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Study on lyotropic liquid-crystalline properties of trimethylsilyl hydroxypropylcellulose

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Abstract

The lyotropic liquid-crystalline behavior of trimethylsilyl hydroxypropylcellulose (TMS-HPC) is reported in this paper. The introduction of the trimethylsilyl (TMS) group in the parent HPC increases the solubility in organic solvents, and the lyotropic mesophase can be formed in concentrated acetone solution. The critical concentration (C*) in acetone is approximately 36%. The liquid crystalline nature of TMS-HPC/acetone solution was confirmed by PLM, and the mechanism of liquid crystallization was studied by FTIR and WAXD methods. © 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Trimethylsilyl group; Hydroxypropylcellulose; Lyotropic liquid crystal; Cholesteric structure

1. Introduction

Many polymers with a rigid or semi-rigid backbone have been reported to show a liquid-crystalline phase.[1] In the past 20 years interest has focused on the study of the liquid-crystalline characteristics of cellulose and its derivatives since Werbowyj and Gray[2] found a cholesteric liquid-crystalline phase in concentrated aqueous solutions of hydroxypropyl cellulose (HPC).[3,4] At the same time, the study on functional cellulosic materials with a liquid crystalline phase such as a cellulose derivative gel or composite retaining liquid crystalline order became attractive also because of the potential advantages such as its high intensity, its toughness, and excellent processability.[5,6]

Although a lot of cellulose derivatives can be found the liquid crystal phase, most of the substituent groups are difficult to remove from the cellulose backbone. The trimethylsilyl (TMS) group is widely used in the protection of hydroxy functional groups as it is easily deprotected in mild conditions.[7,8] Pawlowski and Gilbert[9] studied the synthesis of TMS-cellulose and the cleavage of TMS group, and observed the cholesteric lyotropic liquid-crystalline structure in CH_2Cl_2 solvent. However, studies on the synthesis and liquid crystal properties of TMS-substituted cellulose derivatives have seldom been reported. In previous research, we synthesized a new kind of cellulose derivative, TMS-HPC, and studied its solubility in common organic solvents. We found the liquid-crystalline behavior of hydroxypropylcellulose silyl ethers in acetone. Such cellulose derivative containing the easily deprotected-TMS group is expected to be applied as a new cellulose derivative of a functional material containing a cholesteric liquid-crystalline phase.

2. Results and discussion

The introduction of a TMS group is confirmed by the appearance of a methyl proton signal at δ 0.10 in addition to the broad methyne and methylene proton signals of parent cellulose ethers at δ 3.0–5.0 in the ^{1}H NMR spectra (Fig. 1). The trimethylsilyl substitution (D_{TMS}) of HPC was determined based on the ratio of the integral areas of the signals for the methyl protons of the TMS groups at around δ 0.1 to that for the methyl protons of hydroxypropyl groups at around δ 1.1. In the experiment, the D_{TMS} is approximately 2.2,

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indicating that the hydroxyl groups of HPC were only partly substituted by TMS groups. Comparison of the FTIR spectrum of TMS-HPC to that of parent HPC, shows a new peak in the region 1251 cm^{-1} and three new peaks in the region around 875–752 cm^{-1} all corresponding to the Si–Me group in the product (Fig. 2A). At the same time, a weak –OH stretching peak at around 3485 cm^{-1} is still observed in the FTIR spectrum of TMS-HPC, indicating that the hydroxyl groups of HPC were not completely substituted.

Cellulose and its derivatives readily form cholesteric mesophases in a lyotropic system. HPC has a semi-rigid macromolecular structure and is the most popular cellulose derivative that form cholesteric ordered mesophases in concentrated solution.[1–4] So HPC seems to be a suitable starting material for the preparation of a cholesteric liquid crystal. The peak of associated OH groups shifts upward from 3450 to 3485 cm^{-1} as shown in the IR spectra (Fig. 2A) after the hydroxyl groups of HPC were partly substituted by TMS groups. This indicates that some of the intermolecular and intramolecular hydrogen bonding in HPC was destroyed. Moreover, the incorporation of TMS groups makes the product easily soluble in common organic solvents. Steric hindrance is improved to make the macromolecular chain more unfolded and rigid in solution; hence, it can form liquid crystals more easily. With a polarizing light microscope, the TMS-HPC/acetone solution is observed to be isotropic at room temperature when the concentration is below 36%. But when the concentration is greater, the anisotropic phase begins to appear in the solution. Fig. 3 shows the birefringence texture of the biphasic solutions at different concentrations. It is obvious that the mesophase texture varies with concentration. At the lower concentration, the mesophase is noncontinuous. The mesophase gradually becomes continuous and colored with the increase in concentration. The whole mesophase shows an iridescent texture when the concentration reaches 50%. The band structure in the vertical direction to the shearing direction is observed clearly (Fig. 3d). At the same time, the parallel lines texture can be easily seen in Fig. 3b and c, which also looks like the torsad structures for the sheared sample. Maybe this is the result of the thin sample solution being slightly sheared when pressed between two glass cover-slides.

It is reported that the force of the formation of liquid crystals for cellulose and its derivatives is attributed to both their semi-rigid backbone and molecular interactions in the systems,[10] and most of the molecular interactions are H-bonding interactions.[11] As FTIR spectroscopy is widely used to study H-bonding in many systems,[12] the mechanism of forming liquid crystals and the corresponding texture can be discussed by the frequency change in the FTIR spectra with different concentrations. Fig. 2 shows the FTIR spectra of acetone, solid TMS-HPC and TMS-HPC/acetone solution at different concentrations. In Fig. 2A(c), the peak at 1715 cm^{-1} is due to the stretching vibration of C=O for the acetone. As shown in Fig. 4a, the change of $\nu_{C=O}$ can't be seen in the lower concentrated TMS-HPC/acetone solution (concentration $< 36\%$); however, the peak at 1715 cm^{-1} shifts downward abruptly in a diagnostic concentration (concentration $\approx 36\%$), corresponding with the above discussion on the critical

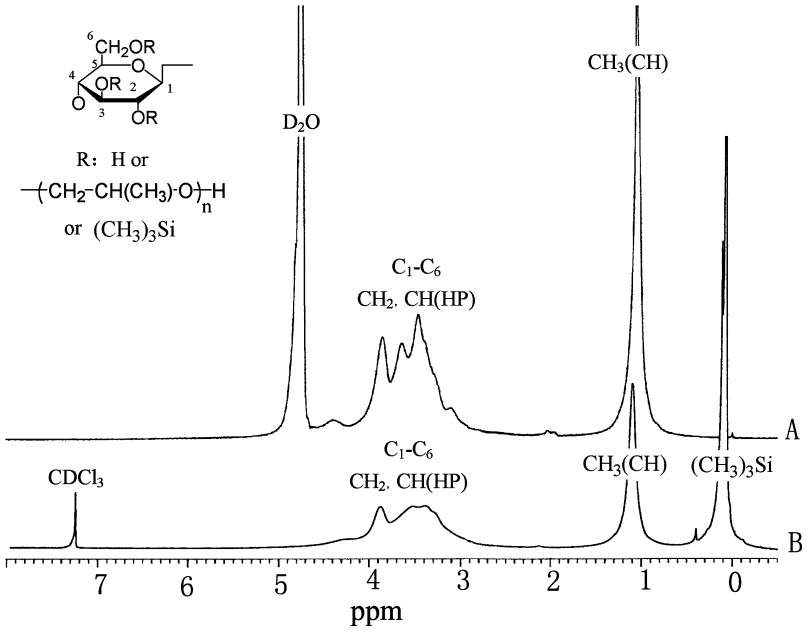

Fig. 1. ^1H NMR spectra of HPC and TMS-HPC. (A) HPC in D_2O; (B) TMS-HPC in $CDCl_3$.

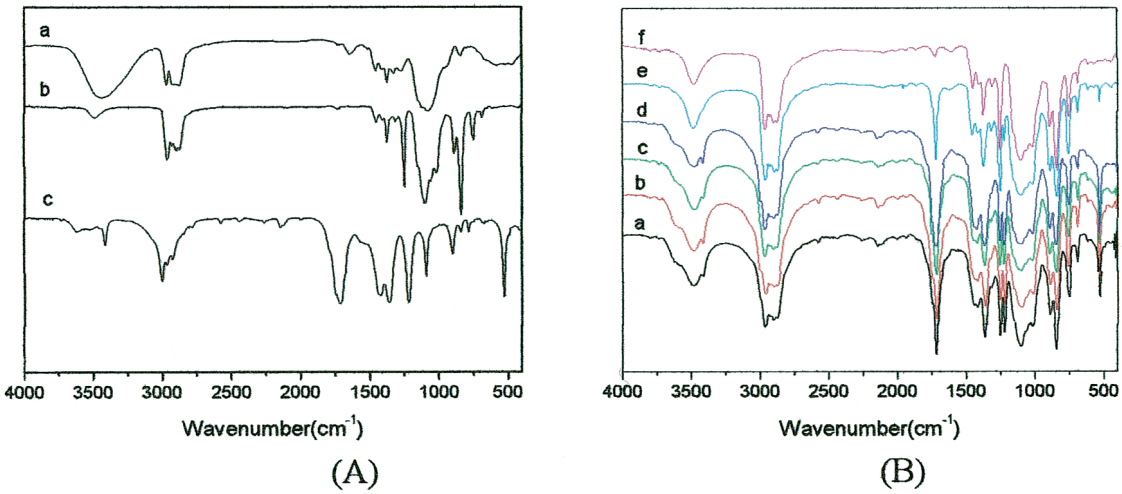

Fig. 2. The FTIR spectra. (A) HPC (a), TMS-HPC (b) and acetone (c); (B) isotropic solution of TMS-HPC/acetone (a: 26%; b: 28%; c: 34%) and liquid crystal solutions of TMS-HPC/acetone (d: 36%; e: 40%; f: 50%).

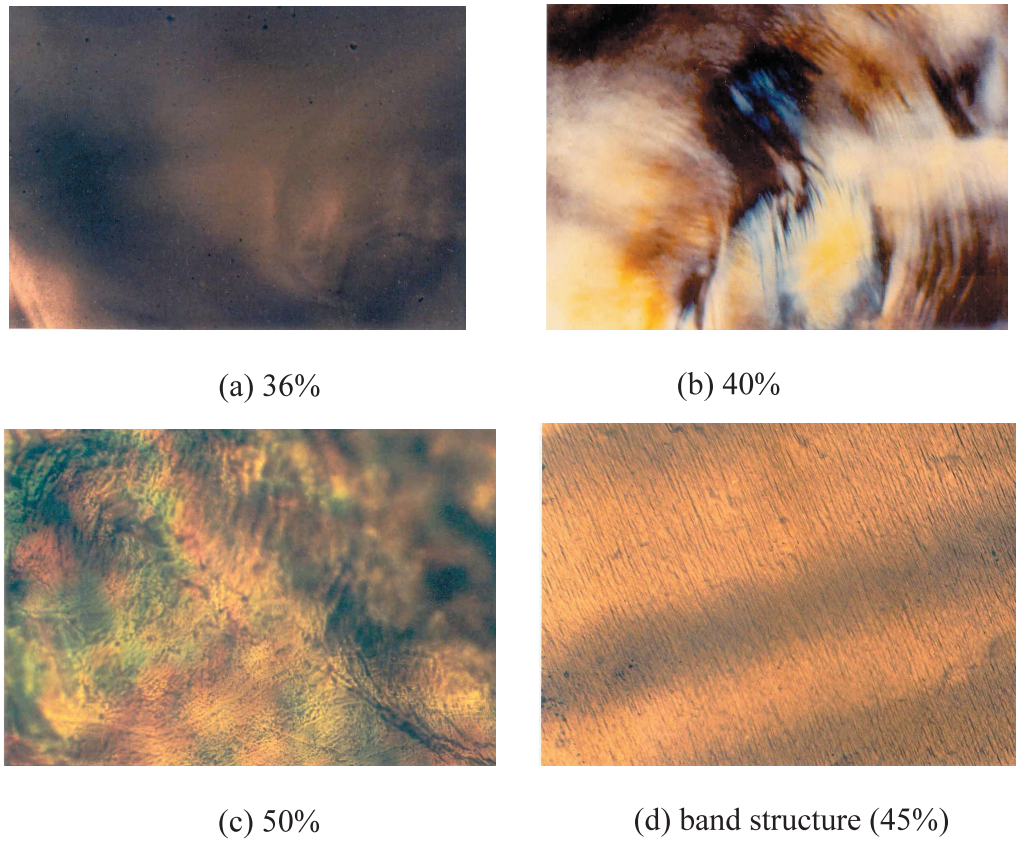

Fig. 3. The polarized light micrographs of TMS-HPC/acetone solutions with different concentrations at room temperature (a, b, c) and the band structure (d).

concentration (C*), after which it shifts to high frequency again with increasing concentration. At the lower concentrations (Fig. 2B a, b, c and d), the three broader peaks centered at 3479 cm^{-1} due to the associated –OH group of TMS-HPC can be observed nearly unchanged. With the increase of concentration, the relative intensities decrease, and the three peaks turn into one narrower peak that shifts in the high-frequency direction, in the end closing up to that of solid TMS-HPC (Fig. 2A(b) and Fig. 4b). The variation of $\nu_{C=O}$

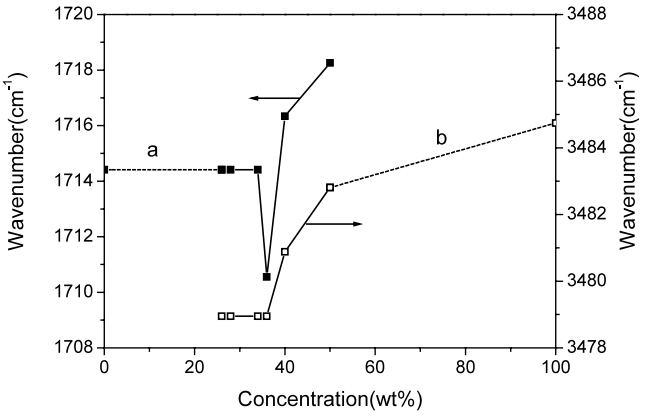

Fig. 4. The FTIR frequency changes observed for some absorption bands as a function of the concentration of solution of TMS-HPC/acetone. a: $\nu_{C=O}$; b: ν_{O-H}.

and ν_{O-H} can be explained as follows. At the lower concentrations, the solution of TMS-HPC/acetone is isotropic, and the TMS-HPC polymer chains are randomly dispersed in the acetone. At this time, there mainly exists intermolecular H-bonding between the TMS-HPC and the acetone and intermolecular H-bonding within the TMS-HPC chains. Although the decrease of carbonyl group number may decrease the probability of intermolecular H-bonding between the TMS-HPC and acetone, the influence is not obvious, and variation of $\nu_{C=O}$ and ν_{O-H} is hardly observed in Fig. 4. Reaching the critical concentration, the TMS-HPC chains transform from a disordered state to an ordered one. This results in the solvent molecules being separated among the layers of ordered polymer chains in the liquid-crystalline phases. The H-bonding between the TMS-HPC and the acetone is strengthened even though the probability of forming intermolecular H-bonding is decreased with the decrease of the carbonyl group number, and correspondingly the $\nu_{C=O}$ shifts downward is shown. However, with the further increase of the concentration of TMS-HPC/acetone, the number of carbonyl groups decrease so that the relative intensity of $\nu_{C=O}$ is observably decreased, and it becomes very weak as shown in Fig. 2B(f) when the concentration reaches 50%. This also means that the influence of carbonyl group number to the probability of forming intermolecular H-bonding between TMS-HPC and acetone is so high that the peak of $\nu_{C=O}$ and the ν_{O-H} shift in the high-frequency direction. At the same time, with the decrease of the influence of molecular interactions on the formation of liquid crystals in solutions, the space for the movement of TMS-HPC chains is very small due to the high density and steric hindrance, where the rigidity of the polymer chains is a key factor that influences liquid crystals.

Fig. 5(A) shows the WAXD curves of solid HPC and TMS-HPC. The broad peaks of HPC and TMS-HPC indicate their amorphous structure. It also can be concluded from the peaks around $2\theta = 6–8°$ and $2\theta = 15–20°$ that they reserve the structural characteristics of cellulose II, and the two peaks are corresponding to the plane of 101 and $10\bar{1}$, respectively. However, a comparison of the curve of TMS-HPC to that of the parent HPC shows broader peaks, lower peak intensities and smaller diffractive angles, which are corresponding to larger d_{101} and $d_{10\bar{1}}$ values calculated by the Bragg formula (Table 1). Combined with the previous discussion on the IR results, this can be explained in that parts of the hydrogen bond were destroyed and the distance of plane added due to the steric hindrance effect of the TMS group after the hydroxyl group in the plane of 101 and $10\bar{1}$ was partially substituted by a TMS group. This results in the structure of TMS-HPC being more unwound and more formless when compared with that of HPC so that TMS-HPC more easily dissolved in common organic solvents. The WAXD curves of different concentrations of TMS-HPC/ace-

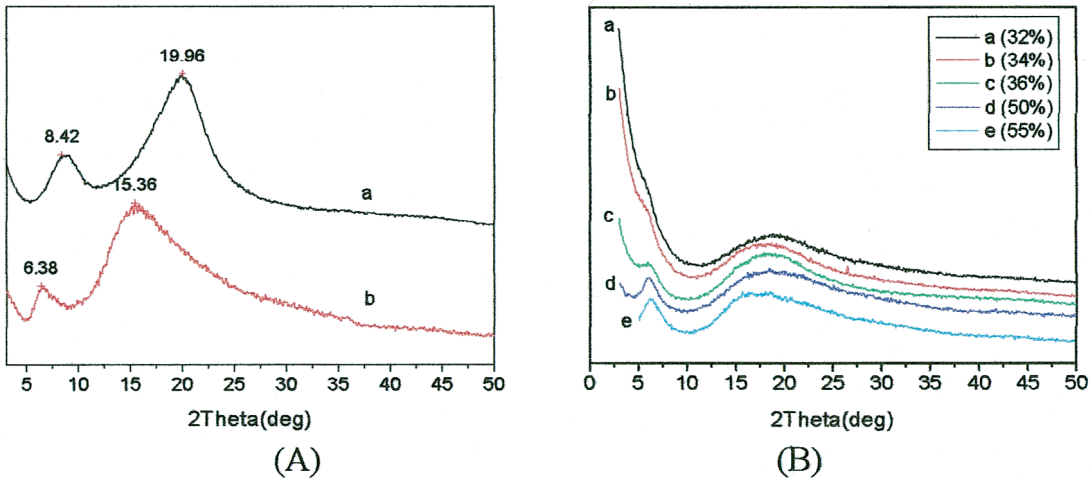

Fig. 5. The WAXD curves. (A) HPC (a) and TMS-HPC (b); (B) TMS-HPC/acetone solution with different concentrations.

tone solution are shown in Fig. 5(B). The corresponding diffraction data are shown in Table 1. The previous discussion indicates the anisotropic liquid-crystal phase begins to appear when the concentration of the solution reaches 36%. Comparison the WAXD curves of those of the solution with those of the solid TMS-HPC shows a broader amorphous peak around 16–18° corresponding to the plane of $10\bar{1}$ of solid TMS-HPC (15.4°). This was observed both in the isotropic and anisotropic solution, along with the peak shifting downward nearly to that of solid TMS-HPC with the further increase of concentration. This indicates that the plane of $10\bar{1}$ is irregular all the time. It is also easily seen that the peak around 5.6–6.2° corresponding to the 101 plane of solid TMS-HPC shows a great difference before and after forming the liquid-crystal phase. The peak of the 101 plane hardly can be seen in the isotropic solution; however, it begins to appear with the forming of the liquid-crystal phase. As the intensity of the peak increases, the shape of the peak becomes more acute, and the position of the peak moves to a lower angle with the increase in concentration. This suggests that the 101 plane changes from an irregular state to a regular state with the forming of a liquid-crystal phase, and the regularity increases and the d_{101} decreases with an increase of concentration. A similar phenomenon was observed by Yoshihike et al.[13] But further research is still needed.

3. Experimental

3.1. Materials

Hydroxypropyl cellulose (molar substitution (MS) 3.8), purchased from Ruitai Cellulose Chemistry, Shandong Province, P.R. China, was dried at 60 °C under vacuum before use. DMF was purified by the usual distillation method. Hexamethyldisilazane and other reagents were used without further purification.

Table 1
X-ray diffraction data for TMS-HPC/acetone solution, TMS-HPC and HPC

Sample	2θ (°)	d (Å)	2θ (°)	d (Å)
a (32%)	5.66	15.6	18.86	4.7
b (34%)	5.86	15.1	18.30	4.8
c (36%)	6.00	14.7	18.18	4.9
d (50%)	6.10	14.5	16.90	5.2
e (55%)	6.16	14.3	16.04	5.5
TMS-HPC	6.38	13.8	15.36	5.8
HPC	8.42	10.5	19.96	4.4

Calculated by the equation of 2d sin $\theta = \lambda$, $\lambda = 1.54056$.

3.2. Trimethylsilylation of HPC

HPC (2 g, 5.32 mmol of glucose units) was dissolved in DMF (concentration $\sim 10\%$), and hexamethyldisilazane (2 mL, 9.55 mmol) was slowly dropped into this solution at 80 °C under a dry nitrogen stream. The mixture was stirred for 3 h. After cooling slowly, the mixture was precipitated in deionized water, and the product was washed three times with water to remove the unreacted HPC. This crude product was purified by repeated dissolution in acetone and precipitation in water, and then it was dried for 72 h at 50 °C under vacuum. The trimethylsilyl substitution (D_{TMS}) of HPC was determined to be 2.2 based on the ratio of the integral areas of the signals for the methyl protons of the TMS groups at around δ 0.1 to that for the methyl protons of hydroxypropyl group at around δ 1.1.

3.3. Preparation of TMS-HPC/acetone solution

Solutions of TMS-HPC in acetone at various concentrations ranging from 20 to 80 wt.% were prepared in sealed vials. The solutions were allowed to age for 1 week at room temperature before evaluation.

3.4. Measurements

^{1}H NMR analyses were carried out by means of a Bruker DMX 300 MHz spectrometer in D_2O or $CDCl_3$ (solvents without Me_4Si). Optical photomicrographs of the solutions were obtained by viewing solutions through a polarizing light microscope (PLM) at magnification range from 100 to 400 ×. Solutions that did not transmit light when examined between crossed polaroid filters were considered to be isotropic. Anisotropic solutions exhibited birefringence. The FTIR spectra of different concentrated TMS-HPC solutions were taken in a Bruker Equinox55 Instrument. Different concentrations TMS-HPC/acetone solutions were scanned by means of a MAC Science wide angle X-ray diffraction spectrometer in the range of 3–50° using nickel-filtered Cu Kα radiation.

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