

Thermotropic Liquid Crystalline Behaviors of Ethylcellulose

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SYNOPSIS

The thermotropic liquid crystalline behaviors of ethylcellulose (EC) were investigated by DSC, polarizing microscope with hot stage, and capillary rheometer. It was found that only those EC that have the ethoxyl content over 45% can exhibit the thermotropic liquid crystalline behaviors: the DSC trace showed the transition from mesophase to isotropic phase, the texture appeared under the crossed polarizer, and the rheological flow curves exhibited two yield points.

INTRODUCTION

According to the Flory theory,¹ the molecular feature responsible for liquid crystallinity are: (i) asymmetry of molecular shape and (ii) anisotropy of intermolecular force. And Papkov² suggested the prerequisite that whether the polymer can transform to liquid crystal or not is the geometry asymmetry of macromolecular conformation but the asymmetry in chemical structure.

Generally, flexible-chain polymers have the conformation of a tangle, that is, the geometric asymmetry of their macromolecules is weakly expressed. Only for the molecules of rigid-chain polymers, which have a drawn-out form caused by the restricted rotation of the units around the bonds which connect them, is a geometric asymmetry possible that does not permit them to be arbitrarily positioned in space. Based on the lattice theory, Flory³ predicted that cellulose and its derivatives can transform into liquid crystalline state. As we know, the basic structure unit of cellulose is cellobiose, which has the asymmetric structure (see Fig. 1). So it is active optically.⁴ This is a precondition responsible for transition into the liquid crystalline state. And from Houwink-Sakurada equation,⁵ that is, $[\eta] = KM^\alpha$, we know that $\alpha = 1.8$ for the rigid chain, $\alpha = 0.5$ for the flexible chain, and $\alpha = 0.9-1.0$ for cellulose. Therefore, cellulose belongs to the semi-rigid conformation. Figure 2 shows that many hy-

drogen bonds exist in intermolecules and intramolecules. Werbowyj et al.⁶ first reported the works on the liquid crystals of cellulose and its derivatives. Subsequently scientists⁷⁻⁹ published many papers on this field, including the material of EC. However, most of them focused their attention on the study of lyotropic not thermotropic liquid crystalline properties. The more detail of the thermotropic liquid crystal of the hydroxypropylcellulose (HPC) had been investigated, but as to EC the similar paper that related to the relationship between the DS and liquid crystallinity has not been found. In this work the investigation of the thermotropic liquid crystalline behaviors of ethylcellulose by means of differential scanning calorimetry (DSC), polarizing microscope, and rheology were carried out.

EXPERIMENTAL

Sample Preparation

Ethylcellulose with various ethoxyl content was made in our laboratory. Cotton linters were pretreated by 50% NaOH at 25°C for 40 mins. The

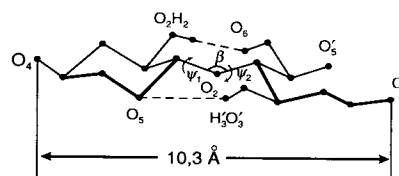


Figure 1 Configuration of cellobiose residue (Ref. 4).

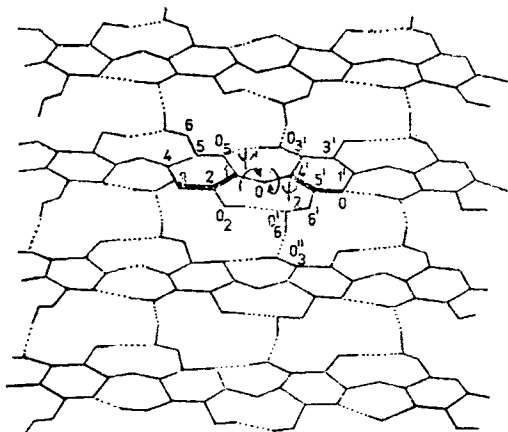


Figure 2 System of intermolecular and intramolecular hydrogen bond in cellulose (Ref. 4).

alkali cellulose, toluene, and ethyl chloride were poured into an autoclave for ethylation. The reaction was carried out in 5–8 h at 130°C. Different degree of substitution can be obtained by changing the usage of ethyl chloride and reaction time.

DSC

Apparatus: Perkin-Elmer DSC-2C.

Conditions: scanning rate 20°/min, sample weight 5 mg, first heating run then cooling run.

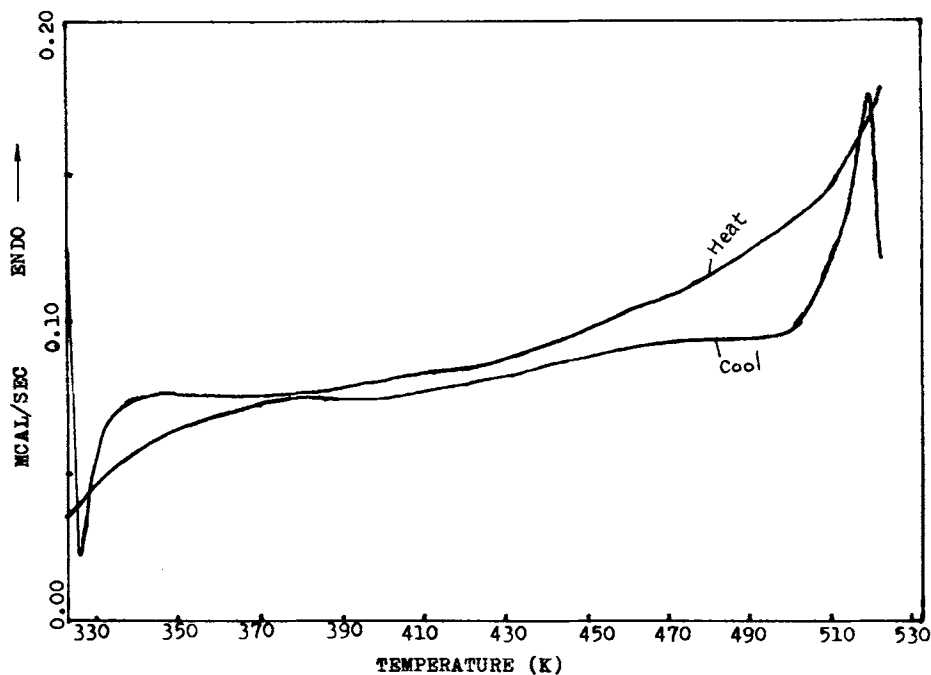


Figure 3 DSC curves of EC sample A.

Table I Preparation Conditions of Samples*

Sample	Toluene/ Cellulose (mL/g)	Ethyl Chloride/ Cellulose (mL/g)	Ethoxyl Content (%)
A	0	10	43
B	6	5	45
C	6	10	48

* The other conditions are the same.

Polarizing Microscope Observation

Apparatus: Orthoplan-01.

Conditions: The sample sandwiched with glass slides was put on the hot stage, the polarizer was crossed, carefully observed, and the magnitude of temperature recorded when the picture was taken.

Rheological Properties

Apparatus: Instron 3211.

Conditions: Die $d = 0.58$ mm, $L_1/d = 10$, $L_2/d = 20$, $L_3/d = 30$ where d is diameter and L is the length, shear rate 0.1–100 s^{-1} , temperature 150–250°C.

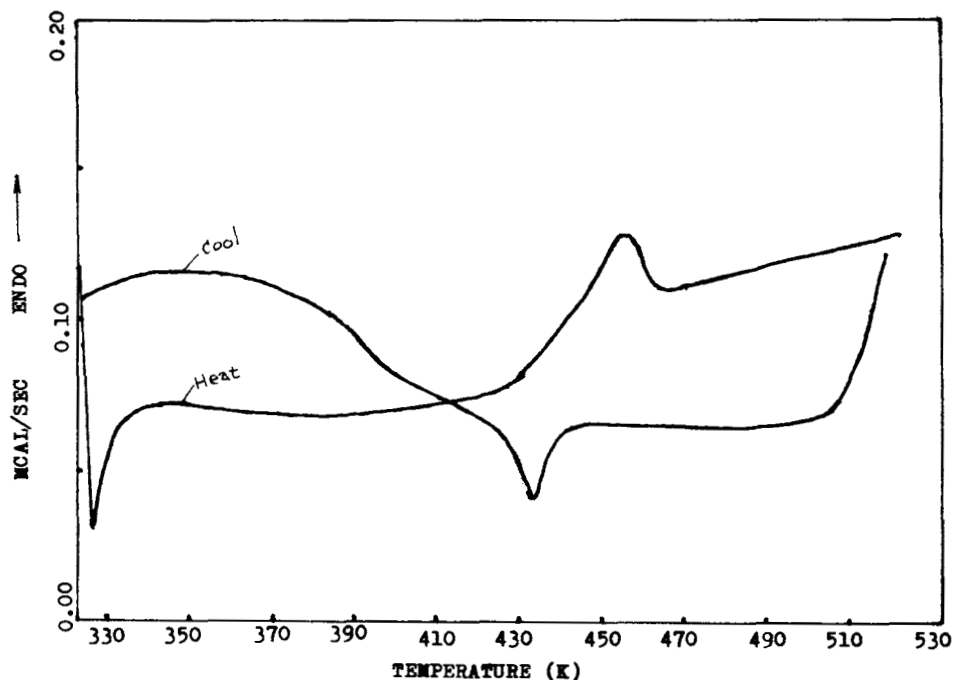


Figure 4 DSC curves of EC sample B.

RESULTS AND DISCUSSION

DSC Interpretation

According to Claudine Noel's paper,¹⁰ the DSC trace exhibits a glass transition, characteristic of the

polymer backbone, and a first-order transformation from the mesophase to isotropic phase due to the mesogenic side chains. The thermal behavior of liquid crystalline main-chain polymer is more complicated. In most cases, samples show a glass transition,

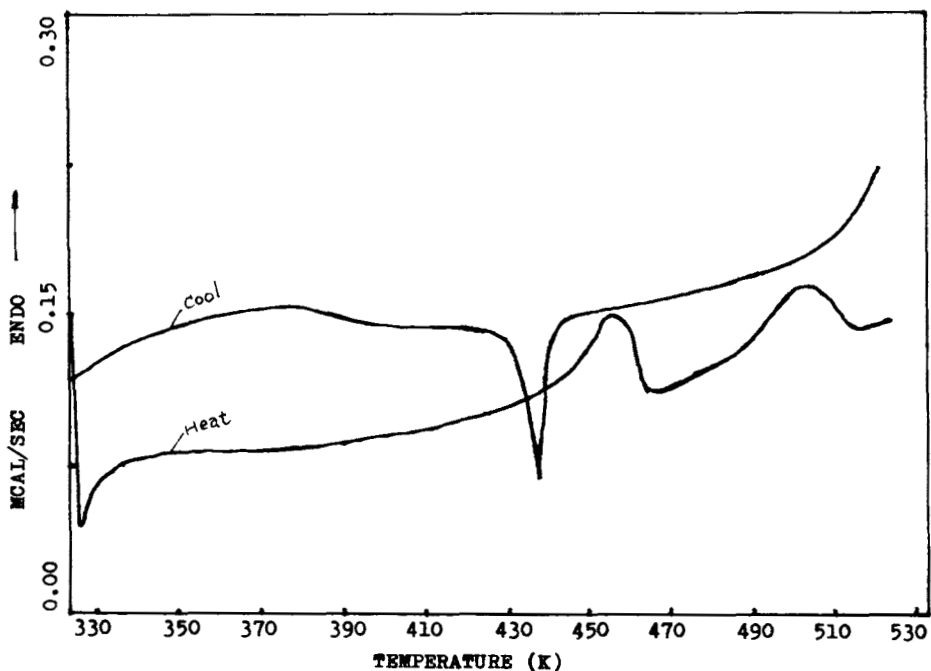
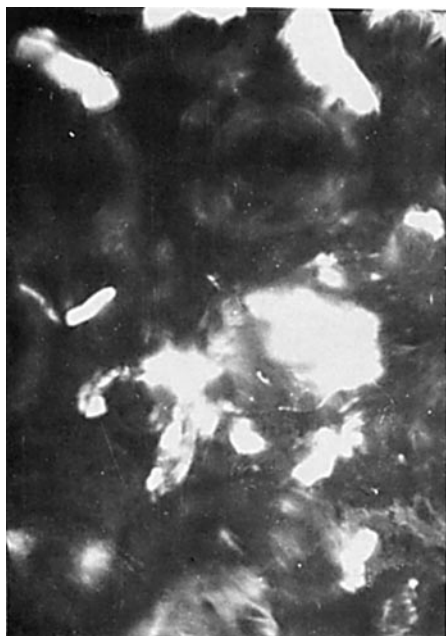
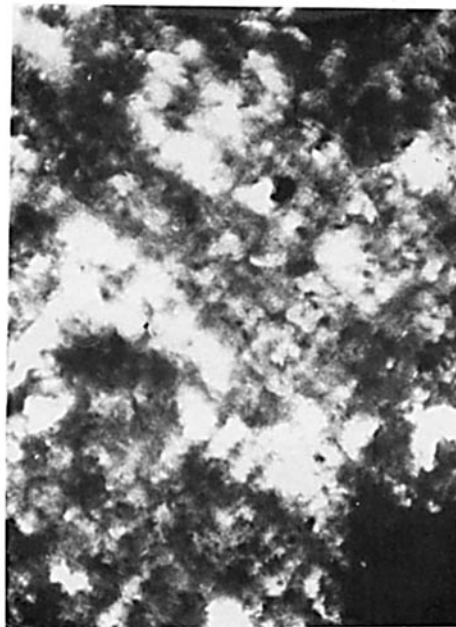


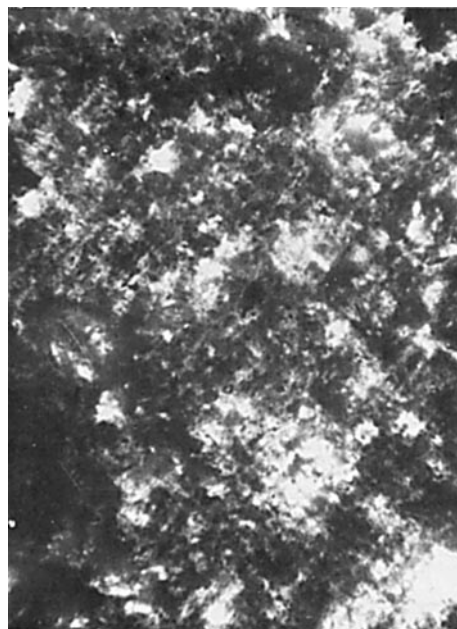
Figure 5 DSC curves of EC sample C.



sample A (178-183°C)



sample B (157-185°C)



sample C (152-227°C)

Figure 6 Polarizing microscope photos of EC samples A, B, and C.

melting, and mesophase-mesophase and/or mesophase-isotropic liquid transitions. For the EC with various ethoxyl content the situation is different

from side-chain or main-chain polymers, the liquid crystallinity gradually perfected by increasing the ethoxyl content. There is no transition peak in sam-

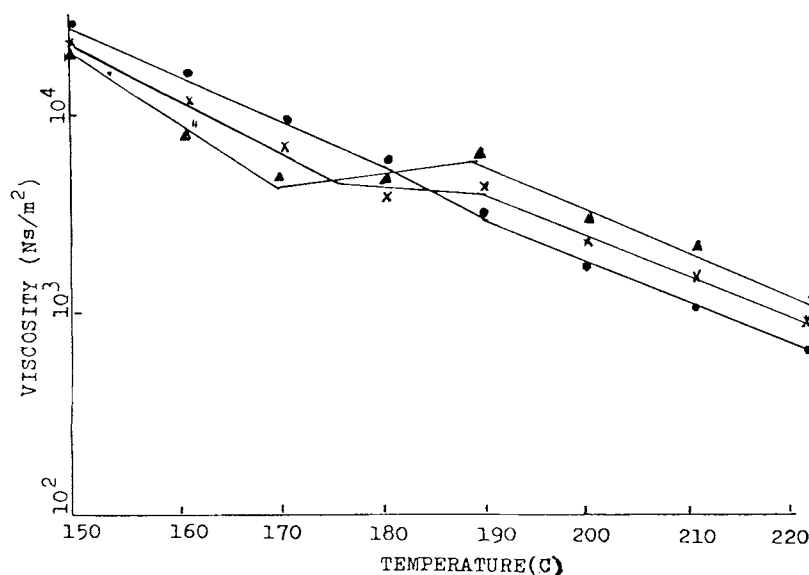


Figure 7 Relationship between viscosity and temperature for EC with different ethoxyl content. (●) sample A; (×) sample B; (▲) sample C.

ple A, its ethoxyl content is 43% (see Fig. 3 and Table I). That means that the liquid crystalline behaviors did not exhibit in sample A. In the case of sample B, the ethoxyl content is 45% (see Fig. 4); one transition peak appeared in the heat run or even cooling run. The transition enthalpy is only 1.39 cal/g (heating run) and -0.66 cal/g (cooling run). It indicated that the liquid crystallinity just occurred. However as we can see in Figure 5, when the ethoxyl content increased up to 48%, the DSC trace exhibits two transition: One is solid phase-mesophase transition; the other is mesophase-isotropic liquid transition. The transition enthalpy are 2.17 and 1.8 cal/g, respectively. This a typical liquid crystalline behavior. However, the peak of mesophase-isotropic phase transition disappeared in the case of the cooling run.

Polarizing Microscope Observation

The thermotropic liquid crystalline polymer would exhibit a characteristic texture under the polarizing microscope when the temperature reaches a certain range. This is also an important method for recognizing liquid crystalline polymer. Figure 6 shows the polarizing microscope picture of three samples. Only a small bright field appeared in sample A; the temperature range of liquid crystalline state is 178–183°C. Sample B shows a larger bright field; the temperature range is 157–185°C. Sample C exhibited well liquid crystallinity; the temperature range is 152–227°C.

Rheological Properties

Many scientists¹¹⁻¹⁴ are interested in the rheological properties of the thermotropic liquid crystalline polymer, which has a close relation to the process and performance of the products. The anisotropic properties will exist in the final products yielded by extruding, injection molding, etc. because of the polymer anisotropy under mesophase condition. As to most of polymer, the relationship between vis-

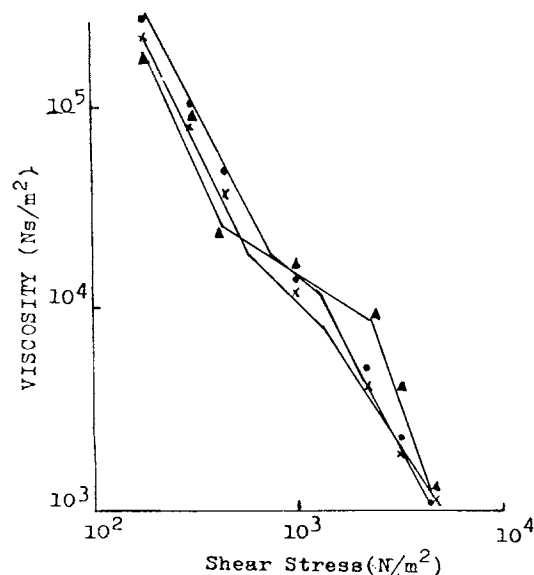


Figure 8 Viscous flow of liquid crystal EC melts (180°C). (●) sample A; (×) sample B; (▲) sample C.

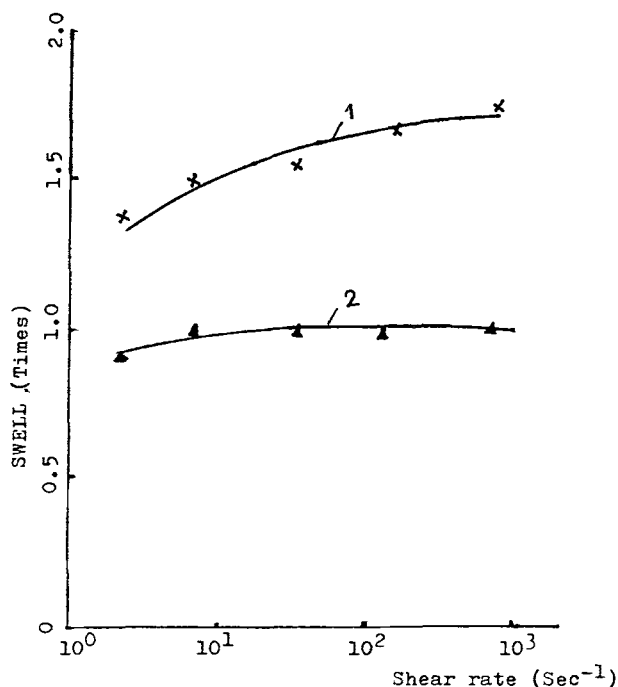


Figure 9 Die swell phenomenon of polymer melts. 1, LDPE; 2, EC.

cosity and temperature follows the Arrhenius equation:

$$\eta = b \exp(-E/RT)$$

$$\ln \eta = \ln B - E/R \times 1/T$$

A straight line should emerge if we plot the $\ln \eta$ to $1/T$. And the viscosity would decrease with increasing temperature. However, for the liquid crystalline polymers, the situation is different. The curve of viscosity-temperature showed a so-called three region flow^{15,16} (Fig. 7). The relationship between viscosity and shear stress also appeared as three region flows (Fig. 8). A similar phenomenon could be seen from Figs. 7 and 8. Sample C with an ethoxyl content of 48% has a wider unusual flow region than sample B and A. These observations of rheological response appear to be associated with texture changes. The polymer chain is easily oriented under the liquid crystalline state during shear flow.

Die swell phenomenon also is very popular in the polymer process. Usually, the die swell increases of shear rate. But the die swell almost equals to zero to EC during shear flow in the mesophase temperature (Fig. 9). That may be due to the easy orien-

tation of the polymer chain. Thus the residual pressure in the exit of the die was low.

CONCLUSION

1. When the ethoxyl content reaches to a certain extent, the EC exhibited the thermotropic liquid crystalline behaviors in a certain temperature region.
2. There are three region flows in the curves of viscosity-temperature and viscosity-shear stress of EC with increasing ethoxyl content.
3. The die swell cannot be observed during extruding.

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Received September 10, 1991

Accepted October 30, 1991