Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 13 Dec 2006.

To cite this article: D. D. Deshpande & V. K. Tiwari (1983): Dynamic Mechanical Behaviour of Some Cholesteryl Liquid Crystals, Molecular Crystals and Liquid Crystals, 103:1-4, 299-305

To link to this article: http://dx.doi.org/10.1080/00268948308071061

Mol. Cryst. Liq. Cryst., 1983, Vol. 103, pp. 299-305
0026-8941/83/1034-0299/$18.50/0

Dynamic Mechanical Behaviour of Some Cholesteryl Liquid Crystals

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(*Received January 28, 1983; in final form May 7, 1983*)

Dynamic mechanical studies of cholesteric liquid crystalline substances in the solid state have been reported using Du Pont's Dynamic Mechanical Analyser, DMA-981. All the substances showed multiple transitions. There is no common transition though the parent structure was similar in the compounds. These weak transitions are not detectable by DSC and hence appear to be second order transitions possibly arising due to rotation of the molecules around the long axis. Alternatively the lattice defects may also be responsible for such transitions.

INTRODUCTION

We are studying the effects of doping of liquid crystalline compounds on the dielectric and viscoelastic behaviour of polymers. The liquid crystalline compounds markedly affect the α- and β-relaxation processes of poly (vinyl acetate),[1] poly (*n*-butyl methacrylate),[2] and poly (vinyl chloride),[3] and thus the glass transitions of polymer + liquid crystals systems are different than those of pure polymers. It was therefore necessary to investigate whether pure liquid crystals at very low temperatures would exhibit some relaxation processes which might be responsible for shift of the glass transition in these polymers. Dynamic mechanical analysis being a very sensitive technique to monitor even very weak transitions, in this paper we have studied dynamic mechanical behavior of some cholesteryl derivates, MBBA, cetyl acetate, and cholesterol in the crystalline state.

EXPERIMENTAL

Materials

The compounds studied were used as received from Aldrich Chemical Co., UK, without further purification (purity 99.9%). These were, Cholesterol (Ch), Cholesteryl chloride (ChCl), Cholesteryl acetate (ChAc), Cholesteryl benzoate (ChBz), Cholesteryl laurate (ChL), Cholesteryl stearate (ChSt), Cholesteryl oleyl carbonate (ChOC), Cholesteryl caprilate (ChCap), Cholesteryl 2-ethyl hexyl carbonate (Ch-2 EHcarb), and MBBA. Cetyl acetate was synthesized in the laboratory from corresponding acid chloride and alcohol.

Sample preparation

Glass cloth was heat cleaned and the material if liquid at ambient temperature, was applied to the glass cloth surface so as to fill all the pores in the cloth. Solid materials were sprinkled on the surface and the glass-cloth was heated by a miniheater so that the molten material spreads uniformly on the glass cloth. It was then cut to 19 × 10 mm size pieces and mounted in the DMA unit.

Apparatus and procedure

Instrument used was Du Pont's DMA-981 model coupled with 990-thermal analyser. The specimens were clamped in horizontal mode to monitor the weak relaxations. The specimens were cooled to $-120\,^\circ\mathrm{C}$ by slow stream of cooled N_2 gas (approximately at a rate of $6\,^\circ\mathrm{C/min}$). The temperature was held at $-120\,^\circ\mathrm{C}$ for about 10 minutes to achieve a thermal equilibrium before starting the heating. The heating rate was $5\,^\circ\mathrm{C}$ per minute.

The raw plots of damping signal and resonance oscillation frequencies versus temperature obtained on $X - Y, Y'$ recorder, were manually treated at closely spaced temperature to obtain $\tan\delta$ values using the following equation,

$$\tan\delta = \frac{C \cdot V}{f^2} \tag{1}$$

where, C = instrumental constant (≈ 0.25), V = the damping signal (mv), f = oscillating frequency (Hz). Figure 1, shows a typical raw plot. As the samples were coated on inert support and clamped

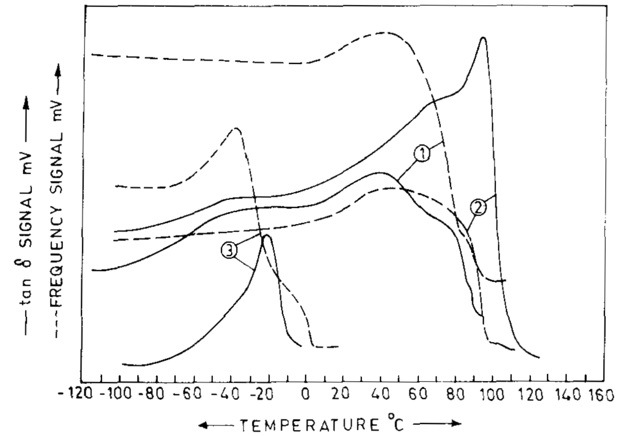

FIGURE 1 DMA-981 module's raw plots for cholesteryl type liquid crystals: ChNOna(1), ChL(2) Ch2EHcarb(3) copper net of 100 mesh size used in horizontal mode of clamping (---)freq (F, Hz), (—) damping signal (mV.) scanning rate: 5 °C/min.

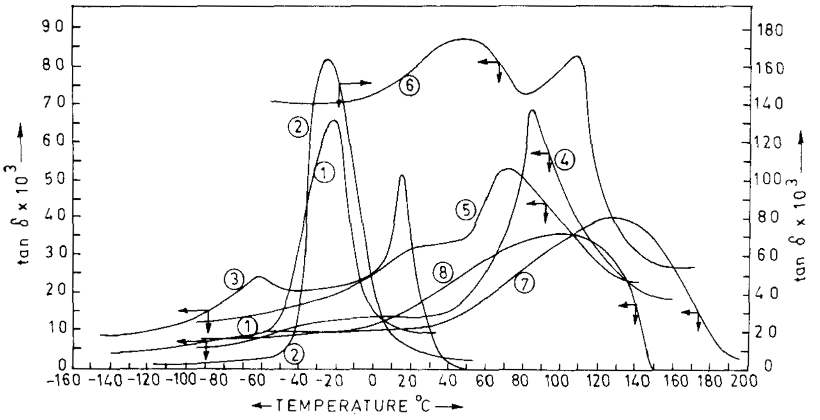

FIGURE 2 DMA loss (tan δ) curves for ChOC(1), Ch2EHcarb(2), MBBA(3), ChCl(4), ChAc(5), ChCap(6), Ch(7) and ChBz(8) [on glass-cloth].

horizontally, the calculation of storage elongation modulus (E') was not possible. The mechanical loss was plotted for various substances, Figures 2 and 3, give such curves. Table 1, shows the various transitions and their temperatures obtained from the raw plots. The last column of the table gives the values of $(\tan \delta)_{\max}$ for major transition. Various weak or broad transitions obtained are also listed in the table.

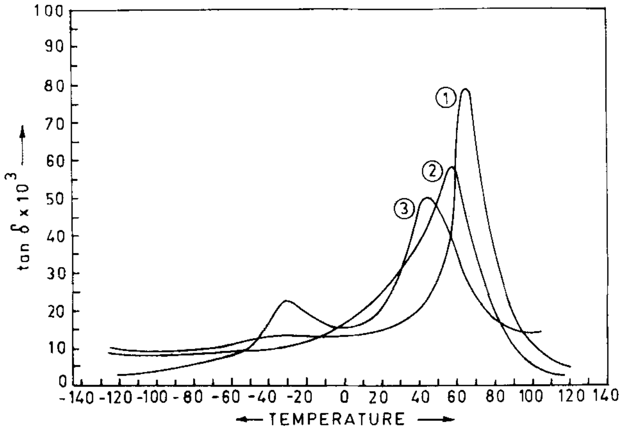

FIGURE 3 DMA loss (tan δ) for ChSt(1), ChL(2) and ChNona(3) [on glass-cloth].

Discussion

Since the reported transitions were weak, we used the instrument in the horizontal mode of operation and with the glass-cloth as an inert support. We had also used copper mesh as a support and found that the observed peaks were shifted to higher temperatures as shown in Figure 4. This effect could be attributed to the high thermal conductivity and the resonance oscillation frequency (which depends on the support material), and hence only the results with glass-cloth as support are tabulated. It was not possible to evaluate the absolute values of the elongation storage modulus, E', and hence only tan δ values were calculated.

As the temperature approaches the value of mesomorphic isotropic transition, the frequency curve showed a rise in frequency of oscillation. This effect was more clear on copper mesh than on the glass-cloth as shown in Figure 1. This increase in frequency indicates in fact increase in the stiffness modulus of the sample and may be attributed to the gross molecular rearrangement occurring before the substance undergoes melting. All the substances studied have shown multiple transitions in the crystalline state. The mechanical loss, tan δ, approaches to the base-line (≈ 0) after the cholesteryl → isotropic or nematic → isotropic transition is complete with a peak maximum occurring at a temperature much below the reported value of transition to isotropic liquid. The materials coated on glass-cloth, when subjected to DSC analysis, did neither reveal any transitions in the crystalline state nor any changes in the mesomorphic range or the

TABLE 1

DMA $(\tan\delta)_{max}$ and transition temperatures for various substances (the observed peaks are designated as S-strong, s-sharp, W-weak, b-broad)

Substance	Transition temperature and its nature °C	$(\tan\delta)_{max}$ $\times 10^3$
Chloresterol	44 (W)	—
	99.8 (Ss)	40
Cholesteryl	−5 (W)	—
Chloride	65 (Sb)	69
Cholesteryl	−7.0 (Wb)	—
acetate	44.0 (W)	53.5
Cholesteryl	−56.5 (W)	—
benzoate	124.0 (Ss)	98.0
Cholesteryl		
laurate	41 (Ss)	58.0
Cholesteryl	−84.5 (Wb)	—
Stearate	13.0 (W)	—
	55.5 (Sb)	78.0
Cholesteryl	−35.5 (b)	—
nonanoate	28.0 (Ss)	50.0
	62.0 (W)	
Cholesteryl	−80.0 (Wb)	—
Oleyl carbonate	−26.0 (Ss)	66.5
Cholesteryl	−50.0 (W)	—
caprilate	36.4 (Sb)	87.5
	103.5 (W)	
MBBA	−101.0 (W)	—
	−65.5 (Ss)	52.0
	6.5 (W)	—
Cetyl acetate	−67.2 (Sb)	60.0
	5.0 (Wb)	—

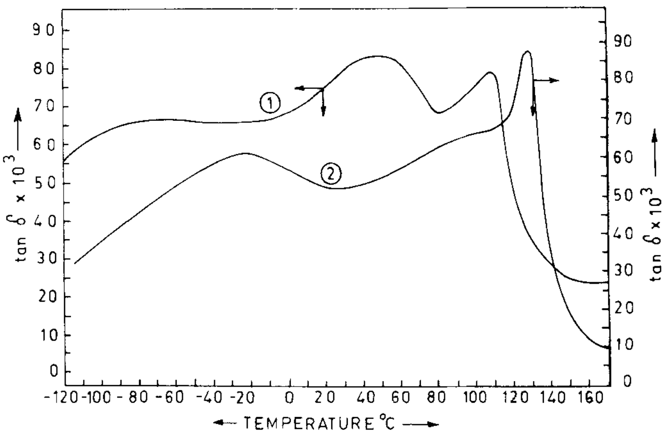

FIGURE 4 DMA loss (tan δ) for ChCap on glass-cloth (1) and copper mesh (2).

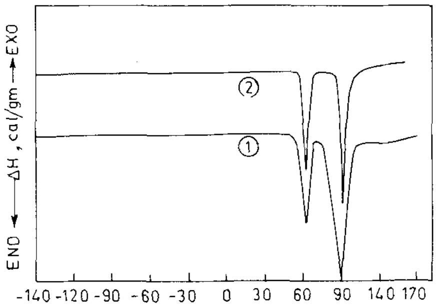

FIGURE 5 DSC thermogram of ChL(1) and ChL coated on glass-cloth(2).

transition temperature of pure substances. Figure 5 shows the DSC thermogram of both pure and coated ChL on glass-cloth.

If all cholesteryl derivates should exhibit a transition due to onset of segment mobility of the aliphatic chain on the cholesterol molecule at low temperature, there should have been a peak common to all cholesteryl compounds. Since there is no such commonness such a possibility is ruled out. It is therefore likely that these transitions are due to the rotational motion of the molecules around the long axis. This fast motion needs little energy and hence appears in these thermomechanical spectra at such a low temperature. Alternatively it is quite likely that during cooling of the coated samples some defects would have been introduced in the crystal lattice and during the temperature scan of the experiments in the heating mode, the transitions are observed as the changes in this defect-state. It may be mentioned here that these are second order transitions only, as the DSC studies have not indicated any enthalpy changes at these temperatures. Changes in C_p could not be detected as these are very weak transitions.

S. Yano[4,5] has observed a low temperature transition in cholesteryl 2,2,3,3 tetra fluoropropionate at $-100\,^{\circ}C$ through dielectric studies. In homologous series of cholesteryl fluoroalkonoates, S. Yano and co-workers[5] attributed these transitions to a phase transition. Bhide and co-workers[7,8] have also reported solid crystalline transitions ScI → ScII → ScIII in M-21 through DSC, polarizing microscopy and IR studies. They also report three such transitions in M-24 compound.

Further work will be required through dielectric and X-ray diffraction studies before a definite conclusion can be reached on the origin of the transitions observed in this work.

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