dimethylphenylcarbamate) (CDMPC) and amylose tris(3,5-dimethylphenylcarbamate) showed a high chiral recognition for a broad range of compounds and nearly 80% of 500 tested racemates can be resolved on these CSPs (Yamamoto & Okamoto, 2004).

Cellulose-based CSPs are usually prepared by physically coating cellulose derivatives on mesoporous silica gel or zirconia (Chen, Okamoto, Yano, & Otsuki, 2007; Ikai, Yamamoto, Kamigaito, & Okamoto, 2007; Okamoto, 2009; Shen et al., 2010; Shen et al., 2013). For coated-type cellulose-based CSPs, the hexane/isopropanol mixture and the water/acetonitrile mixture are typically used as the nonpolar and polar mobile phase, respectively. In most cases, addition of good solvents for cellulose CSPs may enhance the separation

* Corresponding author.
E-mail address: sji@ciac.ac.cn (S. Ji).

http://dx.doi.org/10.1016/j.carbpol.2017.05.049
0144-8617/© 2017 Elsevier Ltd. All rights reserved.

efficiency of racemates. However, the coated-type cellulose-based CSPs can only be used with a limited range of mobile phases and are incompatible with solvents such as tetrahydrofuran (THF), chloroform, and acetone because these solvents can destroy the CSPs by dissolving cellulose derivatives. To solve the solvent compatibility issue, it is necessary to immobilize cellulose derivatives onto the solid support (Okamoto & Ikai, 2008; Zhang et al., 2005; Zhang, Nguyen, Franco et al., 2008; Zhang, Nguyen, Franco, Isobe et al., 2008).

Generally, there are two different types of immobilization approaches: 1) attaching the cellulose derivatives onto the solid support to form a brush layer (Chankvetadze, Ikai, Yamamoto, & Okamoto, 2004; Kitagawa et al., 2006) and 2) crosslinking the cellulose derivatives to form a mat (Chen, Qin, Liu, Huang, & Zou, 2004; Franco, Senso, Oliveros, & Minguillon, 2001; Francotte & Huynh, 2002; Okamoto, Aburatani, Miura et al., 1987; Qu et al., 2011; Shen et al., 2014). Both approaches require efficient functionalization of cellulose derivatives, but the introduction of functional groups onto cellulose derivatives may alter the regular helical structure of cellulose derivatives, which may lower the chiral recognition ability of CSPs. Therefore, it is critical to control the amount and distribution of reactive groups on cellulose derivatives to obtain a CSP with high chiral recognition ability.

In the present study, we developed a homogeneous approach to synthesizing carboxylic acid functionalized CDMPC (CC-X) with controlled amounts of carboxylic acid groups through the reaction between 10-bromodecanoic acid and —NH— in the carbamate group catalyzed by NaH. Condensation of CC-X with amine-modified silica gel gave a series of immobilized CSPs that were evaluated for the separation of racemates with a hexane/isopropanol (90/10, *V*/*V*) mobile phase. The solvent compatibility of the immobilized CSPs was also investigated by addition of good solvents, e.g. THF and chloroform, for cellulose derivatives into the mobile phase. Compared to the coated-type CSPs, the immobilized CSPs had comparable chiral recognition ability but with higher solvent compatibility.

2. Experimental

2.1. Reagents and materials

Cellulose (Avicel® PH-101) was purchased from Fluka and dried at 140 °C for 2 h under vacuum before use. 3,5-Dimethylphenyl isocyanate, 10-bromodecanoic acid, NaH (60% in mineral oil), 1-(9-anthryl)-2,2,2-trifluoroethanol (*1*), trans stilbene oxide (*2*), troger's base (*3*), benzoin (***4***), 2-phenylcyclohexanone (*5*) and flavanone (*6*) were purchased from Sigma Aldrich. The mesoporous amine-modified silica gel (Lot No. KU50308, NH2 SPS 100-5, carbon content: 3.8 wt%, nitrogen content: 1.4 wt%) with a mean particle size of 5 μm and a mean pore diameter of 100 Å was purchased from Fuji Silysia Chemical Ltd. *n*-Hexane, isopropanol, methanol, THF and chloroform in HPLC grade were purchased from TEDIA Company Inc, USA. *N*-Ethyoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (EEDQ), 1-bromopropane, petroleum ether and ethyl acetate were purchased from Aladdin and used as received. Pyridine, *N,N′*-dimethylformamide (DMF), acetone and THF were distilled after CaH_2 treatment. All other materials were used without further purification.

2.2. Synthesis of N-methylcarbonyl-N-propyl-3,5-dimethyl aniline (SB)

As shown in Scheme S1, 3,5-dimethylphenyl isocyanate (0.5 mL, 3.55 mmol) was dissolved in methanol (25 mL), the mixture was stirred under a nitrogen atmosphere at 25 °C for 24 h. Methanol was evaporated and the crude product was purified by silica gel column (petroleum ether/EtOAc, 10/1) to give (3.5-dimethylphenyl)carbamic acid methyl ester (SA) as a white crystal (0.62 g, 97%). ^{1}H NMR and HRMS spectra were shown in Figs. S1 and S2, respectively.

SA (0.5 g, 2.79 mmol) was dissolved in DMF (5 mL) and NaH (60% in mineral oil, 0.22 g, 5.58 mmol) was added in one portion at ambient temperature. After being stirred for 15 min, 1-bromopropane (0.69 g, 5.58 mmol) was added to the suspension via syringe, and the mixture was stirred at room temperature for 12 h. 6 M HCl (~1.5 mL) was then added to acidify the suspension. The mixture was filtered to remove NaCl and the crude product was recrystallized from DMF solution to give a white crystalline *N*-methylcarbonyl-*N*-propyl-3,5-dimethyl aniline (SB) in 93% yield. ^{1}H NMR and HRMS spectra were shown in Figs. S1 and S3, respectively.

2.3. Synthesis of carboxylic acid functionalized cellulose tris(3,5-dimethylphenylcarbamate) (CC-X)

CDMPC was prepared according to a modified literature method (Okamoto, Kawashima, Hatada et al., 1984). Cellulose (3.0 g, 18.5 mmol AGU) was suspended in pyridine (60 mL) and the flask was purged with nitrogen for 15 min at room temperature. 3,5-Dimethylphenyl isocyanate (15.0 mL, 107 mmol, 2 equiv relative to the hydroxyl groups of cellulose) was added to the suspension via syringe. The mixture was stirred at 110 °C under a nitrogen atmosphere for 24 h. Cellulose gradually dissolved as the reaction proceeded. The viscous solution was then precipitated into methanol (~300 mL), and the filtered precipitate was dissolved in acetone, and precipitated in methanol to give 10.0 g (91%) of CDMPC (Fig. 1a). The degree of substitution of CDMPC was >98%, as determined by ^{1}H NMR analysis. The molecular weight (M_n) and polydispersity index (PDI) of CDMPC were determined by gel permeation chromatography (GPC) with THF as the eluent. M_n, relative to a polystyrene standard, and PDI were 53,000 g/mol and 3.39, respectively.

Carboxylic acid functionalized cellulose tris(3,5-dimethylphenylcarbamate) (CC-X), where X is the percentage of the carbamate group functionalized with carboxylic acid, was then synthesized by derivertizing CDMPC with 10-bromodecanoic acid. In a representative synthesis of CC-0.7, CDMPC (3.0 g, 15.0 mmol of carbamate groups) was dissolved in DMF (30 mL), and NaH (60% in mineral oil, 240 mg, 6.0 mmol) was then added to the solution at ambient temperature. The suspension was stirred for 1 h, followed by addition of 10-bromodecanoic acid (88 mg, 0.35 mmol) in 15 mL of DMF via syringe. The mixture was stirred at room temperature for 12 h. The reaction mixture was acidified using 6 M HCl (~3 mL) and the suspension was precipitated in a mixture of methanol/hexane (20/1, *V*/*V*). The precipitate was dissolved in acetone and reprecipitated in methanol to give CC-0.7 (2.4 g, 80%).

2.4. Preparation of cellulose derivatives coated silica gel

In a typical procedure, CDMPC (0.44 g) was dissolved in THF (15 mL) and amine-modified silica gel (2.0) was then added to the solution to form a suspension by sonication for 10 min. The solvent was slowly removed in a rotavap under a controlled constant vacuum (2.0×10^{-2} MPa) for 1–2 h to give coated CSPs with 18% loading of cellulose derivatives.

2.5. Immobilization of cellulose derivatives onto silica gel

The immobilization process is illustrated in Fig. 2. In a typical procedure, CC-0.7 (0.95 g) and EEDQ (0.2 mmol, 50 mg) were dis-

Download English Version:

https://daneshyari.com/en/article/5156702

Download Persian Version:

https://daneshyari.com/article/5156702

Daneshyari.com