

The Physical Properties of Thermotropic Side-Chain Triblock Copolymers of *n*-Butyl Acrylate and a Comonomer with Azobenzene Group

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Abstract: The side chain liquid crystal triblock copolymers (TBCs), which underwent phase transitions below their decomposition temperature, were prepared by copolymerization of poly(*n*-butyl acrylate) and a comonomer containing the mesogenic azobenzene group. The physical properties of TBCs in the distinctive transition temperature ranges were investigated in terms of the liquid crystal (LC) content in the copolymers. The phase transition temperatures traced optically, thermally and rheologically were well coincided one another and clearly exhibited the phase transition of smectic-nematic-isotropic with increasing temperature. In the smectic phase, increasing temperature made the liquid crystal system more elastic, but viscosity (η') remained almost constant. In the nematic phase, increasing temperature abruptly decreased η' and G' , ultimately leading to isotropic phase. Both smectic and nematic phases exhibited Bingham viscosity behavior but the former gave much greater yield stress at the same LC content.

Keywords: side-chain liquid crystalline block copolymer, phase transition, smectic phase, nematic phase, rheology.

Introduction

Liquid crystallinity is a characteristic feature of rod-like molecules, in which strong dipoles with easily polarizable substituents with a tendency of the mesogenic units to point along a common axis, director. So they exhibit very unique mechanical properties.¹⁻⁴ In addition, the high anisotropy of the mesogenic units gives rise to polymorphism, producing a number of thermodynamically stable phases between crystalline and isotropic states.⁵ In consequence, the liquid crystalline polymers (LCPs) produce different patterns of molecular ordering in the solution (lyotropic LCPs) or in the melt (thermotropic LCPs), giving rise to smectic, cholesteric, and nematic phases. Kornfield *et al.*⁶⁻⁸ and Berghausen *et al.*⁹ reported shear-driven alignment of LCPs and Quijada-Garrido *et al.*^{10,11} studied the transient shear flow and flow reversal of the polymers. Thus, LCPs exhibit very complicated rheological responses. In the case of main-chain LCPs (MCLCPs) some consensus on the characteristic rheological responses was reached.¹² This is being effectively utilized in their fabrication processes. Understanding the rheological behavior of side-chain LCPs (SCLCPs) over the range of phase transition temperatures is also very important because

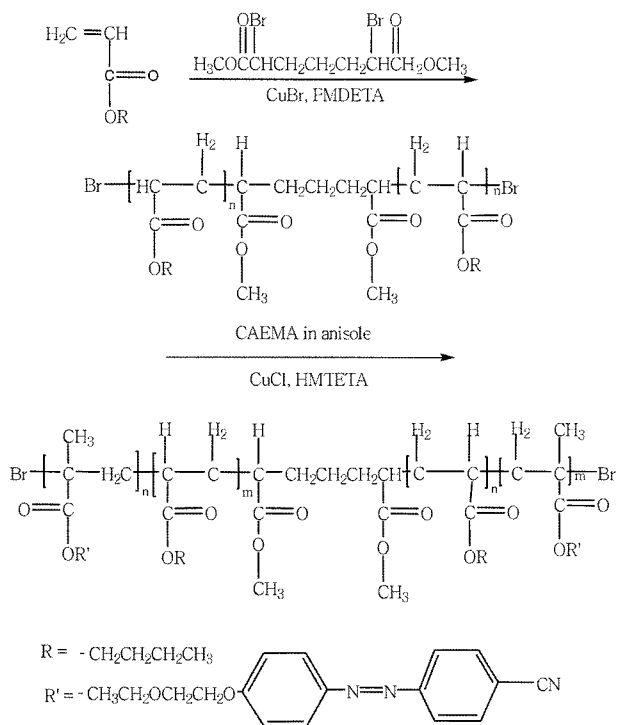
it is prerequisite to control their microstructure during fabrication.

With most MCLCPs the melting temperature is close to the thermal degradation temperature. In the case of SCLCPs, however, the motion of the polymeric backbone and the mesogenic units are partially decoupled due to the presence of a flexible spacer group. This decoupling makes the mesogenic units more mobile and field active. The occurrence of an LC phase depends on the ability of the mesogenic groups to arrange themselves anisotropically, which is affected both by the flexible spacer units and flexibility of the backbone itself. In consequence, one may obtain an LCP whose phase transition temperature range lies in far below the decomposition temperature by tailoring its chemical structure. We prepared such tri-block SCLCPs, and investigated the rheological properties of the polymers over the temperature range where the liquid crystalline phase transition takes place.¹³⁻¹⁵

Experimental

Preparation of Triblock SCLCP (TBC). The synthetic route of the triblock SCLCP is given in Scheme I.¹³ To begin with dibromo poly(*n*-butyl acrylate) macroinitiator was prepared, then TBCs were prepared by copolymerization of

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Scheme I. Synthetic route of the TBCs.

Table I. MW and LC Content of TBCs

Sample ^a	M_n	M_w	M_w/M_n^b	LC Content (%) ^c
TBC-1	29,500	36,900	1.25	17
TBC-2	41,300	51,300	1.24	38
TBC-3	50,400	64,600	1.28	52

^aTriblock copolymer. ^bBased on polystyrene standards. ^cDetermined by ¹H NMR.

2-[2-(4-cyano-azobenzene-4'-oxy)ethyl methacrylate] (CAEMA) and the macroinitiator in the presence of a catalyst, CuCl, by atomic transfer radical polymerization. In CAEMA the azobenzene group plays a role of a mesogen. The LC content in the copolymers was controlled by varying the molar feed ratio of two reactants. The molecular weight and its distribution of TBCs and the content of LC moiety in TBCs are given in Table I.

Measurement of Physical Properties. Thermal properties were measured by differential scanning calorimetry (DSC2010, TA instruments) in nitrogen atmosphere. 4~5 mg sample was heated from 30 to 220 °C and held for 3 min to eliminate the thermal history, the cooled to 30 °C. To obtain the 2nd heating thermogram, this sample was reheated to 220 °C. The scanning rate was 20 °C/min. The thermograms obtained during 1st and 2nd heating scans did not exhibit any notable difference in thermal transition peaks. The liquid crystalline texture in each transition temperature range was examined by optical polarizing microscope (OPM, Leica,

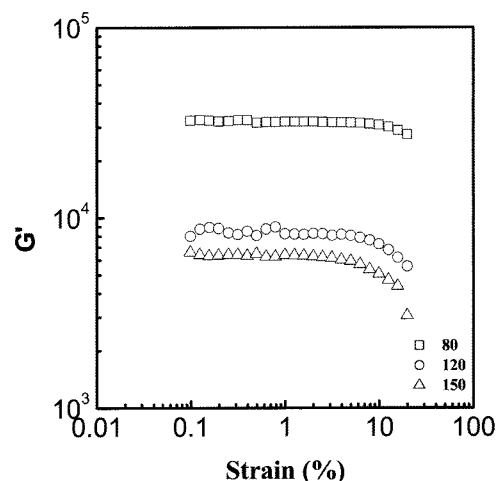


Figure 1. Dynamic strain sweep of TBC-1 at three different temperatures.

DMRXP-MPS 60). The sample polymer was annealed at a given temperature for a given time, then the texture was observed on the cooling cycle at the magnification 200.

Rheological properties were measured by Advanced Rheometric Expansion System (ARES, Rheometric Scientific, Inc.). Parallel-plates, whose diameter and gap were 7.9 and 0.8 mm, respectively, were used. Temperature sweep experiment from 220 to 80 °C was conducted at 0.5 rad/s under isochronal conditions at the cooling rate 1 °C/min. Frequency sweep from 0.1 to 300 rad/s experiment was conducted at the given temperature. The specimen was kept for 5 min at the measuring temperature to remove residual stresses. In the case of LCPs the dynamic rheological properties are very sensitive to the experimental procedure.¹⁶ For a good reproducibility of data rheological measurement was carried out according to the predetermined experimental scheme. The strain level was determined to be 5% by tracing the linear viscoelasticity in the plot of storage modulus (G') vs. strain. Typical dynamic strain sweep result is shown in Figure 1.

Results and Discussion

Thermal and Morphological Properties of TBCs. The DSC thermograms of TBC series obtained during the 1st heating scan are shown in Figure 2. TBCs undergo very complicated phase transitions with temperature. TBC-1 exhibits a very weak endothermic peak, which corresponds to the smectic to nematic phase transition temperature (T_{SN}). The peak gets greater and sharper with increasing LC content. A careful speculation on the chemical structure of TBC series reveals that they can not produce solid crystals because the irregularity of the chains would not allow chain folding. In other words the peak obtained is believed to be associated with the aggregations of mesogenic unit, *viz.*, liq-

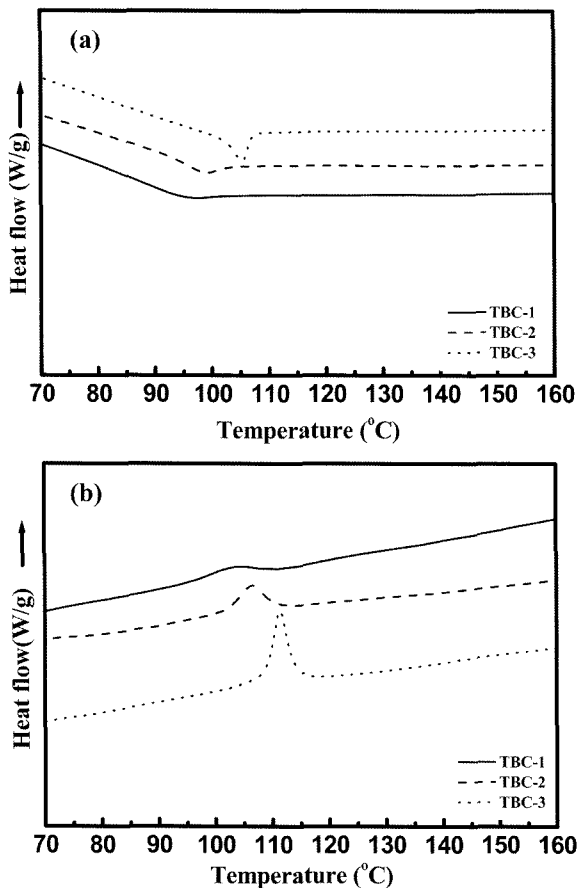


Figure 2. DSC thermograms of TBCs at the scanning rate 20 °C/min: (a) 1st heating scan and (b) 1st cooling scan.

uid crystals. Thus, the DSC peak represents the liquid crystalline phase transition of the mesogenic units of the copolymer.¹⁷⁻¹⁹ The respective endothermic peaks of TBC-1, TBC-2 and TBC-3 at 101, 106 and 111 °C are suggestive of a phase transition from smectic to nematic. The corresponding heats of fusion (ΔH_{SN}) for the peaks are 0.2382, 0.5307 and 1.013 J/g, respectively. TBC-1 and TBC-2 do not give any distinctive peak at the nematic to isotropic phase transition temperature (T_{NI}). However, when the LC content is high (TBC-3), a slight change of slope of the curve is noticed at the T_{NI} .

These thermal transitions accompanied by phase change are further ascertained by the change of liquid crystalline texture with temperature as shown in Figure 3. TBC-2 annealed at 120 °C for 2 h clearly shows a schlieren texture with 2 and 4 brushes typical of the nematic phase but TBC-2 annealed at 97 °C for 1 h clearly shows a batonet texture typical of the smectic phase. TBC-3 annealed at 110 °C for 2 h shows a nematic schlieren texture with 4 brushes but TBC-3 annealed at 62 °C for 30 min shows a smectic texture.

Rheological Properties of TBCs. In the case of SCLCPs temperature dependence of isochronal dynamic moduli proved very sensitive to the phase transition.^{20,21} The rheological

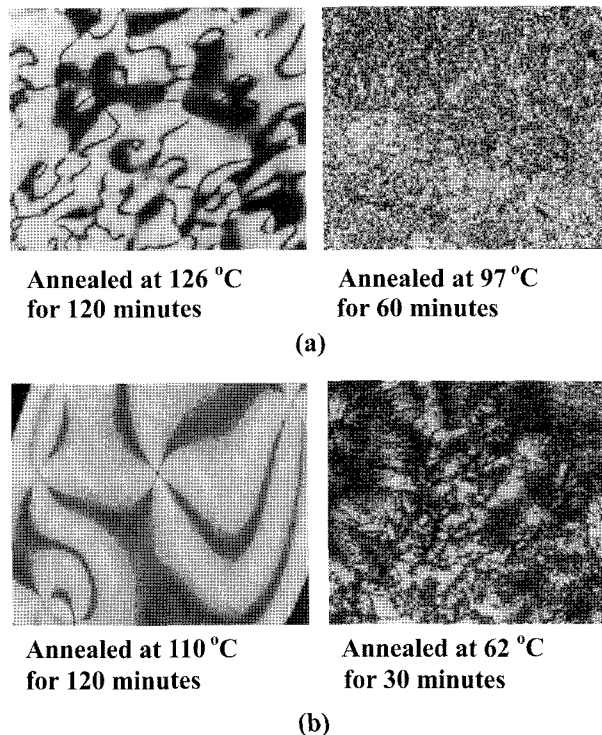


Figure 3. Liquid crystalline textures of TBCs in the transition temperature ranges, showing the transition from nematic to smectic phases with cooling: (a) TBC-2 and (b) TBC-3.

parameters such as dynamic viscosity (η'), storage modulus (G'), loss modulus (G'') and loss tangent ($\tan\delta$) of TBCs at 0.5 rad/s are displayed in Figure 4. In the smectic phase, with increasing temperature, G' was increased and $\tan\delta$ was decreased. However, η' and G'' remained almost constant. In the nematic phase, η' , G' and G'' were decreased with temperature but $\tan\delta$ remained almost constant. Over the T_{SN} range the decrease of viscosity and moduli is more prominent with TBC of higher LC content. The abrupt decrease of viscosity above T_{SN} results from breakdown of 3-dimensional smectic order to 1-dimensional nematic order. That is, molecular orientation under shear is much easier in the nematic phase than the smectic phase. In this temperature range the increase of $\tan\delta$ ascertains this. That is, the lower values of $\tan\delta$ below T_{SN} reflect higher degree of molecular ordering. Further the $\tan\delta$ curve suggests that the physical state is closer to a gel rather than a melt over the temperature range observed. However, little change in rheological parameters appears in the T_{NI} range, corresponding to the DSC curve.

Figure 5 presents the viscosity curve of TBCs over the temperature range of phase transitions. All TBC samples show Bingham body-like flow behavior. Particularly at high LC content, the viscosity curve shows inflection points and three distinct regions as suggested by Onogi and Asada,²² which correspond to breakdown of macro-domains to micro-

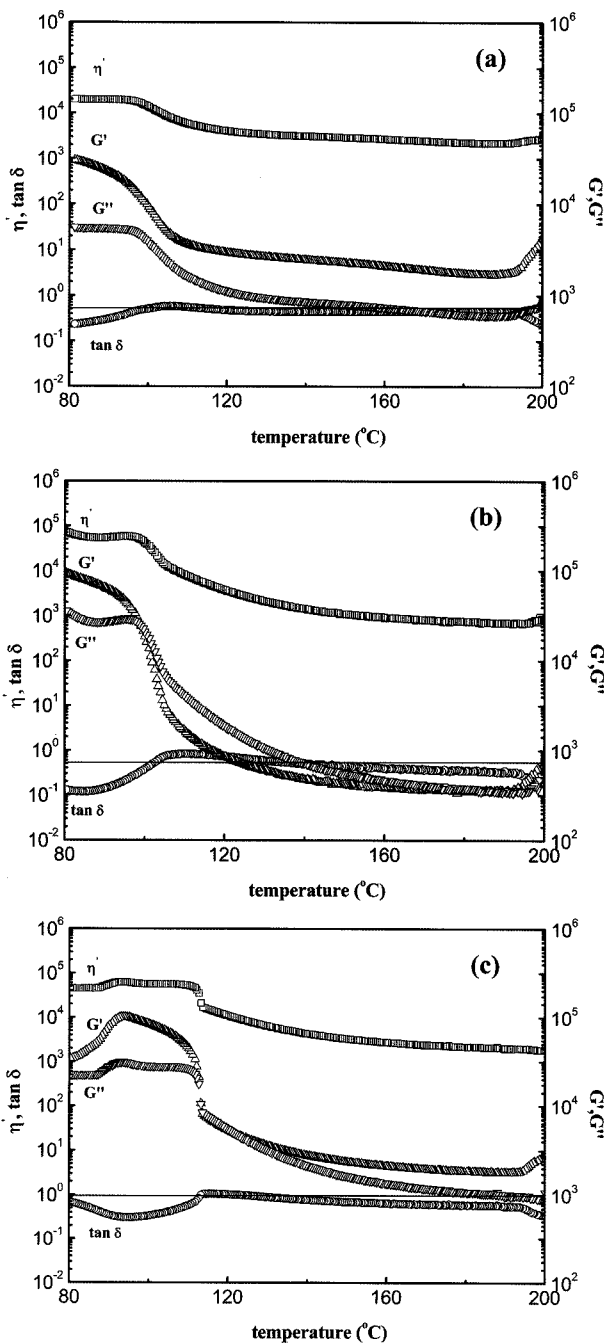


Figure 4. Temperature sweep of TBCs from 220 to 80 °C at 0.5 rad/s: (a) TBC-1, (b) TBC-2 and (c) TBC-3.

domains, breakdown of remaining micro-domain to dispersed poly-domains and rearrangement of poly-domains by shear, and breakdown of poly-domains to the individual mesogens and orientation of the mesogens to the shear direction, respectively. This agrees with the result of Kannan *et al.*,⁶ which suggested that the large amplitude oscillatory shear oriented the SCLCPs.

Disappearance of the lower Newtonian flow region is indicative of yield behavior. In principle, the heterogeneity

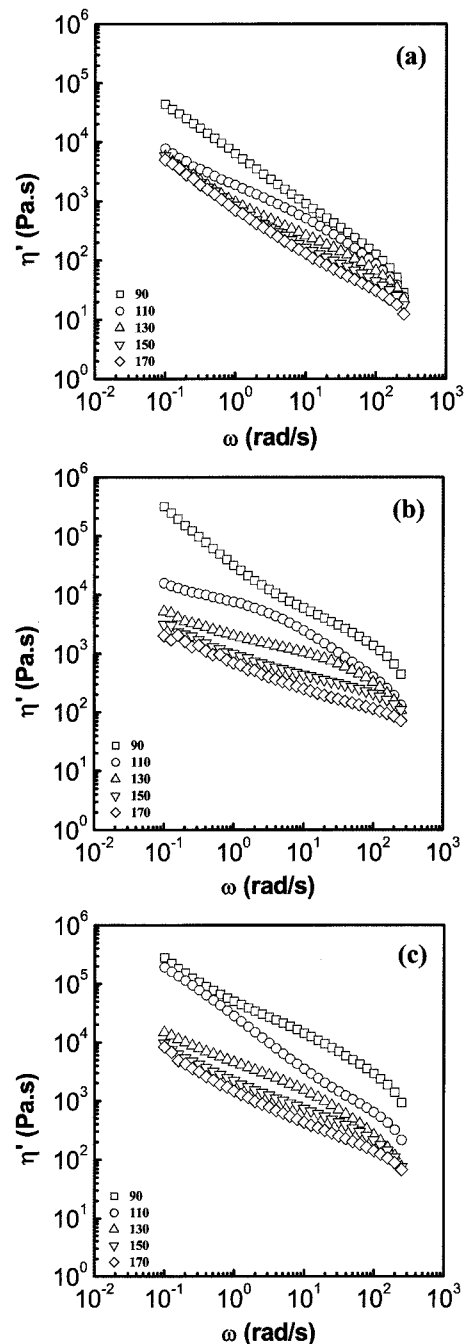


Figure 5. Viscosity curves of TBCs over the phase transition temperature range: (a) TBC-1, (b) TBC-2 and (c) TBC-3.

of a system can be confirmed by the existence of a positive value of yield stress (τ_y), which can be evaluated by modified Casson equation,²³⁻²⁵

$$G''^{1/2} = G_0''^{1/2} + K'\omega^{1/2} \quad (1)$$

in which, ω is angular frequency. The yield stress (G_0'') determined from the intercept of G'' axis is given in Table II. An abrupt decrease of yield stress is observed in the vicinity of 90 °C for TBC-1, 90-100 °C for TBC-2 and 110 °C

Table II. Yield Stress of TBCs

Sample	Temperature (°C)				
	90	110	130	150	170
TBC-1	61	20	20	21	21
TBC-2	175	17	13	12	10
TBC-3	136	130	25	22	23

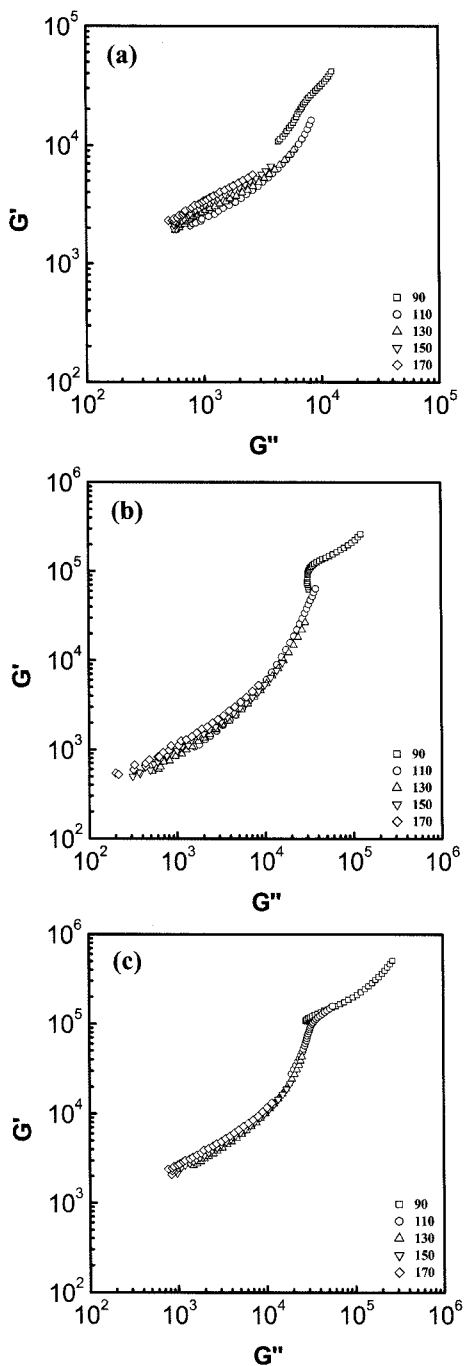


Figure 6. Modified Cole-Cole plot for TBCs over the phase transition temperature range: (a) TBC-1, (b) TBC-2 and (c) TBC-3.

for TBC-3. These temperatures coincide with the T_{SN} of each copolymer predicted by DSC. The high yield stress in the smectic phase reflects the 3-dimensional order of molecules. Thus the abrupt decrease of yield stress is indicative of breakdown of 3-dimensional smectic order to 1-dimensional nematic order.

According to the molecular theories, the homogeneous melts and solutions of polymers give a temperature-independent master curve whose slope is 2 on the double logarithmic $G'-G''$ plot in the terminal zone.²⁶⁻²⁸ However, all TBC samples give slopes much less than 2 on this plot over the temperature range observed as shown in Figure 6. As predicted by viscosity curves the smectic phase exhibits very high elasticity and gives absolutely independent curve probably due to the presence of 3-dimensional molecular order. In the smectic to nematic transition temperature region, 110 °C for TBC-2 and 120 °C for TBC-3, a very complicated behavior is observed which seems to be caused by order-order and order-disorder transition.

It is worth mentioning that Lee and Han¹⁵ reported that G' changes stiffly under the lattice disordering/ordering transition temperature and the slope is slightly increases to 2 at the terminal region above the lattice disordering/ordering transition temperature. In the case of TBC series, however, the slope is less than 2 even above the transition temperature up to 170 °C as shown in Figure 6. This discrepancy can not be explained to the full but it may be attributed to strong interactions between mesogenic units as well as polydispersity in molecular weight and high MW.²⁹ Because of high physical interaction between mesogenic units some heterogeneity may still exist slightly above T_{NI} . Recently we reported that eq. (2) does not hold for highly polar polymer melts and solutions as well.^{25,30,31} Irrespective of the optical transparency some polar polymer solutions in which hydrogen bonding between polymer chains is dominant give slope much less than 2 even at elevated temperature.^{32,33}

Conclusions

The TBCs exhibited distinctive physical properties of the respective smectic and nematic phases with temperature, morphologically and rheologically. The physical properties well reflected the structural order of molecules in the liquid crystalline phase. A notable change in rheological responses was observed at T_{SN} , which indicated the breakdown of 3-dimensional smectic order to 1-dimensional nematic order. The other detailed rheological responses further supported this phenomenon.

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