# Thermotropic Liquid Crystalline Behavior of Cholesterol-Linked Hydroxyethyl Cellulose

# V. A. E. SHAIKH,<sup>1</sup> N. N. MALDAR,<sup>1</sup> S. V. LONIKAR,<sup>1</sup> C. R. RAJAN,<sup>2</sup> S. PONRATHNAM<sup>2</sup>

<sup>1</sup> Shivaji University Centre for Postgraduate Studies, Medical College Old Campus, Solapur 413003, India

<sup>2</sup> Division of Chemical Engineering, National Chemical Laboratory, Pune 411 008, India

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ABSTRACT: A series of monocholesterylsuccinate (ChMS) derivatives of hydroxyethyl cellulose (HEC) were prepared with degree of substitution ranging from 0.6 to 2.0. They were characterized by ChMS content, infrared spectroscopy, polarizing microscopy, and differential scanning calorimetry. All these polymers displayed thermotropic liquid crystalline behavior on heating as well as on cooling. The transformation temperature was found to be influenced by the degree of substitution. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 763–770, 1999

**Key words:** hydroxyethyl cellulose; monocholesterylsuccinate; thermotropic; polarizing optical microscopy

### **INTRODUCTION**

It was predicted that semirigid and rigid polymers would form an ordered phase in concentrated solutions.<sup>1,2</sup> Cellulose and cellulose derivatives exhibiting lyotropic liquid crystalline properties have been reviewed.<sup>1</sup> Werbowyj and Gray<sup>3</sup> first reported the work on liquid crystals of cellulose derivatives. Recently, Guo and Gray<sup>4-7</sup> have investigated chiroptical properties of lyotropic solutions of mixed ester-ether derivatives of cellulose. Acetoxypropyl cellulose,<sup>8</sup> Hydroxypropyl cellulose,<sup>9</sup> and ethylcellulose with ethoxy content over 45% have been shown<sup>10</sup> to exhibit thermotropic liquid crystalline behavior. Bhadani and Gray<sup>11</sup> prepared a series of esters, namely, propionic. *n*-butvric, isobutvric, and phthalic acid esters, of (hydroxypropyl) cellulose that displayed thermotropic liquid crystalline behavior. Hydroxyethyl cellulose acetate also has been shown to be a thermotropic material.<sup>12</sup> In all these investigations, nonmesogenic, flexible substituents were used to render liquid crystalline properties to cellulose or cellulose derivatives.

In a work to be published separately, we have employed a known mesogen monocholesterylsuccinate to confer thermotropic liquid crystalline properties to cellulose acetate, ethyl cellulose, starch, and hydroxyethyl starch. Here, we report the preparation and thermotropic behavior of monocholesterylsuccinate derivatives of hydroxyethyl cellulose with varying monocholesterylsuccinyl content. This cellulose ether was selected as the parent compound because the hydroxyethyl group may act as a flexible spacer and, therefore, would be more amenable to reaction with a bulky subtituent, such as monocholesterylsuccinate.

### EXPERIMENTAL SECTION

#### Materials

Hydroxyethyl cellulose (HEC, MS 2.5) was purchased from Merck. Cholesterol (95%) was ob-

Correspondence to: S. V. Lonikar.

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tained from Aldrich Chemical Company Inc, Hyderabad, India. Succinic acid, acetic anhydride, pyridine, and other organic solvents were purchased from S.d. Fine-chem Ltd., Mumbai, India. Solvents were purified before use by distillation. Succinic anhydride was prepared as per the reported procedure.<sup>13</sup>

#### Preparation of Monocholesterylsuccinate (ChMS)

Cholesterol, 25 g (0.0646*M*), was dissolved in 60 mL of pyridine and succinic anhydride, 18 g (0.18*M*) was added to it. The reaction was allowed to proceed at 90°C for 24 h under stirring under nitrogen atmosphere. At the end of 24 h, the dark brown colored reaction mixture was cooled to room temperature and precipitated into distilled water. The precipitate was extensively washed with distilled water. The product obtained was first air-dried and then purified by recrystallization in acetone. Recrystallized product was then dried under vacuum at room temperature (yield = 28 g; 89% of theorotical; mp 185°C).

### Preparation of Monocholesterylsuccinate Derivative of HEC (Polymers PI–PV)

To a predetermined amount of monocholesterylsuccinate (2 to 10 g), about 30 mL of dry hexane and an excess amount of thionyl chloride were added, and the reaction mixture was stirred at room temperature for 24 h. At the end of reaction time, the solvent and excess thionyl chloride were removed under reduced pressure. Dry benzene, about 15 mL, was added, and the reaction mixture was stirred for 10 min. The benzene was then removed under reduced pressure. Addition and removal of benzene was repeated three times to ensure complete removal of thionyl chloride. Formation of acid chloride was confirmed by infrared (IR). The acid chloride was further dried under vacuum. The product was then dissolved in 6 to 7 mL of dimethyl acetamide, and the solution was added to another flask containing HEC (1 g) and dimethyl acetamide. The total volume of solvent in the reaction mixture was 20 mL. The reaction mixture was stirred at 70°C for 72 h under nitrogen and poured into methanol. The precipitate was filtered, washed with methanol, and airdried. It was then Soxhlet extracted with methanol and dried under vacuum at room temperature.

# **GENERAL ANALYSIS**

Melting point of ChMS was determined by using an electrically heated aluminum metal block melting point apparatus.

IR spectra of the products were recorded on a Perkin–Elmer 883 spectrometer using a nujol mull or KBr pellet technique for sample preparation. Proton nuclear magnetic resonance (NMR) spectra of ChMS was recorded in CDCl<sub>3</sub> with tetramethylsilane as an internal standard on Brucker 200 MHz spectrometer. The thermal properties of the polymer were studied by polarizing light microscopy on a LEITZ LABORLUX 11 POL S polarizing optical microscope equipped with a Leitz Wetzlar Microscope Heating Stage 350 and a WILD MPS  $0.32 \times$  camera. DSC analysis was carried out on a Mettler TA 4000 series instrument. It consisted of a DSC 30 cell coupled to Mettler TC 11 TA processor. The heating and cooling rate was 10°C min.

The degree of substitution (DS) was quantitatively determined by saponification. In a typical

Sample	ChM (S; g)	Temperature (°C)	ChMS Content (%)		
			From Saponification	From Weight Increase	$\mathrm{DS}^{\mathrm{a}}$
PI	2.0	70	51.0	48.40	0.60
PII	2.5	70	61.6	59.18	0.92
PIII	3.5	100	72.0	72.22	1.50
PIV	5.0	70	73.9	75.00	1.63
PV	10.0	70	77.6	76.20	2.00

 Table I Reaction Conditions for Preparation of Monocholesteryl
 Derivative of HEC

HEC, 1.0 g; reaction time, 72 h.

<sup>a</sup> The degree of substitution was determined by saponification.



Figure 1 Infrared spectra of polymers (PI-PV).

run, about 0.3 g of the dried polymer was dissolved in 20 mL of pyridine and then 20 mL of standard NaOH was added. The hydrolysis was carried out for 1 h at the reflux temperature. After cooling it to room temperature, the excess of alkali was back-titrated conductometrically with standard hydrochloric acid. A blank titration was



Figure 2 Photomicrograph (crossed polars) of ChMS  $(\times 100)$  RT.

carried out in similar manner using HEC and cholesterol in weight ratio nearly the same as that of the product which was estimated from the weight increase. The degree of substitution was ascertained using a value of 2.5 for the molar etherification of HEC and considering two ester linkages per ChMS substituent.

# **RESULTS AND DISCUSSION**

#### Monocholesterylsuccinate

Monocholesterylsuccinate (ChMS) was prepared by reacting cholesterol with succinic anhydride in presence of pyridine. It was characterized by elemental microanalysis (calculated for  $C_{27}H_{45}OOC$ .  $CH_2CH_2COOH$ : C% 76.54, H% 10.28; found C% 76.57 and H% 10.45), IR, and proton NMR spectroscopy. IR spectrum of ChMS revealed no hydroxyl stretching vibrations in the 3400–3500



**Figure 3** The DSC thermogram of ChMS in the first heating, cooling, and the second heating mode.

 $\rm cm^{-1}$  region in contrast to that of cholesterol. A strong peak at 1718 cm<sup>-1</sup> indicated formation of ester linkage. Proton NMR spectrum of ChMS showed a multiplet at 2.65 ppm due to two adjacent methylene groups of succinyl moiety. Other spectral characteristics were similar to that of cholesterol.

# Monocholesterylsuccinate Derivatives of Hydroxyethyl Cellulose (PI–PV)

HEC was reacted with ChMS in varying weight ratio to obtain a series of polymers with varying monocholesterylsuccinyl content. The reaction conditions and degree of substitution of the polymers are shown in Table I. The degree of monocholesterylsuccinate substitution was determined in a manner analogous to the determination of acetyl content of acetyl cellulose.<sup>14</sup> The polymer samples were saponified with excess of standard alkali, and the excess of alkali was back titrated against standard acid. Monocholesteryl succinyl content determined by saponification is in good agreement with that calculated from weight increase within experimental error. It can be seen from Table I that the DS increased with increasing quantity of ChMS in the reaction. IR spectra and schematic structure of the polymers PI through PV are presented in Figure 1. The bands

around 3650–3350, 2900, and 1800–1700 cm<sup>-1</sup> are due to —OH, —CH<sub>2</sub>—, and >C=O stretching vibrations, respectively. Since the maximum DS was 2.0, all the samples showed the presence of hydroxyl peak. However, the intensity of the hydroxyl peak decreases, and that of the methylene and carboxyl peak increases with increasing degree of ChMS substitution from PI to PV. No other changes are apparent.

# **Thermotropic Behavior**

ChMS displays monotropic behavior.<sup>15</sup> A small amount of the sample was heated in a microheating stage and was observed under crossed polars using polarizing optical microscope. It does not show any birefringence on heating and isotropization occurred at 176-179°C. The sample was heated further a few degrees above isotropization temperature and held at this temperature for about 5 min. On cooling, the cholesteric phase appeared at 151°C, and the texture was retained at room temperature. Polarizing optical photomicrograph for ChMS is shown in Figure 2. DSC scans of first heating, cooling, and second heating runs are shown in Figure 3. Both first and second heating showed an endotherm at 178-179°C indicating melting. The thermogram for cooling run



PI (X100, RT)



PII (X100, 175 C cooling)



PIV (X100, RT)



PII (X100, 215 C heating)



PIII (X40, 150 C heating)



PV (X100, RT)

Figure 4 Photomicrograph (crossed polars) of polymers PI to PV.

revealed an exotherm at 154°C corresponding to isotropic to cholesteric phase transition.

HEC is not a thermotropic material. It was observed under polarizing microscope that on heating above 180°C, the view field brightened when the sample was slightly pressed, and the brightness disappeared when the deforming force was released. The material decomposed at 250°C without displaying birefringence.

All the ChMS derivatives of HEC showed mesomorphic behavior. Polymers PI through PV revealed strong birefringence on heating, and the birefringence pattern deformed under pressure, indicating that it is a liquid crystalline phase. The mesophase appeared at around 150°C for PI, 140°C for PII, 110°C for PIII, 130°C for PIV, and 150°C for PV, and was observed until isotropization occurred at around 225, 235, 190, 225, and 235°C, respectively. The samples were heated 5 to 10°C above the isotropization temperature, held for about 5 min, and cooled at 10°C min. The anisotropic phase appeared during cooling at

Sample	PI	PII	PIII	PIV	PV
DS	0.6	0.92	1.5	1.63	2.0
$T (^{\circ}C)^{a}$	150 - 225	140 - 235	110-190	130 - 225	150 - 235
<i>T</i> (°C) <sup>b</sup>	200 (RT)	180 (RT)	_	160 (RT)	160 (RT)
Tc-i (°C) <sup>c</sup>	200	160	_		180
It-c (°C) <sup>c</sup>	195	152		—	175

 Table II
 Transformation Temperatures for Polymers PI to PV

RT represents room temperature; T, represents the temperature range over which the mesophase was observed under polarizing microscope (crossed polars).

<sup>a</sup> In the heating mode.

 $^{\rm b}$  In the cooling mode.

<sup>c</sup> The transition temperature is the value at the top of the peak in DSC thermogram (Tc-i, transformation from the mesophase to the isotropic phase; It-c, transformation from the isotropic phase to the mesophase).

about 200°C for P–I, 180°C for P–II, 160°C for P–IV, and 160°C for P–V, and in each case, mesophase texture was retained at room temperature. Polarizing optical photomicrographs for these samples are shown in Figure 4. The results of observation under polarizing optical microscope and DSC analysis are presented in Table II. The mesophase formation occurred at lower temperature in cooling mode compared to the isotropization temperature in heating mode. Similar results have been reported earlier.<sup>12</sup>

It can be seen from Table II that the temperature at which mesophase begins to appear on heating decreases with increasing DS of ChMS substituent; that is, from 150°C for PI with DS 0.60 to 140°C for PII with DS 0.92 to 110°C for PIII with DS 1.5. A further increase in DS results in increase in the temperature at which the mesophase begins to appear to 130°C for P IV with DS 1.63 to 150°C for PV with DS 2.00. This may be explained in terms of the influence of the substituents on the flexibility of the polymer backbone. Though for flexible backbones (polyacrylates, polysiloxanes), attachment of the side chain increases the rigidity of the polymer backbone, attaching a side chain to more rigid backbones (polystyrene and polymethacrylates) increases its flexibility.<sup>16</sup> Cellulosics have a more rigid backbone than polystyrene, as judged from the value of a in the Mark–Houwink–Sakurada equation.<sup>1</sup> Therefore, it is logical to expect that introducing a substituent onto HEC would increase the flexibility of the backbone. Acetylation of HEC gives thermotropic hydroxyethyl cellulose acetate though the parent HEC is not a thermotropic material.<sup>12</sup> This explains the decrease in the temperature at which mesophase begins to appear with increas-

ing DS of ChMS substituent from 0.6 to 1.5. Jinan et al.<sup>10</sup> have reported that the temperature of mesophase appearance decreased from 178 to 152°C as the ethoxy content of ethyl cellulose increased from 43 to 48%. In the present work, the observed increase in the temperature at which the mesophase begins to appear with further increase in DS from 1.5 to 2.0 is probably because of crowding of bulky ChMS substituent on the backbone. Increasing DS generally reduces the overall molecular flexibility as side groupside group interactions become increasingly severe. Flexible substituents, such as ethoxy and side chain containing methylene units, were used in earlier reported works.<sup>10,16</sup> However, on cooling, isotropic to mesophase transition occurred at lower temperature with increasing the DS.

DSC thermograms for PI, PII, and PV obtained in heating and cooling mode are given in Figure 5. On heating, an endotherm was observed from 185 to 210°C for PI, from 135 to 180°C for PII, and from 152 to 210°C for PV, and on cooling, an exothermic peak was observed from 200 to 170°C for PI, from 165 to 130°C for PII, and from 190 to 140°C for PV. These results are in agreement with the observation under polarizing optical microscope and similar to those obtained with hydroxyethyl cellulose acetate.<sup>12</sup> Huang reported that DSC thermogram of hydroxyethyl-cellulose acetate in the heating mode showed a single broad endotherm from 130 to 185°C though observation under a polarizing microscope revealed conversion from solid state to anisotropic fluid at 130°C and to isotropic fluid at about 185°C.<sup>12</sup> The absence of two distinct endotherms in DSC thermograms may be attributed to the high molecular weight, polydispersity, high viscosity, and non-



Figure 5 The DSC thermograms of PI, PII, and PV in (a) the heating mode and (b) in the cooling mode.

uniform substituent distribution of the cellulose derivatives.<sup>17,18</sup> The single exotherm in cooling mode is due to the transformation of isotropic fluid into mesophase, which is retained at room temperature. DSC thermograms for PIII and PIV did not reveal distinct thermal transition even though mesophase formation was observed underpolarizing microscope.

#### **CONCLUSION**

Monocholesterylsuccinate derivatives of HEC display thermotropic liquid crystalline behavior on heating as well as cooling. The mesophase appears at lower temperature in cooling mode compared to the isotropization temperature in heating mode. The temperature region over which the mesophase is observed ranges from 110 to 235°C, depending upon the degree of substitution of ChMS. The temperature of mesophase appearance on heating is lowest when DS is 1.5 and increases when DS is either lower or higher than 1.5.

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