

Synthesis and Lyotropic Behavior of Mesogen-Linked Cellulose Acetates

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ABSTRACT: Three aromatic (*p*-carboxyl phenyl) esters, 4-(benzoyloxy) benzoic acid, 4-(4'-methylbenzoyloxy) benzoic acid, and 4-(4'-chlorobenzoyloxy) benzoic acid, were synthesized and they showed nematic monotropic or thermotropic behavior. The mesogen-linked cellulose acetates were first prepared by the reaction of aromatic (*p*-carboxyl phenyl) esters with cellulose acetate through esterification in the presence of *N,N*-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP). Their degrees of meso-

genic unit substitution (DS_{meso}) were between 0.27 and 0.41. It was found that they can form cholesteric lyotropic phases in dichloroacetic acid and their critical concentration was about 25 wt %. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2693–2697, 2004

Key words: synthesis; lyotropic; cellulose acetate; mesogen; cholesteric

INTRODUCTION

Many cellulose derivatives have been synthesized since the liquid crystallinity of hydropropyl cellulose was recognized in 1976,¹ and such derivatives can form lyotropic cholesteric liquid crystalline phases in a variety of solvents. For example, ethyl-cyanoethyl cellulose can form cholesteric liquid crystals in many solvents, such as dichloroacetic acid (DCA)² and acrylic acid (AA).³ Cellulose 4-methylphenyl urethane exhibits cholesteric liquid crystalline properties in *N*-vinyl pyrrolidinone (NVP) solutions when the polymer concentration is above 35 wt %.⁴ Acetoacetoxypropyl cellulose can form lyotropic phases in acetic acid solution.⁵ In the above investigations, the substituents introduced into the cellulose backbone are nonmesogenic. Recently, the rigid and bulky 4-phenyl-benzoyl group was reported to be introduced to the cellulose backbone and this cellulose derivative can form liquid crystalline phases in *N,N*-dimethylacetamide (DMAc), 1,2-dichloroethane, chloroform, and tetrahydrofuran (THF).⁶ Due to the semi-rigid main chain, the chemical structure of mesogen-linked celluloses is similar to the combined type liquid

crystalline polymers that contain mesogenic units in both main and side chains.^{7,8}

Cellulose acetate (CA) has been known to form cholesteric liquid crystals in some solvents,^{9,10} but to date the lyotropic liquid crystalline properties of mesogen-linked cellulose acetates have not been reported. In this work, three aromatic (*p*-carboxyl phenyl) esters were synthesized and they showed monotropic or thermotropic behavior. The mesogen-linked cellulose acetates were first prepared by the esterification reaction of aromatic (*p*-carboxyl phenyl) esters with cellulose acetate and the lyotropic behavior of the mesogen-linked cellulose acetates was discussed.

Experimental

Materials

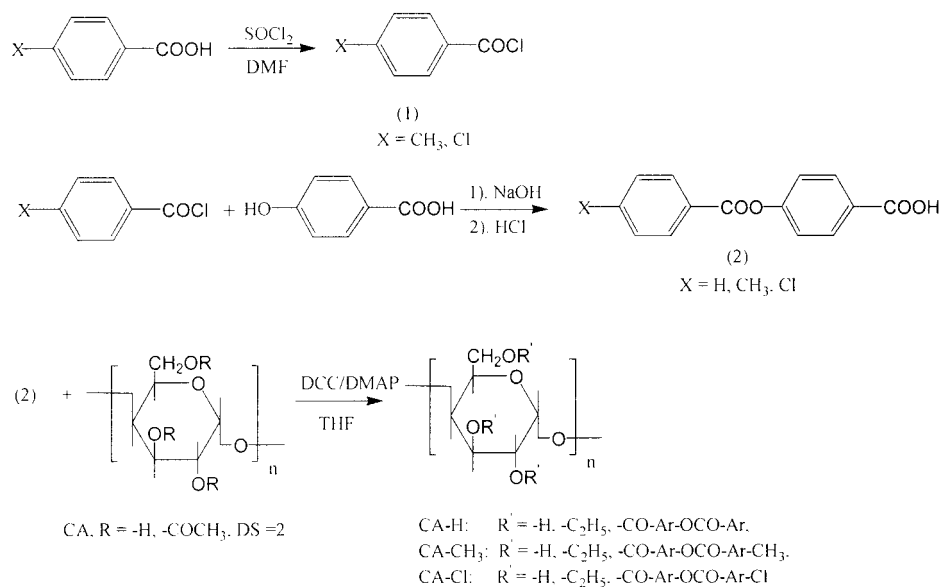
CA with acetyl content of 35% was purchased from Shanghai Factory of Cellulose Acetate (China). *p*-Toluic acid, *p*-chlorobenzonic acid, benzoic chloride, and *p*-hydroxybenzoic acid were analytical reagents (AR) obtained from Beijing Chemical Reagent Company (China). DCC and 4-dimethylaminopyridine (DMAP) were used as received (Arcos). THF was distilled from sodium-benzophenone. Other solvents and reagents were AR grade and were without further purification.

Characterization

Chemical structures of intermediates and polymers were characterized by using a FT-IR spectrometer

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Scheme 1 Synthetic route of mesogen-linked cellulose acetates.

(Bruker EQUINOX55), the $^1\text{H-NMR}$ spectrum was recorded by using Bruker spectrometer (300MHz) with tetramethylsilane as an internal standard, and MS analysis was carried out with an AEI mass spectrometer (MS-50) using the electron ionization method (EI, 70 ev). The melting point and liquid crystalline phase transition of intermediates were determined by means of an Olympus Model BH-2 polarized optical microscope (POM) equipped with a mettler FP-5 hot stage with a heating or cooling rate of $1^\circ\text{C}/\text{min}$. The lyotropic liquid crystalline texture of polymers was studied using the same POM.

Synthesis

The synthesis route of mesogen-linked cellulose acetates is as follows (see Scheme 1).

Aromatic acid chloride [compound (1)]

First, 0.1M aromatic acid was added to a 100-mL round-bottom flask equipped with a reflux condenser and magnetic stirrer and then 25 mL thionyl chloride and two drops of DMF were added to the flask. After the reaction mixture was refluxed for 2–3 h, it was distilled and the desired fraction was collected.

X=CH₃, *p*-toluoyl chloride: bp 225–227°C, yield 68%.

X=Cl, *p*-chlorobenzoic chloride: bp 222–224°C, yield 65%.

Aromatic (*p*-carboxyl phenyl) esters [Compound (2)]

p-Hydroxybenzoic acid (0.1M) and 100 mL 2N NaOH aqueous solution were added to a 500-mL three-neck round-bottom flask and stirred until *p*-hy-

droxybenzoic acid was completely dissolved. Aromatic acid chloride (0.1M) then was added dropwise to the flask with vigorous stirring. The solution was stirred for 2 hours after the acid chloride was added and then was neutralized with concentrated hydrochloric acid. A white precipitate was filtered, washed with cooled and boiled water three times, and then recrystallized from acetic acid twice.

X=H, 4-(benzoyloxy) benzoic acid: mp 227–228°C,¹¹ mp 232.2–232.6°C. Liquid crystalline phase transition: I 224°C N180°C K (in cooling). Yield 54%.

FT-IR (KBr, cm^{-1}): 3,450 (–OH); 1,736; 1,702 (–C=O); 1,604, 1,507 (–Ar); 1,267, 1,165 (C–O–C); 885, 762 (–Ar).

$^1\text{H-NMR}$ (CD_3COCD_3 , δ : ppm): 7.42–7.77 (m, aromatic 5H), 8.04–8.18 (2 days, aromatic, 4H).

MS (EI): = 242 (M^+).

X=CH₃, 4-(4'-methylbenzoyloxy) benzoic acid: Liquid crystalline phase transition: K238°C N > 300°C I. Yield 51%.

FT-IR (KBr, cm^{-1}): 3,000 (–OH); 1,735, 1,701 (–C=O); 1,604, 1,507 (–Ar); 1,273, 1,177 (C–O–C); 885, 740 (–Ar).

$^1\text{H-NMR}$ (CD_3COCD_3 , δ : ppm): 2.46(s, –CH₃, 3H), 7.40–7.45 (d, aromatic, 4H), 8.06–8.17 (2d, aromatic, 4H).

MS (EI): = 256(M^+).

X=Cl, 4-(4'-chlorobenzoyloxy) benzoic acid: Liquid crystalline phase transition: K252°C N > 300°C I. Yield 53%.

FT-IR (KBr, cm^{-1}): 3,100 (–OH); 1,742, 1,688 (–C=O); 1,604, 1,510 (–Ar); 1,261, 1,175 (C–O–C); 878, 745 (–Ar).

$^1\text{H-NMR}$ (DMSO-d_6 , δ : ppm): 7.40–7.46 (d, aromatic, 2H), 7.65–7.70 (d, aromatic, 2H), 8.02–8.17 (2d, aromatic, 4H).

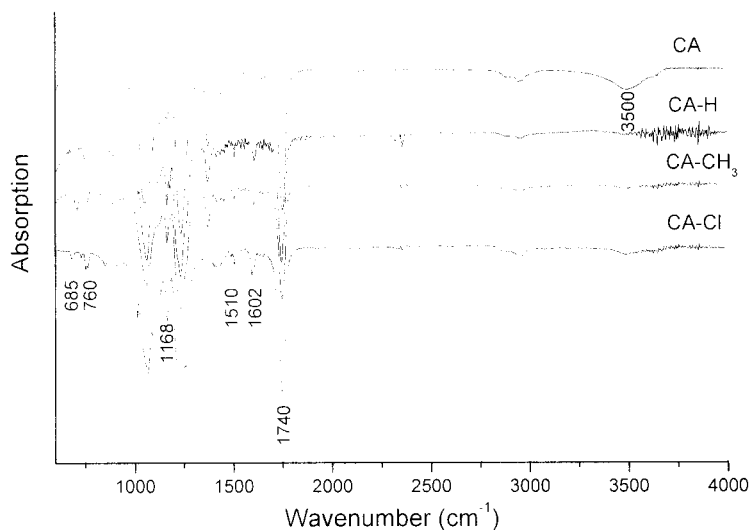


Figure 1 The FT-IR spectra of CA, CA-H, CA-CH₃, and CA-Cl.

MS (EI): = 276.5(M⁺).

Mesogen-linked cellulose acetates (CA-H, CA-CH₃, and CA-Cl)

CA (1 g), 0.75 g DMAP, 6 mmol compound (2), and 40 mL dry TFH were added to a 100-mL three-neck round-bottom flask that was equipped with a condenser and magnetic stirrer. After stirring for 30 min, the solution of 3.2 g DCC dissolved in 10 mL THF was added slowly to the flask. The reaction was carried out at room temperature under the protection of N₂ for 18 h. At the end of the reaction, the reaction mixture was poured into excess of methanol. The precipitate was dissolved in THF and reprecipitated from methanol again. The product was Soxhlet-extracted with methanol and dried under vacuum at 50°C.

X=H, CA-H: DS_{meso} = 0.39, yield 54%.

X=CH₃, CA-CH₃, DS_{meso} = 0.27, yield 52%.

X=Cl, CA-Cl, DS_{meso} = 0.41, yield 59%.

RESULTS AND DISCUSSION

Synthesis

Three aromatic (*p*-carboxyl phenyl) esters were synthesized by the reaction of corresponding aromatic acid chloride with *p*-hydroxybenzoic acid. To avoid hydrolysis, the acid chloride should be added slowly to the aqueous solution of *p*-hydroxybenzoic acid sodium salt with vigorous stirring. The structures of the aromatic (*p*-carboxyl phenyl) esters were confirmed by FT-IR, ¹H-NMR, and MS. The synthesis of 4-(4'-methylbenzoyloxy) benzoic acid and 4-(4'-chlorobenzoyloxy) benzoic acid has been not seen to our knowledge.

The esters of cellulose and its derivatives can be prepared by acid-catalysis from cellulose and its derivatives with acetic anhydride under relatively mild conditions.^{12,13} The reactivity of esterification, however, is markedly decreased and the homologous compounds require more drastic conditions with increasing the chain length of carboxylic acid or using the aromatic acid. The esterification can be carried out by using acid chloride as the reagent and pyridine or triethylamine as chlorine hydride absorber,^{14,15} but the acid chloride is more sensitive to moisture and the thionyl chloride can erode the equipment when it is removed from acid chloride under reduced pressure. Also, esterification of cellulose can be achieved by activating the carboxylic acids using DCC and DMAP as catalysts.^{16,17} It is convenient to prepare the mesogen-linked cellulose acetates from aromatic (*p*-carboxyl phenyl) esters reacting with cellulose acetate using DCC and DMAP as catalysts in this work.

The FT-IR spectra of CA, CA-H, CA-CH₃, and CA-Cl are shown in Figure 1. The decreased intensity of the exceedingly broad hydroxyl peak in the 3,500–3,400 cm⁻¹ regions suggests the occurrence of esterification; the small hydroxyl peaks in CA-H, CA-CH₃, and CA-Cl indicate the incomplete esterification of hydroxyl in cellulose acetate derivatives. The absorption bands at 1,600 and 1,510 cm⁻¹ are attributed to the C=C stretching vibration of the aromatic ring. The peaks at 760 and 685 cm⁻¹ are due to the *para* substituent of aromatic ring. The C=O absorption peak of the new ester bond is covered by the original carbonyl group of the mesogen-linked cellulose acetates at 1,740 cm⁻¹.

The ¹H-NMR spectra of CA-H, CA-CH₃, and CA-Cl (CD₃Cl as solvent) are shown in Figure 2. The peaks at 7.2–8.4 ppm represent the hydrogen of aro-

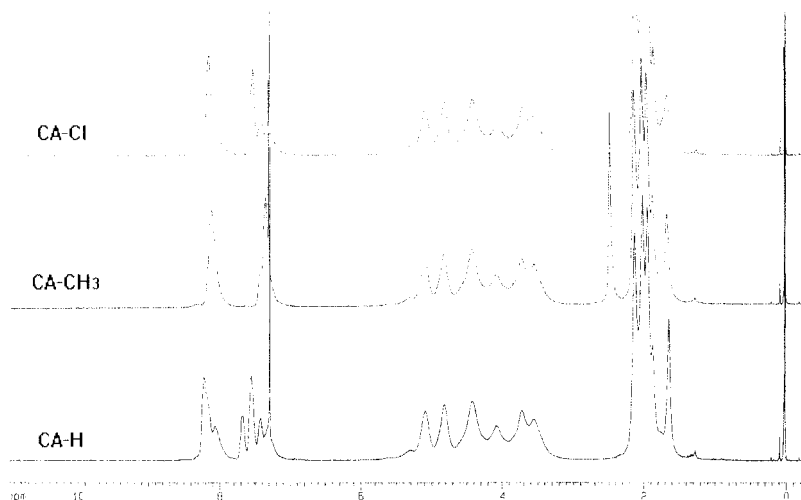


Figure 2 The $^1\text{H-NMR}$ spectra of CA-H, CA-CH₃, and CA-Cl.

matic rings in the mesogen-linked cellulose acetates; the sharp peak of CA-CH₃ at 2.46 ppm is attributed to the hydrogen of methyl group of the mesogenic moiety. The degrees of mesogenic unit substitution (DS_{meso}) can be calculated from aromatic ring hydrogen quantities compared with other hydrogen in the mesogen-linked cellulose acetates. The DS_{meso} of mesogen-linked cellulose acetates calculated from $^1\text{H-NMR}$ were 0.39 (CA-H), 0.27 (CA-CH₃), and 0.41 (CA-Cl).

Liquid crystalline behavior

Thermotropic behavior of intermediates

The three aromatic (*p*-carboxyl phenyl) esters exhibit liquid crystalline behaviors. 4-(Benzoyloxy) benzoic acid displays monotropic behavior and its isotropization occurs at 228°C on heating and the nematic phase appears at 224 to 180°C on cooling; the liquid crystalline texture is schlieren. 4-(Benzoyloxy) benzoic acid is a known compound, but its liquid crystalline property has not been reported. 4-(4'-Methylbenzoyloxy) benzoic acid and 4-(4'-chlorobenzoyloxy) benzoic acid display thermotropic behaviors with nematic phases appearing at 238 and 252°C, their textures are typically schlieren, they have wide temperature ranges of liquid crystalline phase, and their clear temperatures are above the scope of the POM observation (300°C).

Lyotropic behavior of mesogen-linked cellulose acetates

Though the three aromatic (*p*-carboxyl phenyl) esters exhibit nematic phases at the high temperature, the three aromatic (*p*-carboxyl phenyl) ester-linked cellulose acetates do not show any birefringence in the

heating or cooling process; it can be concluded that they cannot form thermotropic liquid crystals.

CA and the mesogen-linked cellulose acetates can form liquid crystalline phases in dichloroacetic acid (DCA) and their critical concentrations are 22 wt % for CA, 24 wt % for CA-H, 25 wt % for CA-CH₃, and 25 wt % for CA-Cl. The liquid crystalline solutions of CA, CA-H, and CA-CH₃ show birefringence under POM observation and the solutions of CA-Cl show parabolic focal conic texture [Fig. 3(a)], which is one of characteristic textures for the cellulose cholesteric phase.^{18,19} The variance of the end group in the mesogenic moiety has little influence on the critical concentrations for grafting polymers. The critical concentrations of the mesogen-linked cellulose acetates are higher than that of cellulose acetate in DCA. In the case of the mesogen-linked cellulose acetates, the residual hydroxyl groups on the main chains of CA are substituted by the bulky and rigid mesogenic units, which may cause the increase of distance between the main chains of CA. On the other hand, the reduction in the amount of hydroxyl groups on the main chain of CA may result in the decrease of inter- and intramo-

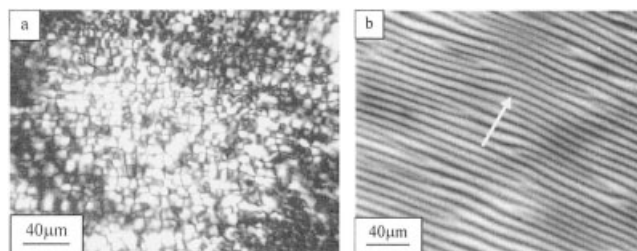


Figure 3 Polarizing optical micrographs of the 30 wt % CA-Cl/dichloroacetic acid cholesteric LC solution (a) and the solution after shearing (b). The arrow represents shear direction.

lecular hydrogen bonds, and the flexibility of polymer main chains is increased. Therefore the critical concentrations of the mesogen-linked cellulose acetates are higher than that of CA. The lyotropic solutions of mesogen-linked cellulose acetates show iridescent colors, which indicates that they are cholesteric liquid crystals. The band texture can also be formed after the CA-Cl lyotropic solution is sheared, in which the shearing direction is vertical to the direction of the band, whose width is about 4 μm [Fig. 3(b)]. The appearance of the band texture under an external force field has been considered to be a typical feature of liquid crystalline polymers.^{20,21}

CONCLUSION

Three mesogen-linked cellulose acetates were first prepared by the reaction of aromatic (*p*-carboxyl phenyl) esters with cellulose acetate through esterification in the presence of DCC and DMAP. Their degrees of mesogenic unit substitution are between 0.27 and 0.41. They are not thermotropic liquid crystals, but they can form cholesteric lyotropic phases in DCA, and their critical concentrations are about 25 wt %.

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References

1. Werbowyi, R. S.; Gray, D. G. *Mol Cryst Liq Cryst* 1976, 34, 97.
2. Huang, Y.; Chen, M. C.; Li, L. S. *Acta Chim Sin* 1988, 46, 367.
3. Jiang, S. H.; Huang, Y. *J Appl Polym Sci* 1993, 50, 607.
4. Arrighi, V.; Cowie, J.; Vaquero, P. *Macromolecules* 2002, 25, 7354.
5. Pawlowski, W.; Gilbert, R. J. *Polym Sci, Part B: Polym Phys* 1987, 25, 2293.
6. Terbojevich, M.; Cosani, A.; Focher, B.; Gastaldi, G.; Wu, W.; Marsano, E.; Conio, G. *Cellulose* 1999, 6, 15.
7. Cha, S. W.; Jin, J. I.; Kim, D. C.; Zin, W. C. *Macromolecules* 2001, 34, 5342.
8. Chen, B. Q.; Kameyama, A.; Nishikubo, T. *Macromolecules* 1999, 32, 6485.
9. Ritcey, A. M.; Holme, K. R.; Gray, D. G. *Macromolecules* 1988, 21, 2914.
10. Shimamoto, S.; Gray, D. G. *Cellulose* 1999, 6, 15.
11. Li, Z. F.; Guo, Y. Z.; Zhang, C. X.; Zhou, Q. F. *Acta Polym Sin* 1995, 4, 414.
12. Huang, Y. *J Appl Polym Sci* 1994, 51, 1974.
13. Heinze, T.; Shaller, J. *Macromol Chem Phys* 2000, 20, 1214.
14. Marsamo, E.; Paz, L. D.; Tambuscio, E.; Bianchi, E. *Polymer* 1998, 39, 4289.
15. Pawlowski, W. P.; Sankar, S. S.; Gilbert, R. D.; Fornes, R. E. *J Polym Sci, Polym Chem Ed* 1987, 25, 3355.
16. Redl, F. X.; Kothe, O.; Bauer, W.; Daub, J. *Macromol Chem Phys* 2001, 201, 2091.
17. Yue, Z.; Cowie, J. *Polymer* 2002, 43, 4453.
18. Demus, D.; Goodby, J.; Gray, G. W.; Spiess, H. W.; Vill, V. In *Handbook of Liquid Crystals*; Wiley-VCH Press: Weinheim, Germany, 1998, chap. IX.
19. Jiang, S. H.; Huang, Y. *J Appl Polym Sci* 1993, 49, 125.
20. Chen, S.; Jin, Y.; Xu, M. *Polym Commun* 1987, 28, 208.
21. Qian, R.; Chen, S. *Makromol Chem, Macromol Symp* 1992, 53, 345.