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Preparation and Chiral Recognition Ability of Crystalline Cellulose Phenylcarbamate

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Abstract As one of the most popular polysaccharide derivatives with high chiral recognition ability, cellulose tris(3,5-dimethylphenylcarbamate) (CDMPC) has been successfully applied in the enantioseparation of a wide range of racemates for various purposes. However, the derivative is usually synthesized with an amorphous structure, and its effect on enantioseparation ability remains obscure. To obtain a better understanding of the correlation between its structure and enantioseparation ability, in this study, CDMPC derivatives with crystalline and amorphous structures were prepared through carbamoylation followed by anti-solvent precipitation. Their chiral recognition abilities were evaluated using high-performance liquid chromatography (HPLC) with chiral stationary phases (CSPs). Interestingly, the ordered arrangement of the helical polymer chains of CDMPC was effectively induced by the aromatic solvent after derivatization, forming a crystalline derivative (**c-CDMPC**) with a uniform and compact worm-like morphology, whereas the amorphous derivative (**a-CDMPC**) was obtained by regular treatment with a polar alcoholic solvent. The **c-CDMPC**–based CSP exhibited higher chiral recognition abilities with much shorter retention times for most racemates in this study, compared to the **a-CDMPC**–based CSP. In particular, flavanone (**Rac-7**), an important chiral drug with anti-inflammatory, anti-tumor, and cardiovascular protective activities, was even better resolved with higher enantioselectivity on crystalline **c-CDMPC** than on Chiralcel OD, a commercialized chiral column based on CDMPC. This indicates that the crystalline ordered arrangement played a critical role in the chiral recognition ability of the cellulose derivative.

Keywords Cellulose derivative; Crystalline structure; Chiral recognition; Enantioseparation; Ordered arrangement

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INTRODUCTION

As one of the naturally available chiral polymers on earth, cellulose macromolecules possess abundant natural resources as well as attractive structural advantages, making them ideal candidates for the preparation of chiral functional materials for various purposes.[1–5] Owing to the regular helical backbone and reactive hydroxyl groups on glucose units, a large number of cellulose derivatives have been developed for chiral recognition *via* different modifications.[6–8] Among these, the development of cellulose phenylcarbamate derivatives and their application as chiral stationary phases (CSPs) for high-performance liquid chromatography (HPLC) has recently achieved significant success.[9–14] In particular, cellulose tris(3,5-dimethylphenylcarbamate) (CDMPC) exhibits powerful chiral recognition ability for a wide range of chiral compounds, including pharmaceuticals, agrochemicals, and food additives.[15–19] Until now, more than 80% of racemic compounds have been efficiently resolved, playing a pivotal role in enantiomeric excess (*ee*) determination and enantioseparation both in analytical- and industrial-scale preparations of optically pure enantiomers. Systematic investigations of the chiral recognition mechanism of cellulose derivatives, especially those of cellulose phenylcarbamates, indicated some close associations between the secondary structure of the derivatives and their chiral recognition abilities. It has been empirically established that their enantioseparation abilities greatly depend on the polymer backbone and the nature and structure of the substituents on the aromatic moieties.[20–23]

Although cellulose derivatives exhibit remarkable advantages in enantiomeric separation, most reported derivatives are fabricated in an amorphous state, lacking long-range order in the polymer chain arrangement. This limitation is restricted, to a certain extent, by the precise matching of chiral recognition sites and the efficiency of intermolecular interactions.[24,25] Only a few cellulose derivatives with specific structures (such as cellulose phenylcarbamate derivatives bearing bulky *para*-substituted benzothienyl or benzofuranyl pendants) can form liquid crystalline phases under specific conditions, and their chiral recognition properties can be improved by relatively regular aggregate structures.[19,26] However, the formation conditions of such liquid crystalline materials are harsh and their stability is limited, which makes it dif-

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ficult to meet the separation requirements in complex scenarios. On the other hand, in recent years, significant progress has been made in the study of crystalline chiral recognition materials, including chiral metal-organic frameworks, covalent organic frameworks and chiral porous organic cages.[27–32] Relying on long-range ordered crystalline structures, a definite arrangement of chiral recognition sites, and a stable chiral microenvironment, these materials were able to establish more selective interactions with enantiomers and exhibited better separation performance than amorphous materials in the resolution of some chiral compounds.[33–39] The ordered arrangement of the polymer chains is a valuable tool for enhancing the chiral recognition properties of polysaccharide derivatives. However, the preparation of crystalline cellulose derivatives has rarely been reported, and the correlations between the crystalline structure and their chiral recognition ability remain unclear.

To investigate the effect of the crystalline structure of the cellulose derivative on the chiral recognition ability and to develop novel polysaccharide derivatives with good enantioseparation ability, crystalline and amorphous states were prepared through carbamoylation followed by anti-solvent precipitation. The structures and morphologies of the two types of CDMPC derivatives were characterized by ^{1}H-NMR, XRD, and SEM. Their chiral recognition abilities were carefully examined as coated-type CSPs using HPLC. The influence of the crystalline structure on the chiral recognition ability of CDMPCs was further studied. The enantioseparation abilities of the two derivatives were also compared with those of the commercially available Chiralcel OD, which is a CDMPC-based chiral column with powerful chiral recognition ability.

EXPERIMENTAL

Chemicals

Cellulose (Avicel, DP=200) was supplied by Daicel Corporation (Tokyo, Japan). *N*,*N*-dimethylacetamide (DMAc), lithium chloride (LiCl), and pyridine were purchased from Guangfu Chemical (Tianjin, China). 3,5-Dimethylphenyl isocyanate, used for cellulose derivatization, was obtained from Energy Chemical (Shanghai, China). Methanol, benzene, dimethylbenzene, and tetrahydrofuran (THF) were purchased from Aladdin (Shanghai, China). Wide-pore silica gel (Daiso gel SP-1000) with a mean particle size of 7 μm and mean pore diameter of 100 nm was kindly gifted by Osaka Soda (Osaka, Japan) and silanized with (3-aminopropyl)triethoxysilane in toluene at 80 °C. All solvents were of analytical reagent grade and dehydrated by fractional distillation prior to use. The racemic compounds used in the experiments were commercially available and their purities met the requirements for HPLC enantioseparation.

Synthesis of Crystalline and Amorphous Cellulose Derivatives

As illustrated in Fig. 1, CDMPC was readily synthesized *via* a one-pot process, according to a previously reported method.[22] After the reaction finished, the mixture was first cooled to room temperature and then isolated through the anti-solvent precipitation procedure using two different solvents, dimethylbenzene and methanol. After sufficient washing with the two solvents, the dimethylbenzene-insoluble fraction and methanol-insoluble fraction were collected as the target products, **c-CDMPC** and **a-CDMPC**, with yields of 86.0% and 85.6% , respectively.

Preparation of Chiral Stationary Phases (CSPs)

According to a previous method, the two obtained cellulose derivatives were dissolved in THF and coated onto aminopropylsilanized silica gel, and the resulting CSPs were designated as **CSP-c-CDMPC** and **CSP-a-CDMPC**, respectively.[22] The silica gels coated with the above derivatives were packed into stainless-steel columns (25 cm × 0.20 cm i.d.) using a slurry technique.

The plate numbers of the two packed columns were measured as 2200 and 2400 for benzene using a mixture of hexane/2-propanol (90/10, *V*/*V*) as the mobile phase at a flow rate of 0.1 mL/min. 1,3,5-Tri-tert-butylbenzene was used as the non-retained compound to determine the dead time (t_0).[40]

Characterization

The ^{1}H-NMR spectra of the cellulose derivatives were recorded on a Bruker 500 MHz spectrometer using pyridine-d_5 as the solvent.

The crystalline structures of cellulose derivatives with different aggregate states were characterized by X-ray diffraction (XRD) on a Rigaku D/Max-TTRIII diffractometer (Japan) in the reflection mode.

The SEM morphologies of cellulose derivatives with different aggregate states were observed using a Hitachi SU8010 field-emission scanning electron microscope (FE-SEM, Japan).

Chromatographic experiments were performed on a JASCO PU-2089 high-performance liquid chromatograph equipped with a JASCO UV-2070 UV-Vis detector, JASCO CD-2095 circular dichroism detector, and JASCO AS-2055 intelligent sampler.

RESULTS AND DISCUSSION

The Structures of Crystalline and Amorphous Cellulose Derivatives

The ^{1}H-NMR spectra of the two cellulose derivatives were

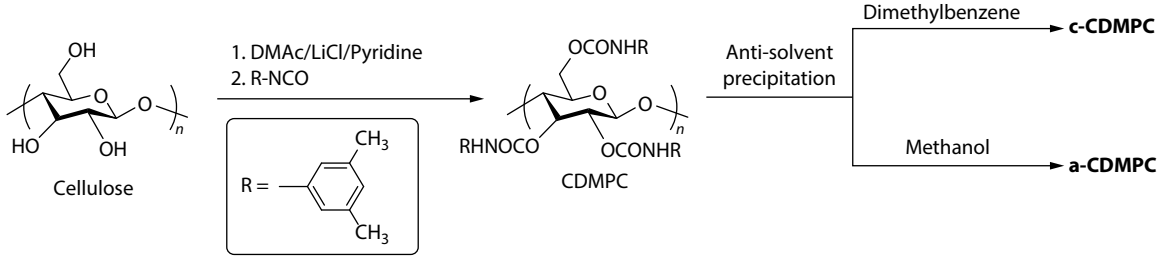

Fig. 1 Scheme for the synthesis of crystalline and amorphous cellulose derivatives.

recorded and analyzed. Fig. 2 displays the ^{1}H-NMR spectra of CDMPCs, in which the characteristic resonance peaks of protons on the glucose units and the N—H of carbamate moieties could be clearly assigned to both **a-CDMPC** and **c-CDMPC**. For **a-CDMPC**, as the cellulose derivative obtained from the conventional treatment using methanol as the solvent, the resonance peaks observed in the range of 3.10–5.70 ppm were assigned to the protons on the glucose units, corresponding sequentially from low field to high field to H3, H2, H1, H6, H4 and H5, respectively, and the peaks of N—H protons of the carbamate groups appeared in the range of 8.9–10.4 ppm.[41,42] Interestingly, compared with **a-CDMPC**, the resonance peaks from protons on the glucose units and the N—H of crystalline **c-CDMPC** shifted to varying degrees. The proton peaks of H2, H3, and H5 in the glucose unit shifted downfield, whereas those of H4 shifted upfield, and the H6 proton peak clearly split into two peaks. In addition, the two N—H proton peaks shifted to a lower field, accompanied by a new shoulder peak at 10.23 ppm. The above spectral differences were probably related to the structural variations between **c-CDMPC** and **a-CDMPC** owing to the different arrangements of the polymer chains.[43]

In addition, compared with the amorphous **a-CDMPC**, the resonance peaks of H_2O in **c-CDMPC** shifted to a lower field, indicating that the deshielding effect on H_2O protons was enhanced in the system formed by the crystalline derivative. It is likely that stronger hydrogen bonding interactions occurred between crystalline **c-CDMPC** and H_2O, which is favorable for improving the chiral recognition ability of the cellulose derivative. Moreover, the degree of substitution of 3,5-dimethylphenylcarbamates in both cellulose derivatives was not altered during the anti-solvent precipitation process, which was determined to be the same at 95.6% for both derivatives.

The crystalline structures and aggregation states of the cellulose derivatives were further characterized by XRD. The XRD patterns of **a-CDMPC** and **c-CDMPC** are shown in Fig. 3. For comparison, the microcrystalline cellulose pattern is also included in the figure. As shown in Fig. 3(a), microcrystalline cellulose exhibits typical cellulose I crystalline characteristic diffraction peaks, appearing at diffraction angles (2θ) of 14.8°, 22.3°, and 34.5°.[44] In contrast to cellulose, in Fig. 3(c), it can be observed that **c-CDMPC** showed much sharper and intense diffraction peaks at 2θ values of 30.1°, 32.9°, and 34.9°, accompanied by several weak diffraction peaks at higher an-

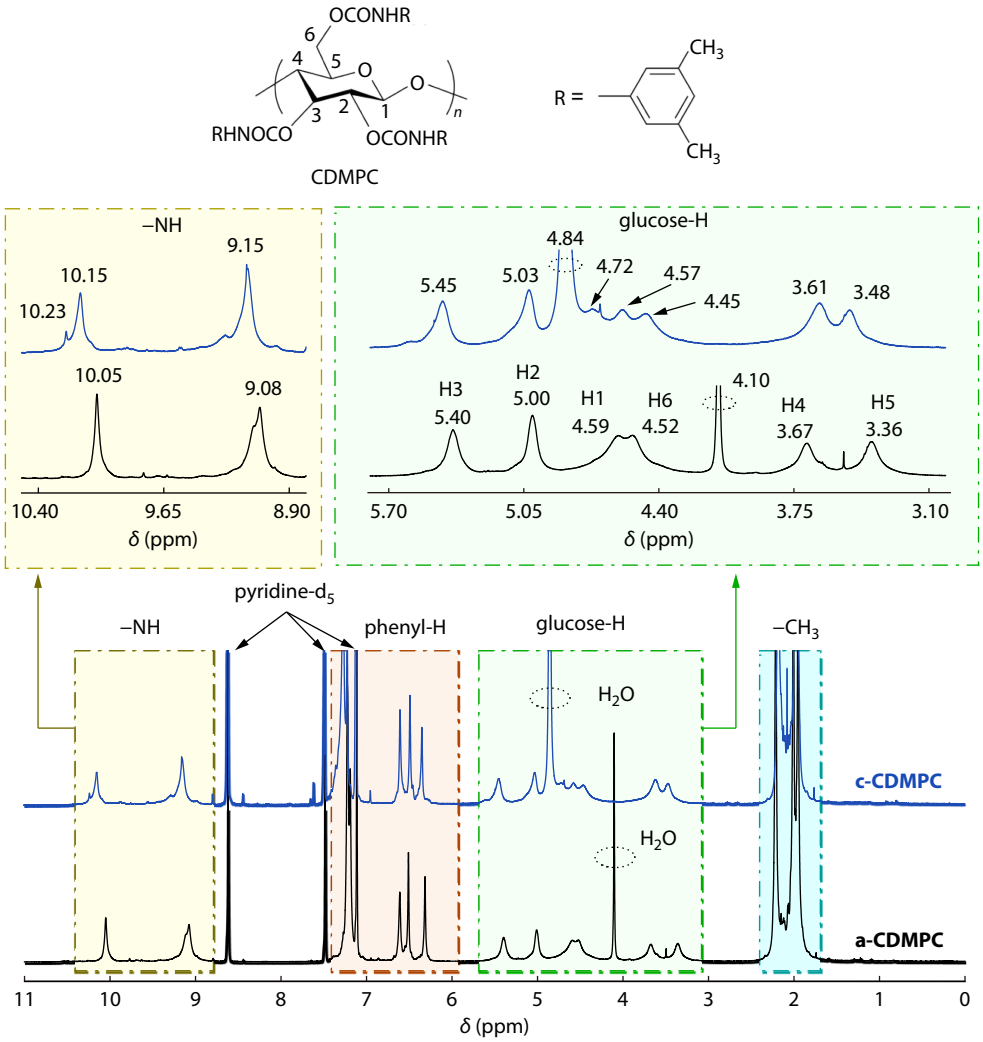

Fig. 2 ^{1}H-NMR spectra of cellulose derivatives in pyridine-d_5 at 80 °C (500 MHz).

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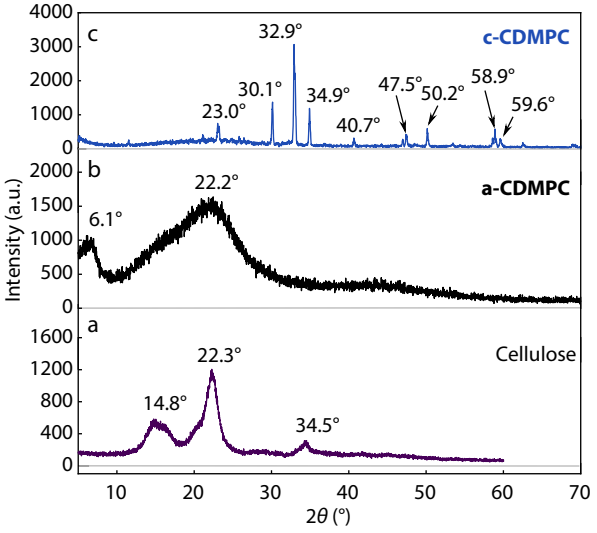

Fig. 3 XRD patterns of (a) cellulose, (b) **a-CDMPC** and (c) **c-CDMPC**.

gles. This indicated that a crystalline CDMPC derivative with a more ordered arrangement than that of microcrystalline cellulose was successfully prepared by anti-solvent precipitation in this study. In contrast, the XRD pattern of **a-CDMPC** (Fig. 3b) showed much broader and more diffuse peaks than those of microcrystalline cellulose, as found within the 2θ range of 5°–35°, the maximum diffraction intensities of which were located at 2θ=6.1° and 22.2°, respectively.[45] This suggests that the carbamoylation reaction probably disrupted the original orderly structure of cellulose, generating a mainly amorphous derivative, **a-CDMPC**. Because of the disordered structure, **a-CDMPC** exhibits higher solubility than **c-CDMPC** in common organic solvents such as pyridine, THF, and DMSO. For instance, **a-CDMPC** showed saturated solubility in pyridine (145 mg/mL) at room temperature, whereas **c-CDMPC** hardly dissolved in pyridine at room temperature and reached a solubility of 115 mg/mL after heating to higher than 40 °C.

From the above, it was revealed that crystalline CDMPC with an ordered arrangement of polymer chains was successfully obtained through anti-solvent precipitation using the aromatic solvent, dimethylbenzene. However, the polar alcohol methanol could only unfavorably form the amorphous structure of the derivative, although it did not influence the degree of substitution of phenylcarbamates as the usual solvent for the post-treatment of polysaccharide derivatives.

Morphological Characterization of Crystalline and Amorphous Cellulose Derivatives

To directly visualize the morphological differences between crystalline and amorphous cellulose derivatives, scanning electron microscopy (SEM) was employed for the systematic characterization of the two derivatives, and the results are shown in Fig. 4. As shown in Fig. 4(a), the amorphous derivative **a-CDMPC** was composed of irregular particles with sizes smaller than 1 μm arranged in a disordered and random style. Nevertheless, crystalline **c-CDMPC** exhibited highly regular worm-like crystalline morphologies, revealing that the precipitation process using a suitable aromatic solvent could effectively induce the ordered arrangement of polymer chains, successfully leading to the formation of a crystalline structure for the cellulose derivative.

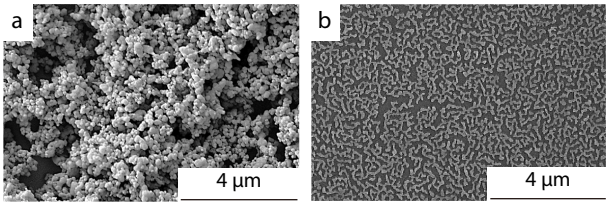

Fig. 4 SEM images of (a) **a-CDMPC** and (b) **c-CDMPC**.

The Structures of CDMPC-based CSPs

To further investigate the influence of the coating process of the chiral stationary phases on the aggregation states of the cellulose derivatives, the obtained coated-type CSPs were characterized by XRD again, and the results are shown in Fig. 5. The coating efficiencies (weight ratio of derivative to silica gel) of the two CSPs were 18.5% and 18.7%, respectively. It was found that **CSP-a-CDMPC** exhibited only a characteristic diffuse peak at 2θ=22.4°, which is a typical pattern of amorphous silica gel. However, for **CSP-c-CDMPC**, a distinct sharp crystalline peak was observed at 26.7° in addition to that of the silica peak, which varied from the XRD pattern of the original **c-CDMPC**, suggesting that recrystallization occurred after coating the derivative onto the silica gel, and a new crystalline ordered structure was formed during the preparation of the coated-type CSP. This phenomenon was in accordance with the improved enantioseparation ability of **CSP-c-CDMPC** as discussed later. The correlation between the crystalline structure and chiral recognition ability of coated CSPs is still in progress and will be reported in detail in due time.

Enantioseparation Abilities of c-CDMPC and a-CDMPC

The enantioseparation abilities of two CDMPC derivatives (**c-CDMPC** and **a-CDMPC**) with different structures were carefully evaluated by HPLC using nine racemates (Fig. 6), and the de-

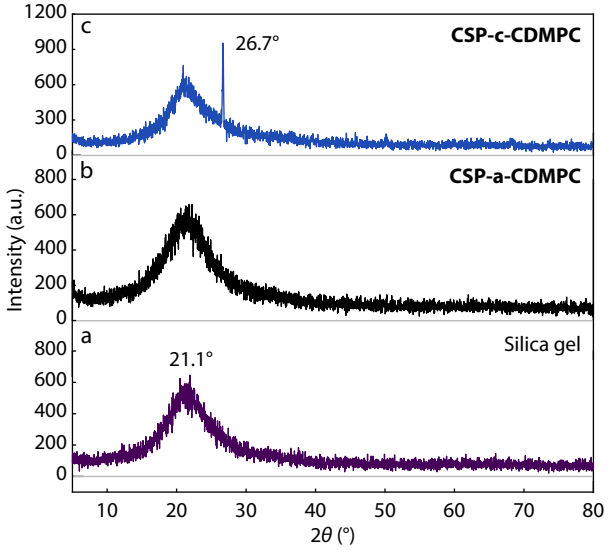

Fig. 5 XRD patterns of (a) silica gel, (b) **CSP-a-CDMPC** and (c) **CSP-c-CDMPC**.

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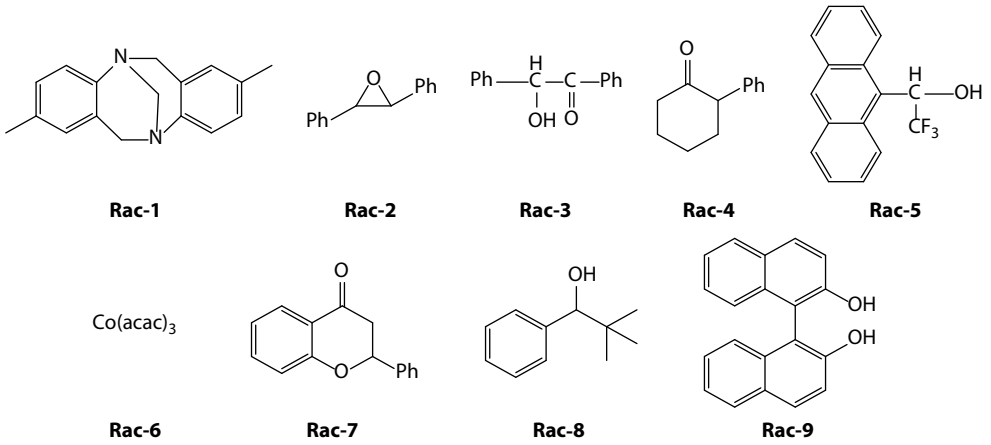

Fig. 6 Structures of the nine racemates **Rac-1**–**Rac-9**.

Table 1 Resolution of nine racemates on cellulose derivatives and Chiralcel OD.

CSPs	**CSP-a-CDMPC** [a]		**CSP-c-CDMPC** [a]		Chiralcel OD [b]	
Racemates	k_1	α	k_1	α	k_1	α
1	0.84(+)	1.19	0.66(+)	1.20	1.05(+)	1.26
2	1.01(–)	1.24	0.47(–)	1.70	0.78(–)	2.11
3	2.22(+)	1.45	1.33(+)	1.58	2.44(+)	1.57
4	1.11(–)	1.11	0.74(–)	1.10	1.17(–)	1.15
5	2.11(–)	1.92	1.45(–)	2.35	2.33(–)	2.59
6	0.52(+)	about 1	0.29(+)	about 1	3.15(+)	about 1
7	1.11(–)	1.30	0.88(–)	1.37	1.13(–)	1.26
8	0.64(+)	1.25	0.42(+)	1.27	–	–
9	4.51(+)	about 1	2.70(+)	about 1	9.56(+)	1.06

[a] Columns: 25 cm × 0.20 cm ID. Flow rate: 0.1 mL/min. Eluent: hexane/2-propanol (90/10 *V*/*V*). The signs in parentheses represent CD signals of the first eluted enantiomer. [b] Data taken from Ref. [46].

tailed results are summarized in Table 1. For comparison, the resolution results obtained on a commercial chiral column, Chiralcel OD, using CDMPC as the chiral selector are also included in Table 1.[46]

In general, the two cellulose-based CSPs exhibited good chiral recognition ability for seven of the nine racemates tested in this study. Interestingly, compared with amorphous **CSP-a-CDMPC**, crystalline **CSP-c-CDMPC** showed superior enantioseparation abilities for six racemates (**Rac-1**, **Rac-2**, **Rac-3**, **Rac-5**, **Rac-7** and **Rac-8**) with higher enantioselectivity. This indicated that the higher-order arrangement could effectively improve the chiral recognition ability of the cellulose derivative, which was in good agreement with previously reported observations.[47] However, both CSPs exhibited the same elution order for all the tested racemates. This indicates that the chiral recognition mechanism was not significantly influenced by the crystalline structure of the cellulose derivatives.

Fig. 7 displays typical chromatograms for the enantioseparation of 2,2,2-trifluoro-1-(9-anthryl)ethanol (**Rac-5**) on both **CSP-a-CDMPC** and **CSP-c-CDMPC**. Using 1,3,5-tri-tert-butylbenzene as a non-retained compound, the dead times (t_0) were determined to be 7.38 and 7.69 min for the two CSPs, respectively. Based on the retention times t_1 and t_2 of the enantiomer pairs, the retention factors $k_1 = (t_1–t_0)/t_0$ and $k_2 = (t_2–t_0)/t_0$ were calculated, and the separation factor $\alpha = k_2/k_1$ was obtained. The separation factors for **Rac-5** on **CSP-a-CDMPC** and **CSP-c-CDMPC** were estimated to be 1.92 and

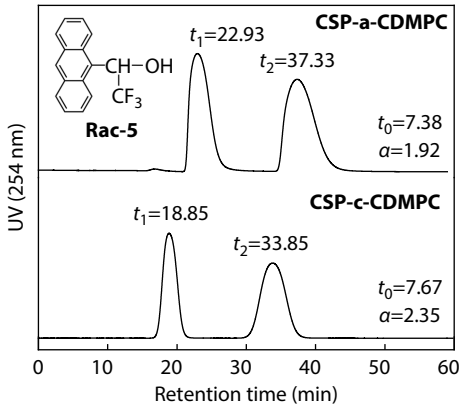

Fig. 7 Chromatograms for **Rac-5** resolution on **CSP-a-CDMPC** and **CSP-c-CDMPC**.

2.35, respectively. This demonstrated that the chiral anthryl compound was successfully baseline resolved on both cellulose-based CSPs, and a higher enantioseparation efficiency was achieved on **CSP-c-CDMPC** than on **CSP-a-CDMPC**, including higher enantioselectivity and shorter retention time. This implies that the crystalline ordered structure of the former was more favorable for improving the chiral recognition ability of the cellulose derivative.

More evidence on the improvement in the enantioseparation efficiency of **CSP-c-CDMPC** can be found in Table 1. In addition to the higher enantioselectivity for the six race-

mates, the retention times for all tested compounds were significantly shorter on crystalline **CSP-c-CDMPC** than on **CSP-a-CDMPC**. Furthermore, compared to the powerful commercially available Chiralcel OD, the former CSP also possessed comparable or better enantioseparation capabilities with much shorter retention times, indicating the clear advantage of crystalline **CSP-c-CDMPC**. This may be closely associated with the long-range ordered arrangement of the crystalline structure, which provides more stable and specifically selective interaction sites for chiral recognition.[29,31] It is worth mentioning that flavanone (**Rac-7**), an important chiral drug, could be better resolved with much higher enantioselectivity on **CSP-c-CDMPC** than on Chiralcel OD. Owing to its multiple pharmacological activities, including anti-inflammatory, antitumor, and cardiovascular protective effects, large-scale preparation of pure enantiomers of this chiral drug is in high demand for the clinical treatment of hepatitis, cirrhosis, and cardiovascular diseases.[48–51] The crystalline cellulose derivative prepared in this study may be a useful tool for the enantioseparation of other chiral compounds, including chiral pharmaceuticals, highlighting the great application potential of chiral recognition materials with crystalline structures.

CONCLUSIONS

In this study, two cellulose tris(3,5-dimethylphenylcarbamate) derivatives with crystalline and amorphous structures were successfully prepared *via* anti-solvent precipitation using different solvents. The structures, crystalline properties, and morphologies of the derivatives were characterized using ^{1}H-NMR, XRD, and SEM. The influence of the crystalline structure of CDMPC derivatives on their chiral recognition abilities was systematically investigated. It was verified that the ordered crystalline arrangement of the polymer chains of CDMPC could be effectively induced by aromatic dimethylbenzene after derivatization, forming a crystalline **c-CDMPC** with uniform and compact worm-like morphology, whereas the amorphous derivative, **a-CDMPC**, was obtained by regular treatment with polar alcoholic methanol. Interestingly, the CSP derived from **c-CDMPC** possessed higher enantioseparation efficiency with higher enantioselectivity and much shorter retention times for most racemates compared to those of **a-CDMPC**. Crystalline CSP-**c-CDMPC** also exhibited comparable or better enantioseparation capabilities with much shorter retention than Chiralcel OD, indicating the clear advantage of crystalline **CSP-c-CDMPC**. This suggests that the ordered crystalline arrangement probably exerts a crucial effect on the chiral recognition ability of the cellulose derivative, favoring more stable and selective interactions for enantioselective recognition. An important chiral drug, flavanone (**Rac-7**), was better resolved on crystalline **c-CDMPC** than on Chiralcel OD, implying that crystalline **c-CDMPC** may have promising potential for the enantioseparation of some chiral compounds, including chiral pharmaceuticals, especially for the large-scale preparation of pure enantiomers. This study provides a new strategy for the development of crystalline cellulose derivatives with high chiral recognition ability and provides a preliminary understanding of the correlation between the crystalline ordered arrangement and chiral recognition ability of cellulose derivatives.

Conflict of Interests

The authors declare no interest conflict.

Data Availability Statement

The related data of this study is data that should not be shared, and can be obtained from the author for reasonable reasons. The author's contact information: shenjun@ustb.edu.cn.

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Graphical Abstract

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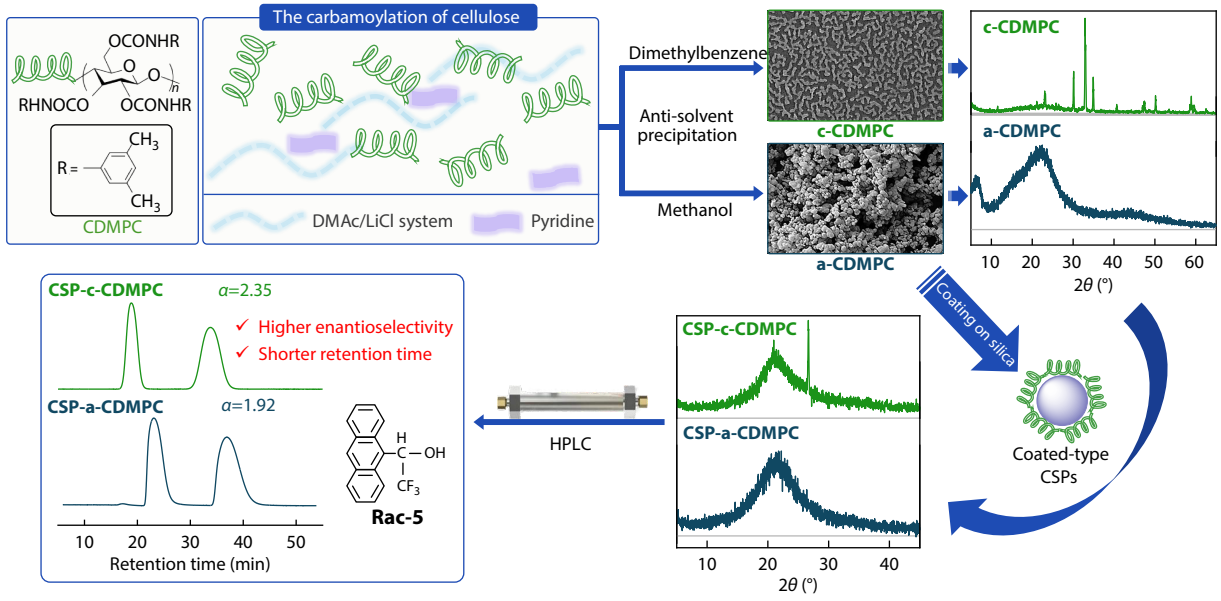
Crystalline cellulose tris(3,5-dimethylphenylcarbamate) exhibited higher chiral recognition abilities with shorter retention times than amorphous derivative and Chiralcel OD. The ordered crystalline arrangement played a crucial role in chiral recognition.



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