The synthesis and thermotropic liquid crystalline behavior of mesogenic moiety-linked ethyl cellulose

Changcheng Wu[1], Yong Huang (✉)[1, 2], Shouxi Chen[1]

[1]State Key Laboratory of Polymer Physics and Chemistry, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China
e-mail: yhuang@cashq.ac.cn, Fax: +86-010-68597356
[2]Laboratory of Cellulose and Lignocellulosics Chemistry, Guangzhou Institute of Chemistry,
Chinese Academy of Science, Guangzhou 510650, China

Summary

In this paper, a new mesogenic moiety was synthesized and characterized by IR, NMR, and MS. The mesogenic moiety-linked ethyl cellulose derivative was prepared by reaction of 4-methyloxyphenyl-4-oxyaceticacid benzoate with ethyl cellulose [EC, degree of substitution (DS) 2.1] through esterification. The polymer was characterized by IR, NMR, DSC, and hot-stage coupled polarizing microscopy. The DS of mesogenic unit is 0.49. The mesogenic moiety-linked ethyl cellulose derivative showed a thermotropic liquid crystalline behavior.

Introduction

Since Werbowyi and Gray[1] first reported hydropropyl cellulose display liquid crystalline properties in 1976, some cellulose esters and ethers with long flexible substitutes [2-3] or aromatic ring[4-6] have been found to be thermotropic and form cholesteric liquid crystals. Hydroxyethyl cellulose acetate[7] and ethyl cellulose with ethoxy over 45 wt.-% have been shown to be thermotropic liquid crystalline behavior[8]. Only a few works about bulky and rigid mesogenic substitutes that are induced to the cellulose side chain have been carried out. Recently, Shaikn et al.[9-10] has reported the preparation and thermotropic behavior of cholesterol-linked hydroethyl cellulose and polysaccharides. Terbojevich et.al[11] have reported the solution properties and mesophase formation of 4-phenyl-benzoylcellulose.

Phenyl benzoate is very popular mesogenic moiety in the field of liquid crystals; side-chain liquid crystalline polymers where phenyl benzoate is used as mesogenic unit have been widely reported[12-13]. In this work, a new end-carbolic acid contain mesogenic moiety, 4-methyoxyphenyl-4-oxyacetic acid benzoate was synthesized. A mesogenic moiety-linked ethyl cellulose derivative was prepared through esterification between 4-methyoxyphenyl-4-oxyacetic acid benzoate and EC. The obtained intermediates and mesogenic moiety-linked ethyl cellulose derivative were characterized by FT-IR, NMR, DSC and polarizing microscopy with hot-stage.

34

Experiment section

Materials

Ethyl cellulose (EC, with degree of substitution of ethyl 2.1) was purchased from Lu Zhou Chemical Factory, Sichuan province, China. p-methoxyphenol and p-hydroxybenzoic acid were analytical reagent (A.R) degree obtained from Beijing Chemical Factory. Other reagents and solvents were A.R or chemical pure (C.P) degree purchased from commercial and the solvents were purified by common ways before use.

Synthesis

The synthetic route of intermediates and polymer in this study was outlined in scheme1.
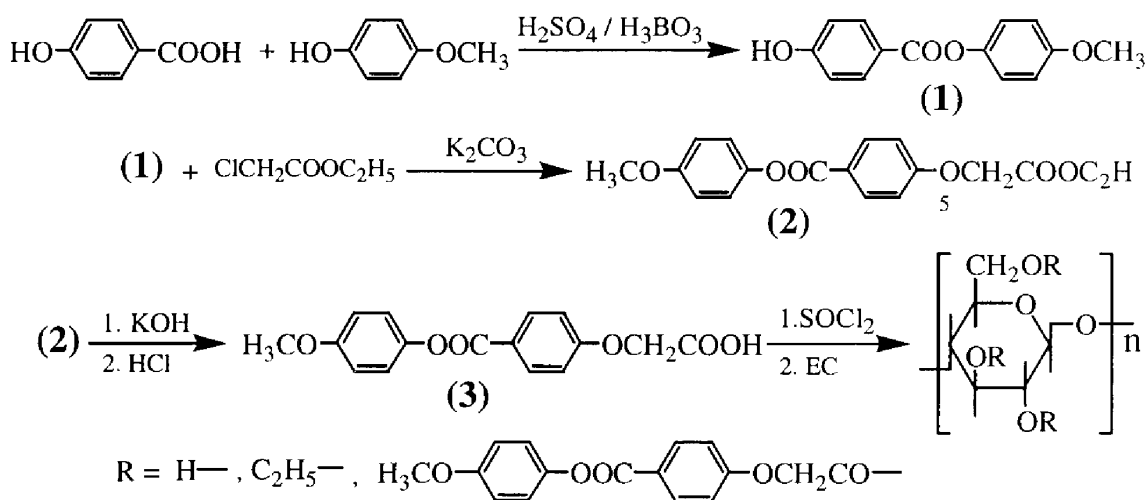
Scheme 1. Synthetic route of intermediates and polymer

4-methoxyphenyl-4-hydroxybenzoate (1)[14]

To a suspension of p-methoxyphenol (18.6 g, 0.15 mol) and p-hydroxybenzoic acid (13.8 g,.0.10 mol) in toluene (500 ml), concentrated sulfuric acid (1.5 g) and boric acid (0.31 g, 5 mol%) were added. The reaction mixture was heated under reflux for 21h under a Dean-stark trap. The solvent was then removed under reduced pressure, and the product was washed with ethyl ether/petroleum ether (1:1) two times, the resulting 4-methoxyphenyl-4- hydroxybenzoate was recrystallized to give 18.3g pure products, yield 75%, m.p. 191-192°C.
FT-IR (KBr): 3388cm^{-1} (-OH), 1708 cm^{-1} (-C=O), 1509 cm^{-1} (-Ar), 1186 cm^{-1} (Ar-OCH$_3$), 858 cm^{-1} (-Ar).
^{1}H-NMR (CD$_3$COCD$_3$): 3.80 ppm (s, -OCH$_3$, 3H), 6.95 ppm (2d, aromatic, 4H), 7.25 ppm (2d, aromatic, 2H), 8.05 ppm (2d, aromatic, 2H), 9.25 ppm (m, OH, 1H).
MS (EI): m/z=244(M$^+$).

4-methoxyphenyl-4-oxyethyl acetate benzoate (2)

0.05 mol (12.2 g) 4-methoxyphenyl-4-hydroxybenzoate, 0.055 mol (6.74 g) ethyl chloracetate and 0.10 mol (13.8 g) potassium carbonate were added to 100 ml 2-butanone, the mixture was refluxed for 12 hours, then cooled to room temperature and poured into 250 ml cooled water, the white crystalline solid was collected and recrystallized from aqueous ethanol. Yield 91.5%, m.p. 103-104.5 °C.
FT-IR (KBr): 1754cm^{-1}(-C=O), 1724 cm^{-1} (-C=O), 1508 cm^{-1} (-Ar), 1199 cm^{-1} (Ar-O-CH$_3$), 845 cm^{-1} (-Ar).
^{1}H-NMR(CD$_3$COCD$_3$): 1.48 ppm (t, -CH$_3$, 3H), 3.80 ppm (s, -OCH$_3$, 3H), 4.20 ppm (q, -CH$_2$CH$_3$, 2H), 4.85 ppm (S, -OCH$_2$-, 2H), 6.93-8.10 ppm (m, aromatic, 8H).
MS (EI): = 330 (M$^+$).

4-methyloxyphenyl-4- oxyacetic acid benzoate (3)

0.025 mol 4-methoxyphenyl-4-oxyethyl acetate benzoate (2) was dissolved in 40 ml of hot ethanol, to this solution added by drops of 0.025 mol potassium hydroxide previous dissolved in 20 ml ethanol. An equal amount (60 ml) of water was added and the mixture was refluxed for 1 h, acidified with conc. Hydrochloric acid and filtered the white precipitate, then recrystallized from isopropyl alcohol. Yield 52%, m.p. 196-197.5 °C.
FT-IR (KBr): 3436cm^{-1} (-COOH), 1735 cm^{-1} (-C=O), 1718 cm^{-1} (-C=O), 1172 cm^{-1} (Ar-O-CH$_3$), 852 cm^{-1} (-Ar).
^{1}H-NMR (DMSO-D$_6$): 3.75ppm(s, -OCH$_3$, 3H), 4.81 ppm (s, -OCH$_2$, 2H), 6.95 -8.05 ppm (m, aromatic, 8H).MS (EI): m/z=302 (M$^+$).

Preparation of mesogenic moiety-linked ethyl cellulose derivative (MMLEC)

3.02 g 4-methyloxyphenyl-4-oxyacetic acid benzoate (3) was placed in a three-necked round-bottomed flask equipped with a reflux condenser, calcium chloride guard tube and magnetic stirrer, excess (10 ml) of thionyl chloride and two drops of DMF were added to the flask, the reaction mixture was stirred at room temperature for 2-3 h, and the clear solution was formed. The excess of thionyl chloride was removed under reduced pressure. The addition and removal of dry hexane (20 ml) was repeated three times to endure complete removal of unreacted thionyl chloride.

The acid chloride in the flask was further dried under vacuum to near dryness and dry, distilled dimethylacetamide (DMAc 10 ml) was introduced into the flask. A clear solution was resulted after stirred for a little moment, and then it was transferred to another flask containing 1.5 g ethyl cellulose, 10 ml DMAc and 1 ml dry pydine. The reaction carried at the temperature of 70 °C under the protection of N$_2$ for 18 h. At the end the reaction, the reaction mixture was poured into excess of methanol. The precipitate was washed with methanol for several times, filtered and dried. The air-dried product was Soxhlet-extracted with methanol to remove the unreacted intermediates completely. 2.4 g products were obtained.

Characterization

Chemical structure of the intermediates and polymers were characterized with FT-IR by using Bruker EQUINOX55 spectrometer, ^{1}H-NMR spectrum by using Brucker 300MHz with tetramethylsilane as an internal standard. MS analysis carried out at

JMS-D300 Chromatography-Mass Spectrometer. The melting point of intermediates were determined by means of Olympus Model BH-2 polarized optical microscope (POM) equipped with a Mettler FP-5 hot stage, the heating rate was 1°C/min. the liquid crystalline texture of polymer was studied by POM with hot stage, the heating and cooling rate was 10 °C/min. A differential scanning calorimeter (DSC) (Perkin-Elmer DSC-2C) was used to measure the transformation temperature and transformation enthalpy at the heating rate of 10 °C/min.

Results and disscussion

Synthesis

4-methyloxyphenyl-4-oxyacetic acid benzoate is a new end-carboxylic Phenyl benzoate intermediates with mesogenic unit and its chemical structure was confirmed by FT-IR, ^{1}H-NMR and MS. The ester of cellulose and its derivatives can be produced by acid-catalysis from cellulose with acetic anhydride under relatively mild conditions[7]. The reactivity, however, is markedly decreased and the homologous compounds require more drastic conditions with the chain length of carboxylic acid increases or the aromatic acid is used. In the synthesis of mesogenic moiety-linked ethyl cellulose, the esterification is carried out in mild conditions using the chloride of 4-methyloxyphenyl-4-oxyacetic acid benzoate as the reagent and pyridine as the catalyst. Excess of chloride acid is used in order to increase the substitute degree of mesogenic unit. The chemical structure of the product is confirmed by using IR and ^{1}H-NMR. The DS of mesogenic unit was 0.45, which was calculated from the increased weight of the obtained polymer.

The infrared spectra of MMLEC and EC are shown in Figure 1. The absorb band at 1770 cm^{-1} and 1735 cm^{-1} are indicative of the ester function. The significant decrease of exceedingly broad hydroxyl peak in 3500-3400 cm^{-1} regions also suggests the esterification. The small hydroxyl peak in MMLEC indicates the incomplete esterification of hydroxyl in ethyl cellulose. The absorb bands at 1600 cm^{-1} and 1510 cm^{-1} are attributed to C=C stretching of aromatic ring. The peaks at 1270 cm^{-1}, 1375 cm^{-1}, and 820-890 cm^{-1} are due to aromatic ether bond, oxymethyl and para substitute of aromatic ring.

^{1}H-NMR spectrum of MMLEC (CD$_3$C1 as solvent) is shown in Figure 2. The peak at 6.90-8.15 ppm indicates the hydrogen of aromatic ring in the MMLEC, a sharp peak at 3.80 ppm is attributed to the oxymethyl group of the mesogenic moiety. The DS of mesogenic moiety can also be calculated from aromatic ring hydrogen quantities compared with other hydrogen in the MMLEC. The DS of mesogenic moiety that calculated from ^{1}H-NMR is 0.49. Which is well agrees with that calculated from the weight increase.

Thermotropic Behavior

Ethyl cellulose can exhibit thermotropic liquid crystalline behaviors[8] only when its ethyloxy content reaches to 45%. In the present work, the ethyloxy content of the ethyl cellulose (DS 2.1) is 42.8 wt.-% and doses not show any thermotropic liquid crystalline behaviors. No birefringence can be observed under crossed polarizing optical microscopy even after it is melted at 182-185 °C in the heating procedure.
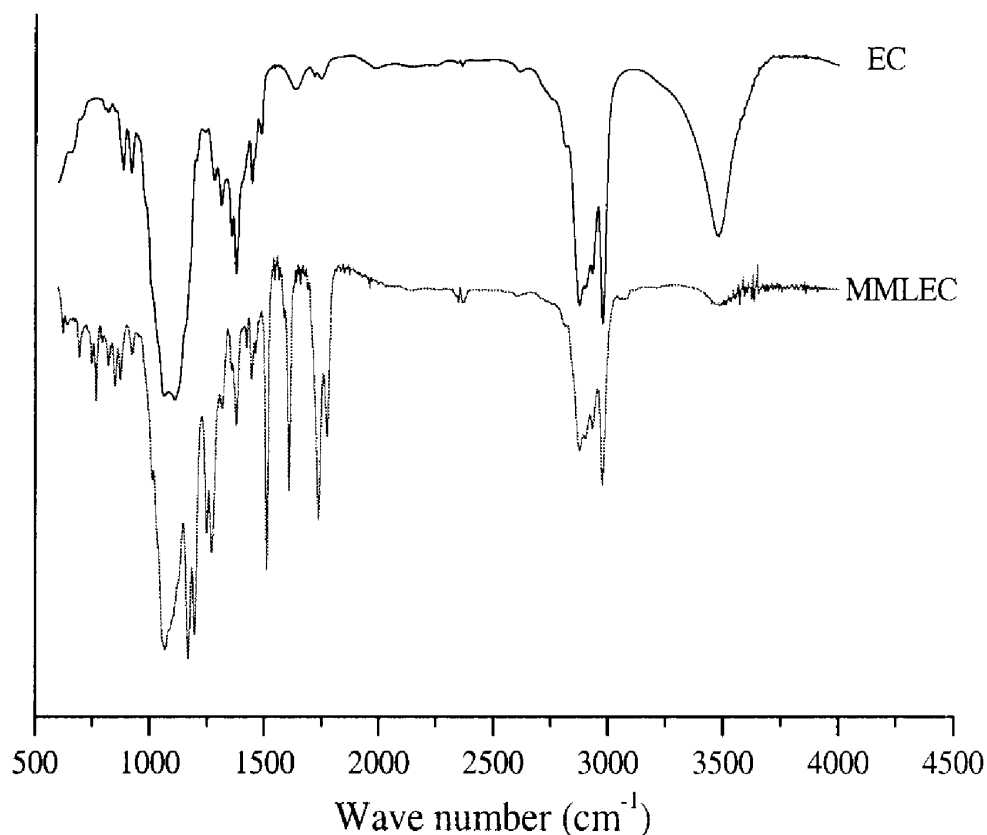
Figure 1. Infrared spectra of EC and MMLEC

After mesogenic units are grafted, the MMLEC exhibits little birefringence at room temperature (Figure 3a). When it is heated to 130 °C, the sample started to melt and birefringence appears (Figure 3b). Irisated birefringence is observed when MMLEC is heated to 150 °C (Figure 3c). When the sample is heated to 170 °C, the birefringence disappears, at which the sample transfer from the mesophase to isotropic phase. No birefringence can be observed during the succeeding cooling procedure. On the second heating procedure, the strong birefringence is observed between 130°C and 160°C and the transition temperature of the mesophase to the isotropic phase changes to 162°C. The difference of the transition temperature may be attributed to the changes heating history of the sample. The DSC results are agreed with the observation by the crossed polarizing optical microscope quite well. In Figure 4, curve 1 is the DSC trace of EC (DS = 2.1). The single endothermic peak at 183°C is attributed to the melt of EC. Curve 2 is the first heating run of MMLEC, there are a plateau at 120°C and a endothermic peak at 169°C. The plateau is attributed to the imperfect crystal structure of MMLEC, which was formed during the precipitation. The imperfect crystals melt and recrystallize during the heating procedure and the endothermo of the crystal melting is equilibrated with exothermo of the recrystallization of the crystals. Therefore, there is a plateau in this temperature range. After the heating history of the sample is eliminated, there are two endothermic peaks at 122°C and 161°C (The second heating procedure, Curve 3). The enthalpies ΔH are 3.89 J/g and 4.26 J/g, which are attributed to solid state- mesogenic and mesogenic-isotropic phase transitions, respectively.

38
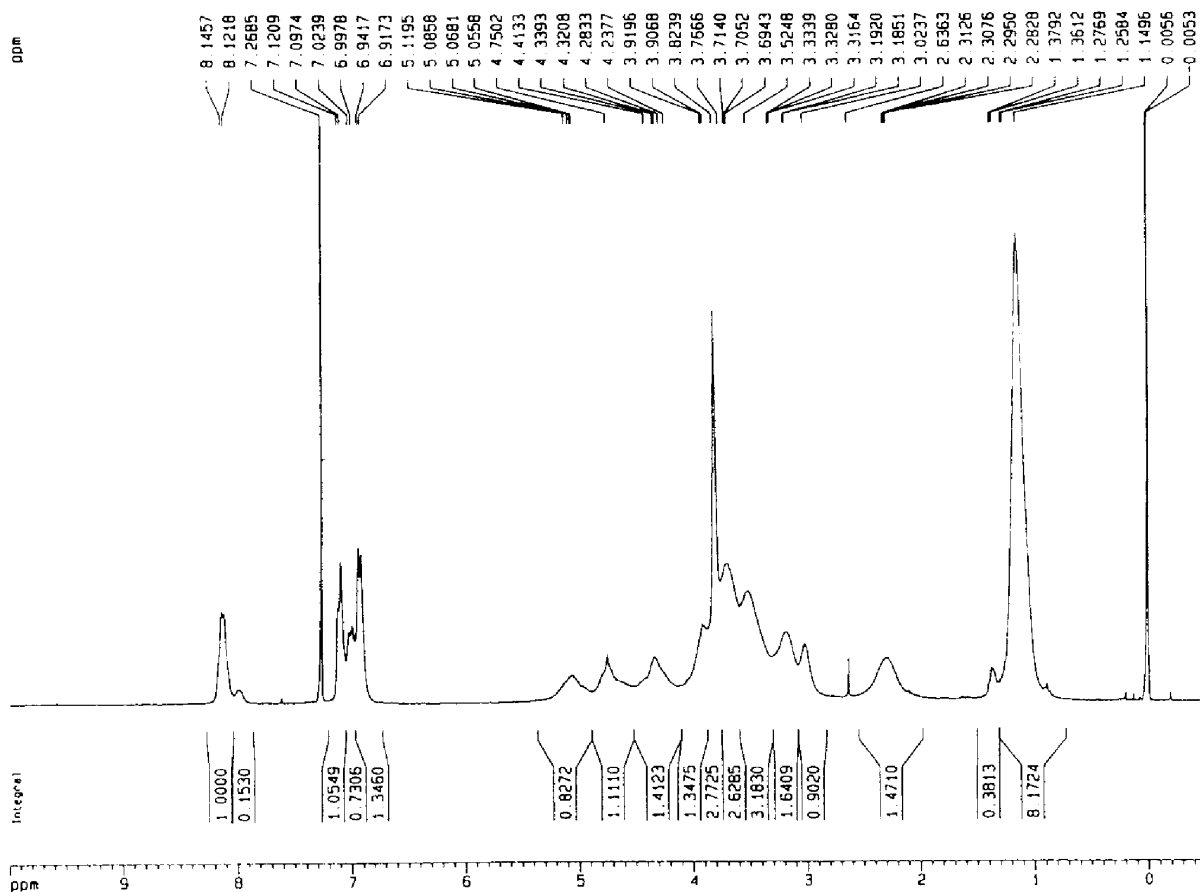
Figure 2. The ^{1}H-NMR spectra of MMLEC

The flexibility of the polymer backbone may be influenced by bulky and mesogenic units that are introduced to the ethyl cellulose chains. In case of polymers with flexible backbone (polyacrylates, polysiloxanes etc.), attachment of the side chain on the main chains may increase the rigidity of the polymer backbone. On the other hand, the flexibility of polymers with more rigid backbones (polystyrene, polymethacrylates etc.) will be increased when side chains are attached to the backbone[15]. The backbone of cellulose is more rigid than that of polystyrene, which can be judged from the value of α in the Mark-Houwink-Sakurada equation[16]. In comparison with the case of EC, the lower melting point of MMLEC suggests a slightly higher flexibility of the polymer chains. The residual hydroxyl groups on the main chains of EC are substituted by the bulky and rigid mesogenic units, which may result in the decrease of the inter and intra molecular hydrogen bonding for the polymers due to the reduction of the amount of residual hydroxyl groups on the main chain of EC and the steric hindrance of the substitution groups. The polymer chains, therefore, are more flexible and the melting point of MMLEC is lower than that of EC. And MMLEC also exhibits the thermotropic liquid crystalline behaviors.

3a (x100)
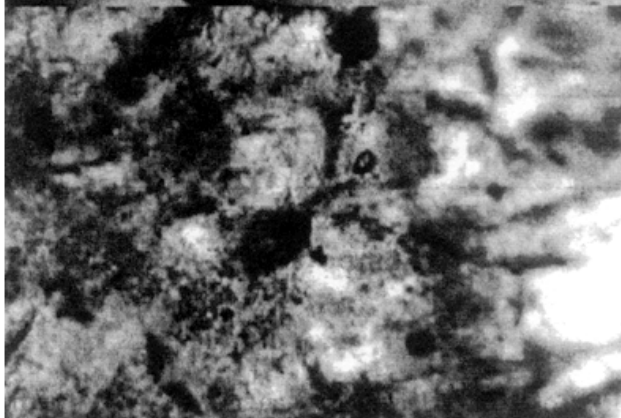
3b (x100)
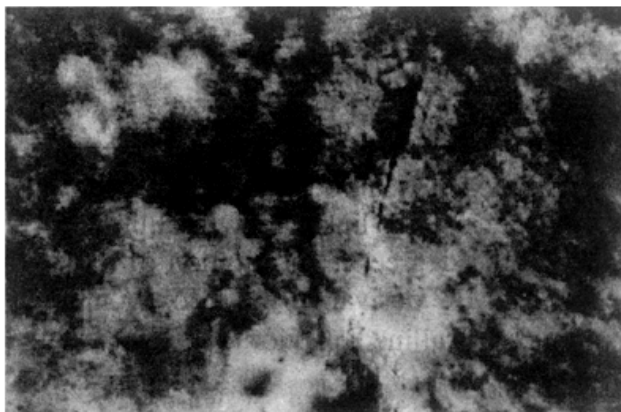
3c (x100)

Figure 3a-c. Photomicrograph (Crossed polars) of MMLEC
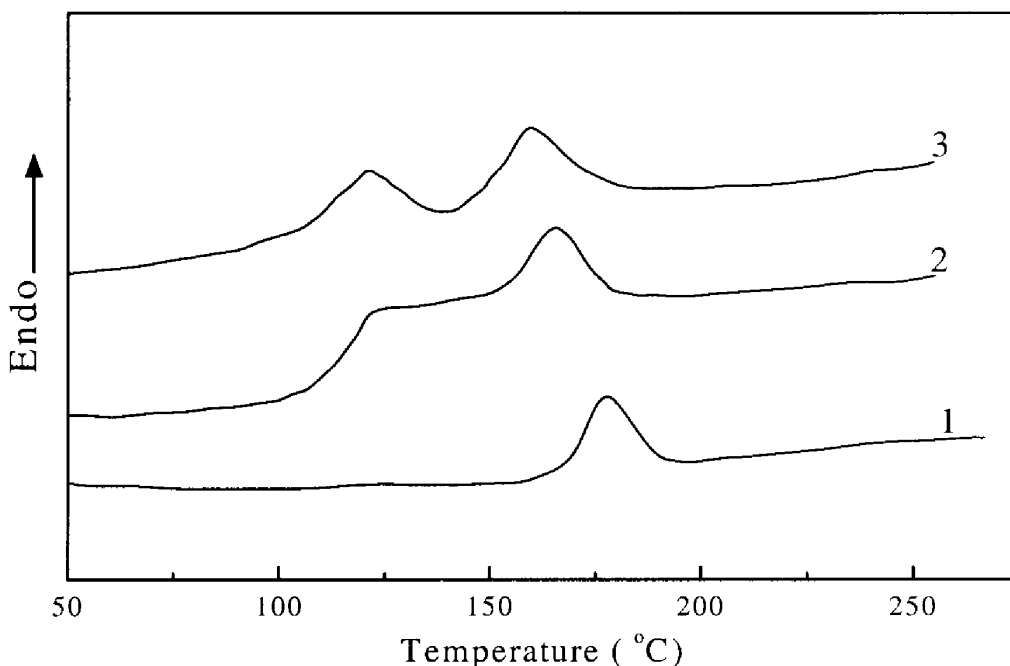
Figure 4. The DSC curves of EC (1. Heating run) and MMLEC (2. The first heating run; 3. The second heating run)

Conclusions

A new end-carboxyl phenyl benzoate immediate (4-methyloxyphenyl-4-oxyacetic acid benzoate) is synthesized and is introduced to ethyl cellulose backbone through esterification. The mesogenic moiety-linked ethyl cellulose is characterized by IR, NMR, MS, and DSC, and the degree of substitution of the mesogenic unit is 0.49. The mesogenic moiety-linked EC derivative has a lower melting point than EC and exhibits thermotropic liquid crystalline behavior at the temperature region of 120°C to 169°C.

References

[1] Werbowyi RS, Gray DG (1976) Mol Cryst Liq Cryst 34:97
[2] Yamagishi T, Fukuda T, Miyamoto T, Watanabe J (1988) Polym Bull 20:373
[3] Jiang SH, Huang Y (1993) J. Appl Polym Sci 50: 607
[4] Pawlowski WP, Sankar SS, Gilbert RD, Fornes RE (1987) J Polym Sci, Polym Chem Ed, 25:3355

[5] Bhadani SN, Gray DG (1983) Mol Cryst Liq Cryst 99:29

[6] Isogai, Ishizu A, Nakano J (1984) J Appl Polym Sci 29:2097

[7] Huang Y (1994) J Appl Polym Sci, 51:1974

[8] Chen J, Huang Y, Yuan J, Yan S, Ye H (1992) J Appl Polym Sci 45:2153

[9] Shaikn VAE, Madar NN, Lonikar SV, Rajan CR, Ponrathnam S (1998) J Appl Polym Sci 70:195

[10] Shaikn VAE, Madar NN, Lonikar SV, Rajan CR, Ponrathnam S (1999) J Appl Polym Sci 72:763

[11] Terbojevich M, Cosani A, Focher B, Gastaldi G, Wu W, Marsano E, Conio G (1999) Cellulose 6:15

[12] Finkelmann H, Ringsdorf H, Wendorff H (1978) Makromol Chem 189:273

[13] Portugall M, Ringsdorf H, Zentel R (1982) Makromol Chem 183:2311

[14] Van Meter JP, Klanderman BH (1973) Mol Cryst Liq Cryst 22:285

[15] Imerie CT, Karsaz FE, Attard GS (1993) Macromoleculaers 26:3803

[16] Gilbert RD, Patton PA (1983) Prog Polym Sci 9:115