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Thermotropic Cellulose Derivatives with Flexible Substituents. I. Preparation of Tri-o-(β-methoxyethoxy)ethyl Cellulose and its Cholesteric Mesophase Properties

T. Yamagishi [a] , T. Fukuda [a] , T. Miyamoto [a] & J. Watanabe [b]
[a] Institute for Chemical Research, Kyoto University, Uji, Kyoto, 611, Japan
[b] Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, 152, Japan
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Thermotropic Cellulose Derivatives with Flexible Substituents. I. Preparation of Tri-o-(β-methoxyethoxy)ethyl Cellulose and its Cholesteric Mesophase Properties

T. YAMAGISHI, T. FUKUDA and T. MIYAMOTO

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

and

J. WATANABE

Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

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Tri-o-(β-methoxyethoxy)ethyl cellulose was prepared by reacting the regenerated cellulose with 2-(2-methoxyethoxy)ethyl iodide and characterized as a fully substituted derivative. The resultant derivative forms a thermotropic liquid crystal in the wide temperature range from room temperature to the isotropization temperature of 180°C, showing that the (methoxyethoxy)ethyl side-chain substituent is long and flexible enough to inhibit crystallization of the extended cellulose chains and facilitate formation of liquid crystals. This is the first example of a thermotropic liquid crystalline cellulose derivative with a homogeneous side chain. This type of liquid crystal is cholesteric with a right-handed helical structure. The cholesteric pitch increases with increasing temperature, with the magnitudes comparable to the wavelength of visible light in the temperature range below 120°C.

Keywords: tri-o-(β-methoxyethoxy)ethyl cellulose, cellulose derivatives, cholesteric mesophase, thermotropic liquid crystal

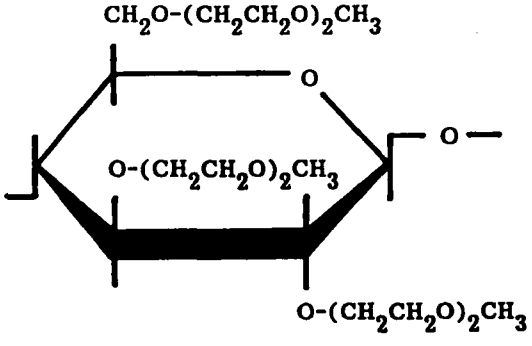
INTRODUCTION

The rigid or semirigid biopolymers such as polypeptide, cellulose and chitin can form liquid crystalline phases in lyotropic systems, and their mesophase properties have been widely studied. The liquid crystalline state of such rigid molecules is of great interest because of the unusual flow behaviors and the preferential orientation of the polymer chains to the flow direction, which leads to an easy preparation of uniaxially oriented fibers and films with superior tensile modulus and strength. In addition, the unusual optical properties characteristic of the cholesteric liquid crystals of chiral biomaterials are also of special interest.

In recent years, the transformation of a lyotropic liquid crystalline polymer to a thermotropic one has been successfully performed by attaching long and flexible side chains to the stiff main chain. This transformation is very attractive since one no longer has to use a solvent, which may sometimes be volatile, toxic, or even corrosive; and thus one can more easily carry out fundamental studies on the liquid crystalline structure and properties as well as their commercial utilization.

A typical example of such transformation can be seen in the α-helical polypeptide system as reported by Watanabe et al.[1-4] In this system, it was found that the thermotropic nature arises in the homopolymers of *L*-glutamate which have *n*-alkyl side chains longer than a decyl group and also in the copolyglutamates which have two kinds of side chains fairly different in length. The spontaneous formation of the liquid crystalline state in this system, even in the absence of solvent, indicates that the long and flexible side chains act rather like a solvent and allow the central α-helices some mobility. The cholesteric mesophase properties of these thermotropic polypeptides have been widely reported in relation to their chemical structure.

Similarly, cellulose, another lyotropic liquid crystalline biopolymer, has been transformed into thermotropic ones. These include the acetic, acetoacetic, propionic, *n*-butylic and isobutylic acid esters of hydroxypropyl cellulose.[5-8] In each of these polymeric systems, a cholesteric mesophase has been found to be formed, and the relationship between cholesteric pitch and temperature is established. It should be noted here that all these cellulose derivatives have been prepared from the commercial hydroxypropyl cellulose obtained by heterogeneous etherification of cellulose. Here, the reaction for the etherification proceeds as graft copolymerization; each of the hydroxypropyl substituents carries a hydroxy group which is capable of undergoing further reaction and so a possible structure is fairly heterogeneous. As a result, some ambiguity in the chemical structure is included in these derivatives of hydroxypropyl cellulose, and this seems to make it difficult to clarify the relationship between the mesophase properties and chemical constitution of the component polymer. In order to avoid this ambiguity, more recently, we have prepared a series of homopolymers with long and flexible side-chain substituents which were directly derived from the cellulose by the etherification or esterification of hydroxy groups.[9-10] In this paper, as a first paper of this series, we will report the mesophase properties of the following cellulose derivative with the (methoxy-ethoxy)ethyl group as a side-chain substituent;



This polymer interestingly forms a thermotropic cholesteric liquid crystal in the wide temperature region extending from room temperature to the isotropization temperature of 180°C. The preparation of this polymer and its thermotropic mesophase properties will be described in detail.

EXPERIMENTAL

Materials

Tri-o-(β-methoxyethoxy)ethyl cellulose was prepared by reacting the cellulose with 2-(2-methoxyethoxy)ethyl iodide, the details of which will be shown later in RESULTS AND DISCUSSION. The regenerated cellulose which was prepared from cellulose acetate with a degree of polymerization of 200 by treatment with 14% aqueous ammonia, was used as a starting cellulose. 2-(2-Methoxyethoxy)ethyl iodide was prepared by *p*-toluenesulfonylation (tosylation) of diethylene glycol monomethyl ether (DEGM), followed by the reaction with sodium iodide.[11] The chemicals for the reaction, DEGM, dimethy sulfoxide (DMSO), diethylamine (DEA), dichloromethane and pyridine, were purified according to the standard procedure. All other chemicals were of reagent grade and used without further purification.

Methods

DSC measurements were performed with a Perkin-Elmer DSC-II calorimeter. The sample of about 10 mg in weight was examined at a scanning rate of 10°C/min. The selective reflectance of circularly polarized light was detected by circular dichroism (CD) using a Jasco Model J-20 automatic recording spectrometer in the wavelength range 400—700 nm. In this experiment, the dry specimens were placed between glass plates, heated at the desired temperature by a heater and spread under a slight pressure. The specimen was tightly sealed with special glue to avoid the absorption of water moisture. The thickness of the film specimen was less than 50 μm. The maximum wavelength of reflection, λ_m, was related to the optical pitch, nP, by the equation $\lambda_m = nP$ where n and P are the average refractive index and the cholesteric pitch, respectively. Wide-angle X-ray patterns were recorded with a flat-plate camera using a Rigaku Denki X-ray generator with Ni-filtered Cu Kα radiation. Photomicrographs were taken with an Olympus BH-2 photo attachment with a Mettler FP 80. ^{1}H-NMR spectra were obtained by using a Varian model VXR-200 Spectrometer.

RESULTS AND DISCUSSION

(A) Preparation of tri-o-(β-methoxyethoxy)ethyl cellulose

Tri-o-(β-methoxyethoxy)ethyl cellulose was obtained by a two-step procedure. The first, the etherification of cellulose, was performed according to the method of Isogai et al.[12] which is a very convenient method for preparing highly-substituted cellulose ethers by use of a nonaqueous solvent. As a second reaction, the resultant

derivative was further treated with 2-(2-methoxyethoxy)ethyl iodide and methysulfinyl anion (DMSO-NaH) to assure a full substitution.

In the first step, cellulose was dissolved in a nonaqueous solvent, SO_2-DEA-DMSO, and then powdered sodium hydroxide was added. To the suspension thus prepared, 2-(2-methoxyethoxy)ethyl iodide was added dropwise at room temperature. The mixture was stirred at room temperature for 2h and then heated at 60°C for 24h. After cooling to room temperature, the sample product was recovered by dialysis and subsequent lyophilization. In the second step, it was treated with 2-(2-methoxyethoxy)ethyl iodide and methylsulfinyl anion in DMSO according to the method due to Hakomori.[13] Methylsulfinyl anion was prepared as described in the literature[13] and the reaction was carried out at 50°C for 24h. The reaction mixture was poured into a large amount of water, and the resulting solution was dialyzed against deionized water. After the insoluble fraction was removed by filtration, the filtrate, i.e. the final derivative was concentrated and freeze-dried.

The DS value of the derivatives was determined with the ^{1}H-NMR spectra of sample solution in $CDCl_3$ by calculating the relative ratios of the peak areas in the following manner. Figure 1 shows the ^{1}H-NMR spectra of the first derivative (curve A) and the second derivative (curve B) of tri-o-(β-methoxyethoxy)ethyl cellulose. It can be seen that peaks *a*, *b* and *c* are strong and sharp as compared with the others. It is evident that the three peaks are assigned to the protons of oxyethylene (OE) units and the methoxy protons, because the mobility of these units is much higher than that of rigid anhydro-glucose (AHG) units. A strong peak at a higher field (peak *c* at 3.35 ppm from internal TMS reference) may be assigned to methoxy protons, while the other two peaks (peaks *a* and *b*) at 3.52 and 3.59 ppm to methylene protons. The relative intensity of peak *a* is weaker in curve B than in curve A, i.e., it becomes weaker with an increase in the DS value. This implies that peak *a* overlaps with the ring proton signals of the cellulose skeleton. The peaks due to cellulose skelton protons are broad and indistinguishable from others, but this is unimportant for the present purpose of determining DS value. If one designates the integrated area from methoxy protons as P and the area of remaining protons as Q, one can readily calculate the DS value of the sample derivatives by the equation;

$$DS = 10\,P / (3\,Q - 7\,P)$$

The DS value thus evaluated was found to be 3.0 for the final derivative, which indicates a perfect substitution of 2-(2-methoxyethoxy)ethyl group on cellulose. This contrasts to the relatively low DS value of 2.3 to 2.5 found for the intermediate derivative obtained in the first step reaction. A final derivative was used for the following examination of the mesophase properties.

(B) Cholesteric mesophase properties of tri-o-(β-methoxyethoxy)ethyl cellulose

In Figure 2 are shown the DSC thermograms of bulk polymer measured in the temperature range from 20°C to 200°C. On heating, only one endothermic peak can be seen at 183°C. On cooling, the corresponding exothermic peak appears at

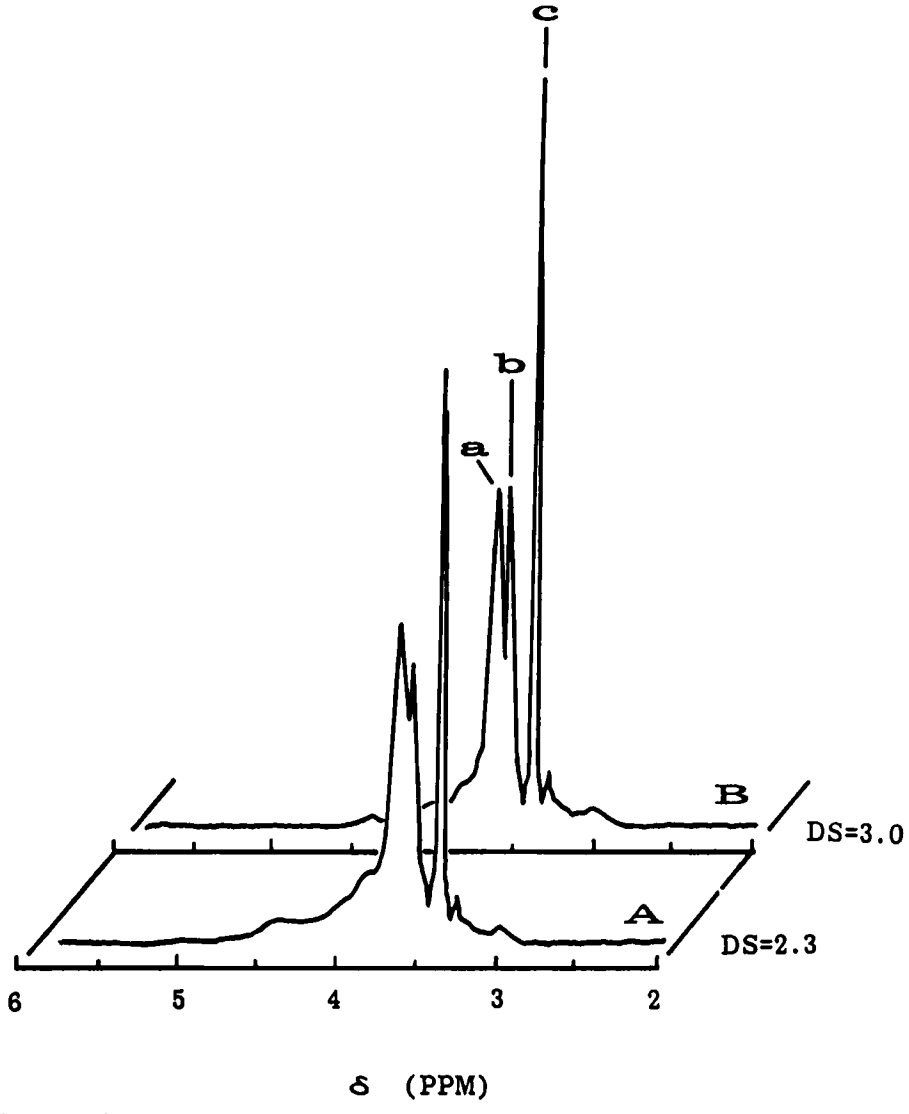


FIGURE 1 ^{1}H-NMR spectra of sample solutions in $CDCl_3$: curve A for the derivative obtained in the first step reaction and curve B for the derivative obtained in the second step reaction.

174°C. Heating-cooling cycles repeatedly given did not alter this thermal behavior and hence the transition is fairly reproducible. The average transition enthalpy and entropy are 0.45 kcal/mol and 1.0 cal/mol K, respectively.

The microscopic observation under cross polarizers dictates that the above-mentioned transition is associated with the isotropization of anisotropic birefringent phase; on heating, the bright birefringent phase gradually disappears into a dark field of isotropic phase at around 180°C and on cooling the dark field becomes gradually bright at around 170°C. Even though there is no clear appearance, on

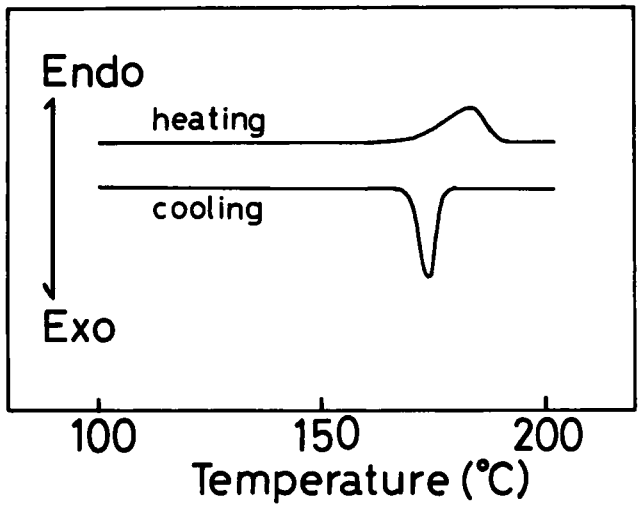


FIGURE 2 DSC thermograms of tri-o-(β-methoxyethoxy)ethyl cellulose.

cooling, of droplets of anisotropic phase out from the isotropic phase, the anisotropic phase is appreciably fluid and, hence, one can easily envisage that it is a kind of liquid crystal. By microscopic observation as well as by DSC analysis, no other physical transition can be detected in the temperature range of 20°C to 180°C, indicating that the mesophase character is retained even at a room temperature.

The mesophase character is also confirmed by the X-ray observation. Figure 3 shows the illustration of the X-ray pattern recorded at room temperature for the oriented mesophase. Here, the oriented specimen was prepared by stretching the highly viscous mesophase at room temperature by tweezers. The X-ray pattern consists of two broad reflections at 4.2 A and 11.8 A and another weak but sharp reflection at 5 A. The latter sharp reflection appears on a meridional direction along a fiber axis and its spacing of 5 A corresponds to the axial length of cellulose backbone in a crystalline form.[14] We can thus conclude that the reflection arises from an axial repeating of the main chain; in other words, the main chain is in an extended form in this phase. On the other hand, the broad reflection of 11.8 A

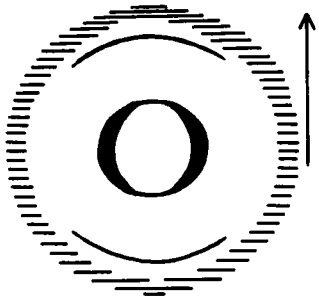


FIGURE 3 X-ray pattern of the oriented mesophase taken at room temperature. The arrow indicates the stretching direction of mesophase.

appears on the equator and so can be assigned to the lateral packing of cellulose chains. Its assignment is also justified by the density consideration; in the tentative hexagonal- and tetragonal-packing modifications of extended chains, the densities are calculated to be 1.0 g/ml and 1.1 g/ml, respectively, which are reasonable for this kind of polymer. No appreciable orientation is seen for the broad reflection at 4.2 A, which may possibly arise from the amorphous domain of the side-chain substituents. The overall features of the x-ray diffraction pattern, far from the crystal pattern, are to be expected for a liquid crystalline phase.

This type of mesophase is a cholesteric. This can be first presumed from the microscopic observation of Grandjean-like texture with the oily streaks as shown in Figure 4. Secondly, this is obvious from the exhibition of cholesteric reflection colors; upon standing, the mesophase between microscopic slides in the form of a thin film at temperatures below 120°C, the mesophase exhibits the characteristic cholesteric colors which sensitively change from blue to red with the temperature.

For evaluating the cholesteric pitches, the circular dichroic (CD) spectra of thin layer (around 20 μm) were obtained at different temperatures. Here, the spectrum was recorded after each sample was maintained at the desired temperature for 2h. The duration of 2h may be long enough for the equilibrium for the formation of the helical cholesteric structure to be reached at the respective temperatures, since after this duration the maximum wavelength of CD peak becomes constant irrespective of prior conditions. Typical CD spectra thus obtained are shown in Figure 5. A fairly sharp peak with the negative sign can be observed. The negative CD indicates a right-handed helical structure for the present cholesteric mesophase. Figure 5 also shows that the maximum wavelength (λ_m) of CD and hence the optical pitch (nP) increase from 400 nm to 700 nm by an elevation of temperature from

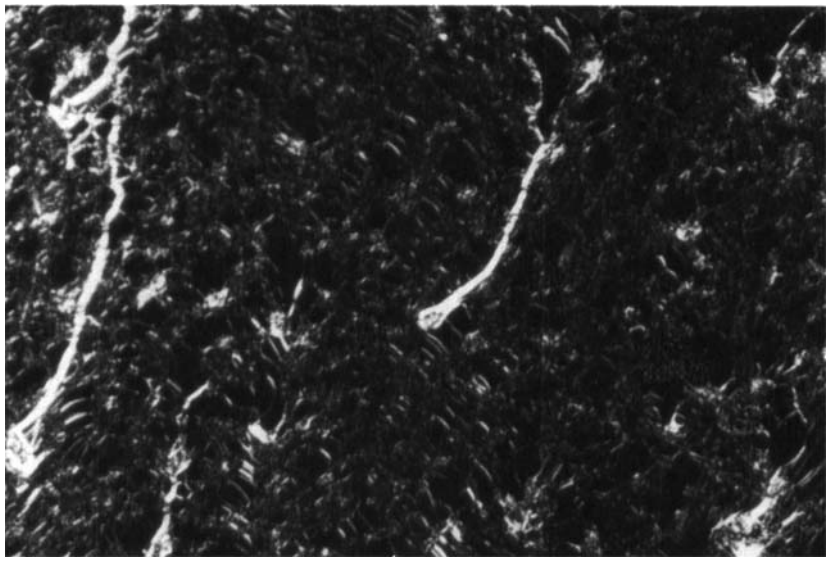


FIGURE 4 Microscopic photograph of thin mesophase (~20 μm) at 150°C exhibiting the cholesteric Grandjean-like texture with oily streaks.

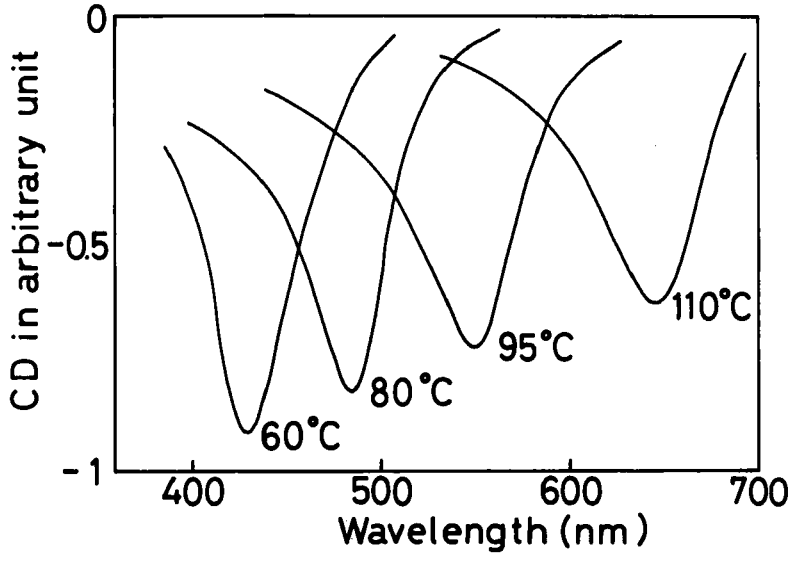


FIGURE 5 CD spectra of cholesteric mesophases measured at the different temperatures.

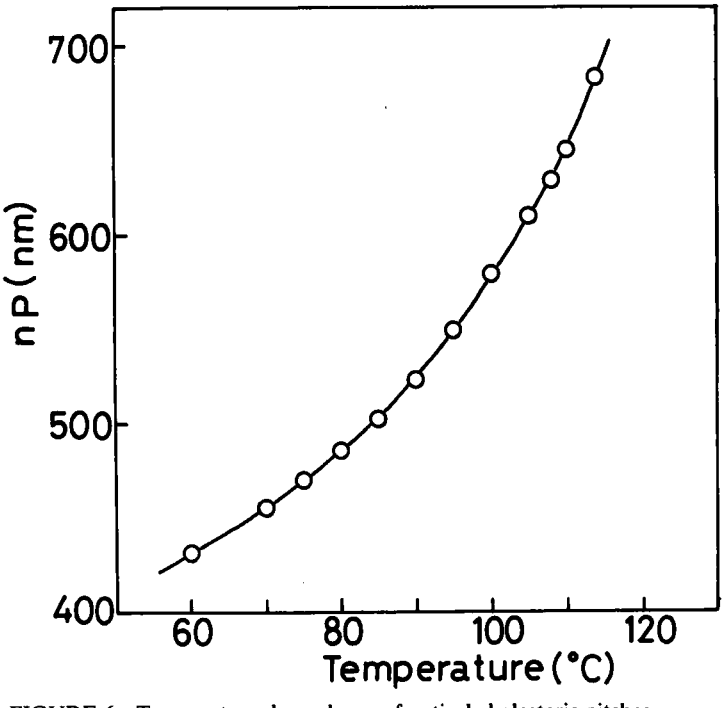


FIGURE 6 Temperature dependence of optical cholesteric pitches.

60°C to 120°C. Detailed temperature dependence of the optical pitch based on this observation is illustrated in Figure 6, consistently showing a positive temperature dependence. The increase of pitch with temperature may be also expected in a higher temperature region beyond 120°C. However, the pitch was not so much increased as to be detected by the polarized microscopic observation although the right-handed cholesteric structure was found to be maintained up to the isotropization temperature from the exhibition of positive optical rotation in a wavelength region of 400 to 700 nm.[15] Similar positive temperature dependence of the pitch for the right-handed helical cholesteric configuration has been observed for other cholesteric liquid crystals in both thermotropic and lyotropic systems of cellulose and its derivatives.[6,7,16-19] Only one example of negative temperature dependence has been reported for a left-handed helix by Vogt and Zugenmaier.[19]

We thus presented the first example of a thermotropic cellulose derivative with a homogeneous long side chain. In the same vein, we can expect the induction of the thermotropic liquid crystalline nature also for other kinds of cellulose derivatives, the preparation of which is now proceeding. The effect of side-chain substitution of the cellulose derivatives on their thermotropic behavior and their cholesteric mesophase-forming properties will be reported in the near future.

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