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(*S*)-4-(2-Methylbutyl)-4′-Cyanobiphenyl (5*CB) Glass Former: Are the Crystalline Polymorphs Ordered?

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*The studies performed for right-handed (*S*)-4-(2-methylbutyl)-4′-cyanobiphenyl glass former using calorimetry (down to 0.35 K) and spectroscopy methods are reviewed. The substance reveals isotropic and cholesteric liquid phases, glass of cholesteric phase and two crystalline polymorphs, one of which transforms to glass. Two anomalies in heat capacity below 5 K and their relation to ordering of the molecules in three solid phases are discussed.*

Keywords Enthalpy relaxation; glass transition; heat capacity; solid state polymorphism

PACS 61.43.Fs; 64.70.Md; 65.50.+m

1. Introduction

Universal features of organic glass formers are in the focus of soft-matter studies [1,2]. Long lasting non-exponential structural α-relaxation related to reorientations of the whole molecules [3] and its superarrhenius temperature dependence reflecting a slowing down phenomenon [4,5] are thoroughly observed. Both features are the evidence of the cooperativity of molecular dynamics in a supercooled liquid [6] that grows dramatically on approaching a glass transition temperature T_g. Due to a growing viscosity, fluctuations of a structural disorder hardly relax. Liquid is no longer ergodic and finally, below T_g, a dynamical disorder of the molecules is frozen-in. The next universal property of glass formers is the so-called Boson peak at low energy (∼3 K, ∼3 meV) [7–9], observed in glass by the adiabatic calorimetry and the Raman and neutron scattering. It is related to the excess of vibrational

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density of states, caused by a lack of long range order of the molecules in glass, with respect to that of phonons propagating in ordered crystals. In addition, below 1 K a T-linear anomaly in heat capacity related with tunneling levels was reported in various disordered glassy states [7,9]. In this respect studies of glasses of plastic crystals [10–12] and of liquid crystalline phases [13,14] are of growing interest as there are some well defined forms of long range order present. Recently, glass transition has been also found in crystalline phases with dynamical disorder of intra molecular degrees of freedom [12,15].

In this paper a detailed review of the features found for the right handed (*S*)-4-(2-methylbutyl)-4′-cyanobiphenyl (5*CB), using several experimental methods [8,14,16–23], has been undertaken to understand better the nature of solid state polymorphism. Due to the chirality center in the molecular chain, cholesteric phase, easily supercooled and vitrified on cooling, and crystalline polymorphs on heating were identified, contrary to the linear pentylcyanobiphenyl isomer 5CB, revealing nematic liquid crystalline phase which crystallizes on cooling [24].

2. Polymorphism of a Solid State

Measurements of complex electric permittivity of 5*CB [14,18–21] have shown the transition from the isotropic liquid to cholesteric liquid crystalline phase at about 246 K and glass transition at about 210 K on cooling with a standard cooling rate of about $-1\,\mathrm{K\,min^{-1}}$. On cooling neither crystallization nor glass of isotropic liquid has been found but glass of cholesteric phase. On heating it softens to cholesteric phase and at about 246 K a spontaneous crystallization of a phase II[1], lasting about 2 h, has been detected. Melting of the phase II has been observed around 280 K. In both liquid phases reorientational motions of molecules, around short axes mainly, have been evidenced. The FIR studies [17] have shown that spectra of glass of cholesteric resemble that of cholesteric liquid. Spectra of the phase II in the lattice vibration region suggest that it is a poorly ordered crystal. An extra crystalline phase I[1], melting at higher temperature than phase II, was registered in the time evolution of the main maxima of the far infrared interferogram. Identification of three solid phases have been confirmed using the adiabatic calorimetry down to 100 K [16,18].

In order to obtain a full insight into the phase diagram of 5*CB compound the adiabatic measurements of the heat capacity $C_p(T)$ have been extended down to 5 K in numerous series with various thermal treatments applied to the sample [22]. A liquid sample has been first heated up to 350 K and then cooled down to 5 K (with $-15\,\mathrm{K\,min^{-1}}$ at 280 K and $-8\,\mathrm{K\,min^{-1}}$ at 210 K). On subsequent heating the heat capacity $C_p(T)$ has not shown any extra anomaly up to 100 K but a glass-like transition at $T_g = 210$ K related to softening of the glass of cholesteric phase as shown in Figure 1 (squares). Then, an asymmetric peak with the finite height due to cholesteric to isotropic liquid phase transition has appeared at 246.78 K. It has been immediately followed by a spontaneous crystallization to the phase II. Such process was observed on heating with $1.4\,\mathrm{K\,min^{-1}}$ at several temperatures: when the sample was undercooled from the isotropic liquid down to 238 K crystallization occurred at 254 K and for undercooling down to 244 K it occurred at 250 K. A warming drift,

[1]In papers [14,16–19] the phase II has been called a metastable crystal, crystal I or C1 while the phase I – a stable crystal, crystal II or C2.

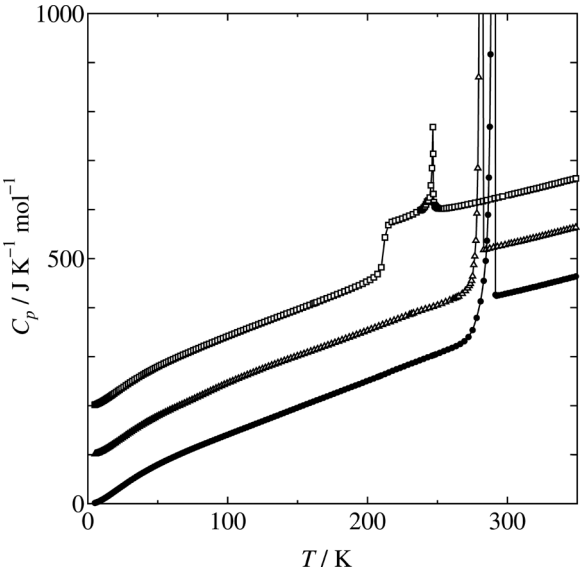

Figure 1. Molar heat capacity $C_p(T)$ of 5*CB in the temperature range from 5 K to 350 K as measured in [22]. Meaning of the symbols: (●) – phase I which undergoes melting, (Δ) – glass G_{II} and phase II which undergoes melting and (□) – isotropic and cholesteric liquid phases and glass of cholesteric phase. For better presentation the experimental points (Δ) and (□) are shifted along the vertical axis by 100 and 200 JK^{-1} mol^{-1}, respectively.

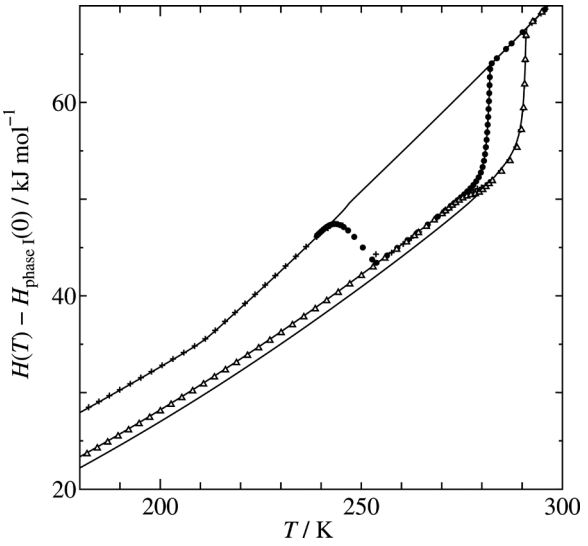

Figure 2. The enthalpy H *vs.* T calculated in [22] presented down to 160 K. The value of enthalpy of phase I extrapolated to 0 K has been subtracted. Meaning of the symbols: (Δ) – pure phase II undergoing transition to phase I which undergoes melting, (●) – cholesteric liquid phase crystallizing spontaneously to the phase II which undergoes melting and (+) – cholesteric liquid phase crystallizing to the phase II transforming into phase I which undergoes melting. The lower solid line – pure crystalline phase I, the upper solid line – supercooled isotropic liquid phase.

a signature of crystallization, has been always detected. In order to obtain the pure phase II the sample has been left at 255 K for 10 h and a temperature growth of 3 K has been measured. In case when phase II has been cooled down only to 240 K it melted at about 281.93 K (single peak in Figure 1 shown by triangles). When cooled down to lower temperature, phase II transformed on heating to the phase I slightly below 280 K. The pure phase I has been obtained only after many steps of a special thermal treatment: first it has been annealed for 10 h at 284.6 K, then cooled to 5 K, heated slowly (1 K min^{-1}) up to 285 K, cooled slowly (−1 K min^{-1}) to 240 K and finally cooled rapidly to 5 K. For the pure phase I the heat capacity $C_p(T)$ shows only a single peak of melting at 291.39 K (see filled circles in Figure 1). In order to show the details of various experimental runs the corresponding excess enthalpies $H(T) - H_{\text{phase I}}(0)$ *vs.* T are presented in Figure 2, where the $H_{\text{phase I}}(0)$ means the enthalpy of phase I estimated to 0 K.

3. Glass of Crystalline Phase II

There were several steps undertaken for the investigation of the phase II. First the sample in phase II was cooled down to 5 K with the cooling rate equal to −6 K min^{-1}. On subsequent heating (9 K h^{-1}) the heat capacity has shown a small step-like anomaly around 100 K along with the exothermic process observed in the rate of temperature drift $\Delta T/\Delta t$ *vs.* T. Next, the phase II was cooled down to 78 K and annealed there for 5 h for the clarification of the step anomaly. Then, when measuring $C_p(T)$ again with a slow heating of 2.7 K min^{-1}, a shift of the $C_p(T)$ step-like anomaly to lower temperature was observed along with the endothermic process detected by the $\Delta T/\Delta t$ *vs.* T dependence. This result was a signature of a glass transition, i.e., softening of glass of phase II, labeled G_{II}. The glass transition temperature T_{gII} was determined as 105 K [22]. In Figure 3 a small increase of $C_p(T)$

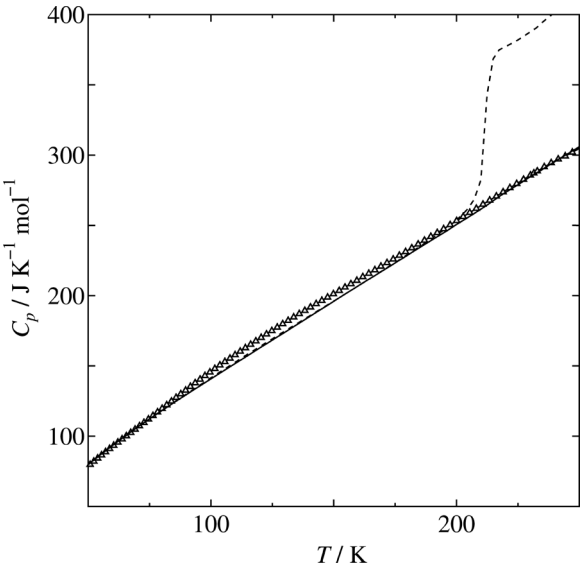

Figure 3. Softening of two glasses: $G_{II}(\Delta)$ and glass of the cholesteric phase (dashed line). Solid line gives $C_p(T)$ for the phase I.

corresponding to softening of the glass G_{II} is shown together with large jump related to softening of the glass of cholesteric phase (dashed line). The thermal effects observed at softening of the cholesteric glass and of the glass G_{II} differ by two orders of magnitudes. Jump of the heat capacity of about $110\,J\,K^{-1}\,mol^{-1}$ at $T_g = 210\,K$ can be related mainly to the activation of the reorientational motions of the whole molecules around short axes [18,14]. Softening of glass of cholesteric liquid is visible also in the entropy changes presented in Figure 4 (upper curve). An intensive increase of the configurational entropy $S_c(T) = S(T) - S_{phaseI}(T)$ near T_g is due to a change from a static disorder of the translational and rotational degrees of freedom in glass to a dynamical one in cholesteric phase. One can see that $S_c(T)$ value near melting of the cholesteric phase is nearly two times larger than the residual entropy, a measure of a static disorder of molecules in glass, equal to $14.28\,J\,K^{-1}\,mol^{-1}$ [22]. The Adam-Gibbs-Vogel-Fulcher formula [25] was used for extrapolation of $S_c(T)$ to the Kauzmann temperature T_K (see solid line in Figure 4). $S_c(T_K) = 0$ allowed to estimate $T_K = 184\,K$. A softening of glass G_{II} gives a very small jump of $C_p(T)$ of $1.36\,J\,K^{-1}\,mol^{-1}$ at about $T_{gII} = 105\,K$. One can attribute it to the activation of the conformational degrees of freedom of molecules frozen-in at T_{gII} on cooling. Probably it concerns a twist angle in biphenyl core of molecules, as was suggested in case of a similar 8*OCB compound [26] basing on the spectroscopic results. Residual entropy of glass of phase II is equal to $2\,J\,K^{-1}\,mol^{-1}$ only. Large difference in residual entropies of both glasses is caused mainly by the fact that in the glass of phase II a long range positional order of molecular centers of gravity is present while in the cholesteric glass only some cholesteric order of long molecular axes exists and a positional distribution of molecules is random. For glass of crystalline phase C2 of liquid crystalline material 8*OCB the value of residual entropy was mentioned to be negligible [15] while in case of the glasses of liquid crystalline phases it varies from

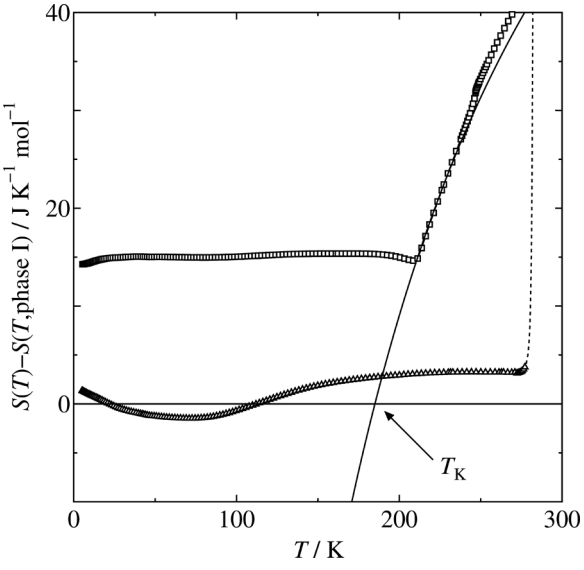

Figure 4. The excess of entropy, $S(T) - S_{phaseI}(T)$ with respect to phase I for glass of cholesteric phase, cholesteric and isotropic phases (□) and for glass of phase II and phase II (Δ). The meaning of the solid line is described in the text. Dashed line shows melting of phase II.

about $13\,J\,K^{-1}\,mol^{-1}$ for nematics to about $9\,J\,K^{-1}\,mol^{-1}$ [13] for smectic G phase. For glass of crystalline phase in cyclohexanol and in cyanoadamantane, where intramolecular rotations in molecular clusters are assumed to be activated at softening of glass, the residual entropy is equal to $6.0\,J\,K^{-1}\,mol^{-1}$ and to $2.7\,J\,K^{-1}\,mol^{-1}$, respectively [27].

One can compare these data with residual entropy estimated for ethanol, a substance of small molecules: about $13\,J\,K^{-1}\,mol^{-1}$ for glass of the isotropic phase and $4.2\,J\,K^{-1}\,mol^{-1}$ for glass of orientationally disordered crystalline phase [12].

4. Is the Phase I Disordered?

In studies of three solid phases of 5*CB by the inelastic incoherent neutron scattering method [8] neither diffraction patterns nor the density of states $G(\nu)$ obtained at 20 K occurred to be typical for fully ordered crystal. Even for both crystalline phases the diffraction patterns point to poor structures given by distribution of the hydrogen atoms of 5*CB molecules; the phase II seems to be of lower symmetry than phase I. In addition the low-energy Debye frequency dependence of the density of states typical for ordered crystals was not found in any of the solid phases. Moreover, at 20 K the spectra of density of states for glass G_{II} occurred to be of lower intensity than that of the phase I. It is in accordance with our finding that in the temperatures between 20 K and 110 K the entropy of the phase I is larger than that of the glass of phase II as is shown in Figure 4 (lower curve). It is unusual as the phase I is a stable phase having the lowest values of the Gibbs energy [22]. Temperature dependence of entropy for all phases is sketched in Figure 5 to help understanding of such a behavior. One can see that a larger values of $S_{phaseI}(T)$ (dotted line) than of $S_{phaseII}(T)$ (solid line) near T_{gII} temperature may be caused by the difference in vibrational parts

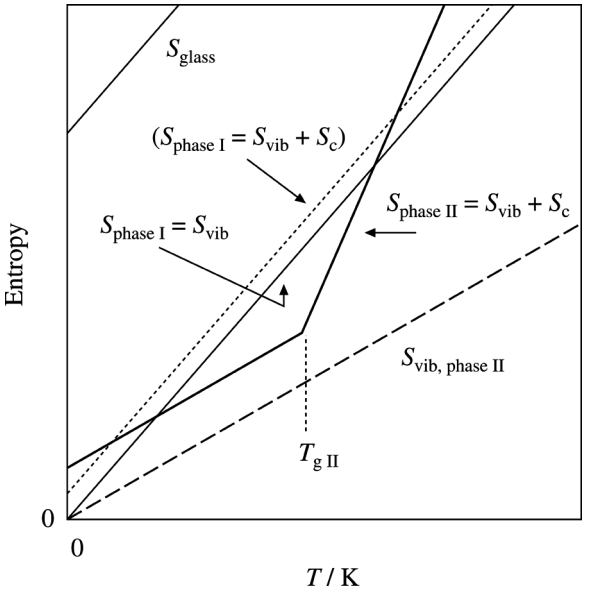

Figure 5. Schematic diagram for entropy $S(T)$ for three solid phases of 5*CB. Description in the text.

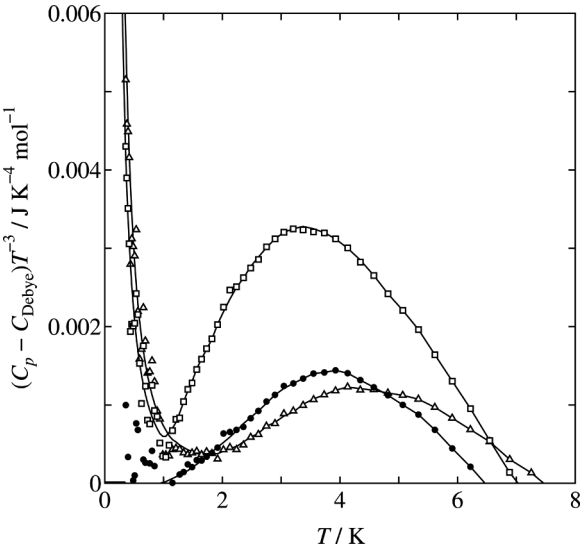

Figure 6. Molecular heat capacity $(C_p(T) - C_{\mathrm{Debye}}(T))T^{-3}$ for three solid phases of 5*CB in the temperature range 0.35 K – 8 K calculated basing on data measured in [23].

of entropies S_{vib} (T) (for phase I – a solid line and for phase II – a dashed line). Probably, some molecular motions, frozen-in in the phase II at T_{gII}, in the phase I are active down to low temperatures. Besides, librational motions of the whole molecules located in the centers of crystalline lattice and/or anharmonicity of vibrational modes may give larger contribution to the density of states in phase I than in phase II. In view of that, the phase I is not a fully ordered crystal. Thus, the fact that it has been found to be less ordered than the glass of the phase II is no longer peculiar.

In order to know deeper the details of thermodynamic features of solid phases of 5*CB at lower temperatures the measurements of the heat capacity were extended to 0.35 K by the relaxation calorimetry method [23]. In the temperature below 10 K the $C_p(T)$ of glasses can be divided into three parts

$$C_p(T) = aT + b_{\mathrm{Debye}}T^3 + b_{\mathrm{excess}}(T).$$

The Debye-type contribution to the measured heat capacity is given by $C_{\mathrm{Debye}}(T) = b_{\mathrm{Debye}}T^3$, the term describing fully ordered crystal with phonon vibrations. Two anomalies detected for disordered phases are given by first term, associated with tunneling in a nearly symmetric potential well [9,28,29], and by the third term due to the excess vibrational contribution, the so-called Boson peak [7–9] giving bump in the C_p/T^3 presentation of the data. For 5*CB the $C_{\mathrm{Debye}}(T)$ contribution related to lattice vibrations was calculated by fitting the first two terms to the measured $C_p(T)$ below 1 K, with a and b_{Debye} being the fitting parameters [23]. Then, the $(C_p(T) - C_{\mathrm{Debye}}(T))T^{-3}$*vs.* T dependence was obtained in the temperature range up to 8 K for three solid phases as shown in Figure 6. One can see that glassy phases, i.e., the glass of cholesteric phase and the glass of phase II, reveal both anomalies. Detection of the glass transition anomalies and the non-zero entropies at 0 K corroborate with these features. In both glasses of 5*CB densities of tunneling levels

estimated from the *a* parameters are similar [23]. The difference in intensity of the humps at 4 K, identified with the Boson peaks, seems to reflect a difference in the magnitude of the residual entropies. No *T*-linear anomaly is visible for the crystalline phase I. It means that the density of tunneling levels, if they exist, is too small to be detected. However, the hump at about 4 K is of similar intensity as for the glass of crystalline phase II. In the phase I, where no glass transition has been detected, it reflects probably the excess density of states related to degrees of freedom mentioned earlier. Density of material at low temperature corresponds to the Debye temperature Θ_D estimated using the equation $b_{\text{Debye}} = (12/5)\ \pi^4 R\ (\Theta_D)^{-3}$, assuming the translational degrees of freedom only, where R is a gas constant [29]. It was found that the density of glass of phase II is higher than of the stable crystalline phase I [23]. It means that in phase I there may be enough room for motions that are frozen in glass of phase II.

5. Conclusions

The results of calorimetry down to 0.35 K and of complementary methods for the right-handed (*S*)-4-(2-methylbutyl)-4′-cyanobiphenyl (5*CB) glass former have been reviewed. The substance reveals isotropic and cholesteric liquid phases, glass of cholesteric phase and two crystalline polymorphs, one of which (phase II) transforms to glass. The existence of some molecular motions in phase I down to low temperatures is proposed to explain the unusual feature namely that in the stable crystalline phase I the entropy at low temperatures was found to be larger than in the glass of phase II. Further, two anomalies in heat capacity observed below 5 K in both glasses of 5*CB have been described using conventional picture of the tunneling and the so-called Boson peak. Lower density of material in phase I than in phase II, estimated from the Debye temperatures seems to justify that some motions frozen-in in the phase II may be active in the phase I and give the extra non-Debye density of states at about 4 K. The understanding of the physical nature of tunneling entities in the solid phases of 5*CB is necessary to explain the lack of *T*-linear anomaly in the heat capacity in the not fully ordered crystalline phase I below 1 K.

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