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A Dendronized Cellulose Derivative and Its Thermotropic Liquid Crystal and Lyotropic Cholesteric Liquid Crystal Behaviors

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Abstract. A novel dendronized cellulose， ethyl cellulose grafted 3,4,5-tris[4-(dodecyloxy) benzyloxy] benzoate (EC-g-DOBOB), which is comprised of ethyl cellulose (EC) backbone with mesogenic moiety DOBOB (3,4,5-tris(4-(dodecyloxy)benzyloxy)benzoic acid) dendron grafted, was designed and synthesized. The structure of EC-g-DOBOB was investigated by means of FTIR, Both thermotropic liquid crystal and lyotropic liquid crystal behaviors of EC-g-DOBOB were studied by combination of DSC, POM and XRD. At room temperature EC-g-DOBOB demonstrated hexagonal columnar mesophase (Φ_h), with the column diameter 5.8 nm, besides it formed lyotropic cholesteric liquid crystal in concentrated chloroform solution with a planar texture.

Introduction

Dendrimers are attractive molecules owing to their multifunctional properties[1, 2]. Several groups focused on the self-assembling of dendrimers in liquid crystal and reported many types of liquid crystalline phase, which covered almost all the liquid crystalline phase reported in other polymers[3-5]. 3, 4, 5-Tris (*p*-dodecyloxybenzyloxy) benzoic acid (DOBOB) was first reported by Malthete et al.[6]. DOBOB has been used to design molecular[7] and supramolecular[8-9] liquid crystals. Percec and coworkers reported that DOBOB and its corresponding polymethacrylates self-assembled into a tubular supramolecular architecture displaying a columnar hexagonal (Φ_h) mesophase[10]. Most of the dendronized polymers developed by Percec base on the flexible chains such as poly(methyl methacrylate) or polystyrene, but the semi-rigid backbones such as polysaccharide have never been researched. Much of our work focuses on grafting DOBOB mesogen onto polysaccharide ethyl cellulose (EC). It was reported by Zhang et al. that grafting rodlike cellulose nanocrystals spontaneously exhibits fingerprint texture in both lyotropic and thermotropic states[11]. As per our knowledge, the researches of dendronized polysaccharide mostly concentrated on without self-assembly and liquid crystalline properties except our report on dendronized chitosan and its lyotropic liquid crystalline behavior[12].

This article aims at the design and synthesis of a new liquid crystalline nano-molecule EC-g-DOBOB, which is comprised of natural bio-macromolecular backbone with mesogenic dendritic moieties grafted. Besides a quite broad temperature range thermotropic liquid crystal Φ_h

phase EC-g-DOBOB formed a lyotropic cholesteric texture. It is expected to be a functional liquid crystal polymer material.

Experiment

Preparation of EC-g-DOBOB: EC-g-DOBOB was prepared by reaction of EC with carboxyl ending DOBOB using dicyclohexylcarbodiimide (DCC) and (dimethylamine) pyridinium-4-toluenesulfonate (DPTS) as the catalyst. The product was purified by column chromatography (silica gel, $CHCl_3$ eluent).

General methods: The infrared spectra were measured with a Nicolet Avator 360 FTIR by the KBr pellet method. ^{1}H NMR (500 MHz) spectra were obtained with a Varian Unity NMR spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as the internal reference. The micrographs were obtained with an Olympus BH-2 polarized optical microscope (POM). A Netzsch DSC204 differential scanning calorimeter was used to determine the thermal transition. Small-angle X-ray diffractograms from powder samples were recorded with an image plate area detector using graphite-monochromatized Cu Kα radiation.

Results and discussion

Structure characterization of EC-g-DOBOB. The structure of EC-g-DOBOB has been confirmed by FTIR and ^{1}HNMR. In FTIR results, compared with raw material EC, the structure of EC-g-DOBOB was verified by 1722 cm^{-1} (the esterified carboxylic groups, -COOR), 3039 cm^{-1} stretching vibrations of the C-H on benzene, 1511 and 1610 cm^{-1} vibrations of backbone of benzene ring, and 822 cm^{-1} out-of-plane bending vibrations of C-H on benzene. The ^{1}H NMR ($CDCl_3$, ppm) spectrum of EC-g-DOBOB showed resonance signals at δ 0.88–1.8 ppm corresponding to the protons of aliphatic saturated hydrocarbon, δ 3.0–5.0 ppm corresponding to both protons which connected with oxygen protons of the dendrimer and EC, and δ 6.5-7 ppm corresponding to the protons in benzene ring. The degree of substitution was about 0.50 per glucose unit via the calculation of the integral ratio of δ 3.0–5.0 and δ 6.5–7 ppm.

Thermotropic liquid crystalline behavior of EC-g-DOBOB. The thermotropic liquid crystalline behavior of EC-g-DOBOB were characterized by a combination of techniques consisting of differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction experiment (XRD).

The thermal transition temperature of EC-g-DOBOB was analyzed by a combination of thermal polarized optical microscopy (TPOM) and DSC. The samples were heated above the clearing point (T_c) to erase any previous thermal history, and quenched for measurement. Fig. 1 presents DSC trace of EC-g-DOBOB. During the DSC scan, we observed transitions at -0.5 and 107.5℃, which were assigned as the ordered solid state-to-Φ_h and the Φ_h-to-isotropic (i) transitions, respectively. EC-g-DOBOB showed a quite broad temperature range Φ_h phase stable up to 107℃. By means of TPOM, the transition from the isotropic (i) to the Φ_h phase was qualitatively assigned through the broken fan-shaped texture observed on the polarized optical microscopy. Compare with DOBOB, introduction of the macromolecules backbond and restricted substitution increased the space between dendrimers, weakened the inter-molecular interaction. So the T_c of EC-g-DOBOB (107˚C) was lower than DOBOB (145˚C) [10].

Representative textures of the Φ_h mesophase of the EC-g-DOBOB are shown in Fig.2. As observed, EC-g-DOBOB form thermotropic liquid crystalline phase, showing broken fan-shape textures similar to DOBOB reported previously[10].

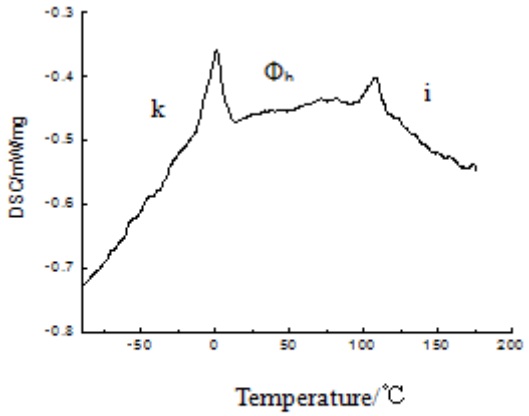

Fig.1. Second heating DSC trace of EC-g-DOBOB

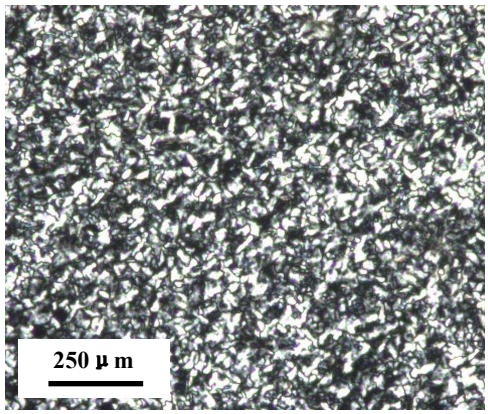

Fig.2. Photographs of the fan-like texture for EC-g-DOBOB

The identification of the Φ_h phase of EC-g-DOBOB was accomplished by small-angle XRD experiment (Fig. 3). In Fig.3 a strong narrow peak was observed at 1.77° and two week peaks at 3.07° and 3.56°. The d spacings of all reflections are presented in Table 1. As we all know, geometric considerations result in the characteristic rations of $1:1/\sqrt{3}:1/\sqrt{4}$ for the d spacings of the (100), (110) and (200) reflections of a two-dimensional hexagonal lattice in the small-angle regime. EC-g-DOBOB have X-ray reflections in the ratio, $d_{100} : d_{110} : d_{200} = 1:1/\sqrt{3}:1/\sqrt{4}$, this is indicative of a Φ_h mesophase. The hexagonal columnar lattice parameter *a* is measured to be 57.6 Å. Compare with DOBOB, the hexagonal columnar lattice parameter of EC-g-DOBOB is larger than DOBOB (40.9 Å) [10].

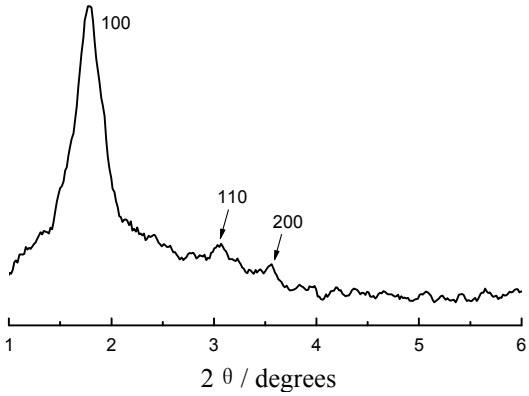

Fig. 3. Small-angle X-ray diffractogram of EC-g-DOBOB at room temperature (Miller indices of the observed peaks are indicated).

Table 1. X-ray Diffractions Observed in the mesophase of EC-g-DOBOB

2 θ (deg)	d spacing (Å)	Miller indices *(hkl)*
1.77	49.9	(100)
3.07	28.7	(110)
3.56	24.8	(200)

Lyotropic liquid crystal behavior of EC-g-DOBOB. Besides thermotropic liquid crystal behavior EC formed a cholesteric texture, showing a typical fingerprint texture in several organic

solvents like most of cellulose derivatives[13]. While it was observed that EC-g-DOBOB solutions in chloroform formed another typical cholesteric texture in very high concentration, i.e. a planar texture (Fig. 4) in 80% (w/v) EC-g-DOBOB / chloroform solution. It is well known that the cholesteric phase usually demonstrates a planar texture, while the axes of spirals are almost vertical to the sample plane. EC and EC-g-DOBOB both display lyotropic liquid crystalline behavior like others derivatives, whereas the appearance of textures are different.

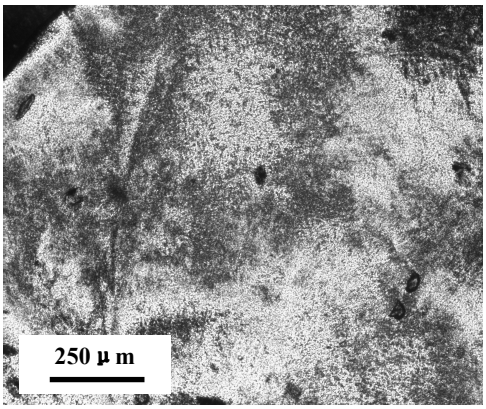

Fig.4. Photographs of the planar texture for EC-g-DOBOB

Conclusions

A new liquid crystalline nano-molecules EC-g-DOBOB was designed and synthesized. Both thermotropic liquid crystalline behavior and lyotropic liquid crystal behavior were studied. Broken fan-shaped texture was observed at room temperature while a quite broad temperature range Φ_h phase stable up from -0.5℃ to 107℃ was measured by means of DSC. EC-g-DOBOB solutions in chloroform formed typical cholesteric texture in very high concentration. EC-g-DOBOB is the first dendronized cellulose showing both thermotropic liquid crystalline behavior and lyotropic liquid crystal behavior. Dendronized cellulose can be a series of potential functional LCP materials.

Acknowledgements

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