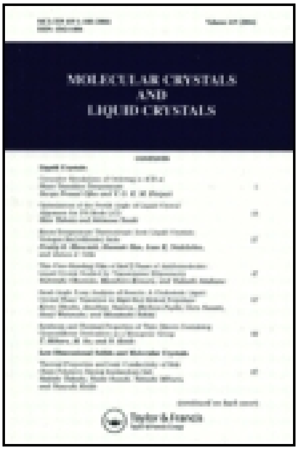

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Studies of Polymorphism of Right Handed (S)-4-(2-Methylbutyl)-4′-Cyanobiphenyl

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Studies of Polymorphism of Right Handed (S)-4-(2-Methylbutyl)-4'-Cyanobiphenyl

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Basing on the results of polarizing microscopy, differential scanning calorimetry (DSC) and infrared spectroscopy (in the range 70 –700 cm^{-1}) in the temperature range from 100 K to 320 K the phase diagram of right handed (S) 4-(2-methylbutyl)-4'-cyanobiphenyl was established. On cooling an isotropic phase transforms at 246 K into a cholesteric phase which can be easily supercooled to a glass at *ca.* 210 K. On heating this sequence of transitions reverses. Further heating of the sample leads to crystallization of supercooled isotropic phase at about 250 K. The crystal phase melts at 276 K. It was clarified that process of nucleation starts on cooling below 240 K. The shape of the far infrared bands (lattice vibration range) suggests that the crystal phase is highly disordered.

Keywords: phase diagram; DSC; polarizing microscopy; FIR spectra

INTRODUCTION

The right handed (S)-4-(2-methylbutyl)-4'-cyanobiphenyl known also as isopentyl cyanobiphenyl was synthesized by Gray and McDonnell[1] by incorporating the chiral center into the alkyl group of 4-n-alkyl cyanobiphenyl homologous series reported first by Gray *et al.*[2] some time earlier. This compound is interesting because of its low melting temperature, relatively high twisting power and strong positive dielectric anisotropy[1]. However its phase diagram was unclear and from first information about two mesomorphic phases i.e. cholesteric and smectic A[1] only appearance of the cholesteric phase was confirmed later.[3,4] Dielecric relaxation experiments carried out recently[3] showed very pronounced relaxation and existence of glass state that was not detected earlier.[1]

The aim of this paper is to summarize the last results of DSC and polarizing microscopy experiments[4] together with new infrared spectroscopy measurements taking into account the dielectric data which illustrate the observed phase transitions.

EXPERIMENTAL

All measurements were performed on the sample of isopentyl cyanobiphenyl of 97% purity synthesized at the Organic Chemistry Laboratory of WAT (Warsaw, Poland). This sample was used before in papers.[3,4] The values of the transition temperatures[1,3] and low level of electrical conductivity[3] prove that the sample purity was acceptable.

Polarizing microscopy experiments were performed using Biolar PI (PZO, Warsaw, Poland) microscope equipped with Linkam (UK) THM 600 heating stage and TMS 90 controller. The sample was placed on silver block of heating stage between microscopic cover glasses or as a droplet lying on cover glass. Hitachi CCD camera and videorecorder were used for registration of observed textures. Different heating / cooling rates were applied in the temperature range 130 K- 320 K. In some cases the sample was additionally annealed at chosen temperatures.

Calorimetric measurements were performed in the temperature range from. 130 K up to 320 K using Perkin-Elmer DSC-7 differential scanning calorimeter. The output signal (heat flow - dQ/dt) proportional to the difference between the power input to the sample and that to the reference (empty sample pan), is registered as a function of the sample temperature. The input heating power is appropriate for given scanning rate, so the measured heat flow reflects the specific heat of the sample. The measurements were performed for five samples (5 mg to 35 mg) closed in the aluminum sample pans with different scanning rates, typically 2.5, 5, 10 and 20 K/min both for heating and cooling.

The infrared experiments were performed on the up-graded Digilab (USA) FTS 14 spectrometer in the range 70 - 700 cm $^{-1}$ from 100 to 320 K. Both interferograms and FT (Fourier Transformed) spectra were analysed. Similar to other techniques different rates of cooling and heating of the sample as well as annealing were applied.

RESULTS AND DISCUSSION

The observations of polarizing microscopy show that on cooling at about 246 K the texture of isotropic phase transforms to the texture of an anisotropic phase which can be attributed as a cholesteric phase.[5,6] On further cooling one can observe a gradual cracking of the sample around 212 K. No other changes were observed until 80 K. During heating that followed the crackings were gradually disappearing and the texture of cholesteric phase was observed. In that observations no crystal phase was formed and cholesteric transforms into isotropic phase at 246 K. But when the sample was cooled only to *ca.* 233 K and there annealed for some time then upon sequential heating slightly above the transition from cholesteric to isotropic phase a crystal was formed in process lasting of about several minutes. On cooling the crystalline sample a gradual cracking was detected as previously. Contrary to the glass in crystal the fractures were not disappearing on heating up to melting at 280 K

The results of DSC experiments are in agreement with the above features. Figure 1 presents typical thermogram obtained on heating with anomalies connected with reversible phase transitions from a glass into cholesteric phase and from cholesteric into isotropic phase (upper curve). Special thermal treatment leads to formation of the crystal phase and its melting (lower curve) as in similar microscopic observations.

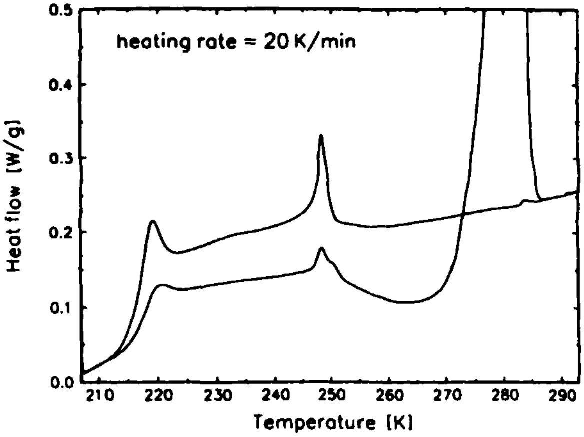

FIGURE 1 Thermogram for a raw sample (upper curve) and for a sample partially transformed into crystal phase (lower curve, peak of melting cut off)

The analysis of DSC results allows to determine thermodynamic parameters describing the phase transitions. Comparing to melting the thermal effect observed for cholesteric-isotropic phase transition is small.

TABLE I Thermodynamic parameters of transitions observed on heating

Phase transition	Temperature [K]	Enthalpy [J/mole]
Glass	$T_g = 212.5 \pm 0.2$	
Cholesteric-isotropic	$T_{tr} = 246.4 \pm 0.1$	$\Delta H = 360 \pm 30$
Melting	$T_m = 276.4 \pm 0.3$	$\Delta H = 10700 \pm 0.5$

In Figure 2 there is a schematic graph of free energy *vs.* temperature. It shows also the temperature ranges where the most effective nucleation of crystals occurs as well as the growing of crystal phase. The results are in

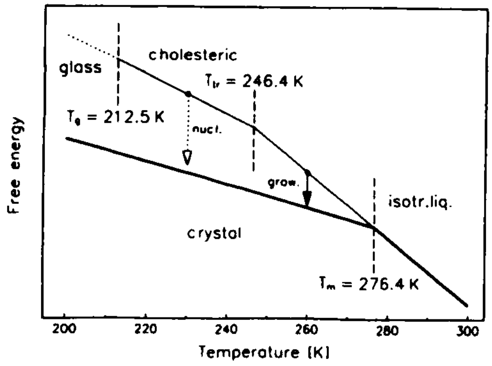

FIGURE 2 Schematic graph of free energy temperature dependence showing relations between detected phases.

agreement with earlier dielectric studies. [3] Due to rather fast cooling rate applied in that method and larger size of the sample the crystallization on heating was observed there without any special annealing procedure.

In order to elucidate the differences among phases on molecular level the infrared spectroscopy experiments were carried out. The results are shown in Figures 3 - 5. Fig.3 presents the spectrum of a glass recorded at 100 K after fast cooling the sample (top curve) and the spectra of the crystal phase at 100, 200 and 260 K which grows due to application of the thermal treatment discovered in earlier studies. Fig.4 points out specially the far infrared region (50-500 cm^{-1}). In Fig.4a the upper curves are for the crystal phase and lower curves are for the isotropic phase. It is worth to note that phases clearly seen as different in macroscopic experiments (i.e. in temperature dependence of dielectric permittivity[3]) are very difficult to distinguish on a molecular level point of view. The FTIR spectra for the isotropic and cholesteric liquids as well as for a glass (frozen liquid) are very similar in a broad range of temperatures (Fig.4b-two lower curves and Fig.3 - the top curve). Fig.4b gives the evidence that crystallization was observed also in a very slow cooling process. The crystal phase of isopentyl cyanobiphenyl is still far from perfect ordering as the lattice vibration region below 150 cm^{-1} presents one irregular broad band similar to that observed for the glass (Fig.3). It seems that at very low temperatures there is possible an extra phase transition to more ordered solid phase (such studies are under way now). Due to large degree of disorder (chiral molecular chains) the formation of a glass is very easy whereas growth of a crystal requires special long lasting thermal treatment in which the nuclei of crystals are formed. Only after that the crystal phase was growing from the supercooled isotropic liquid. Experiments when cooling were performed only to 240 K never succeeded in crystallization in subsequent heating.

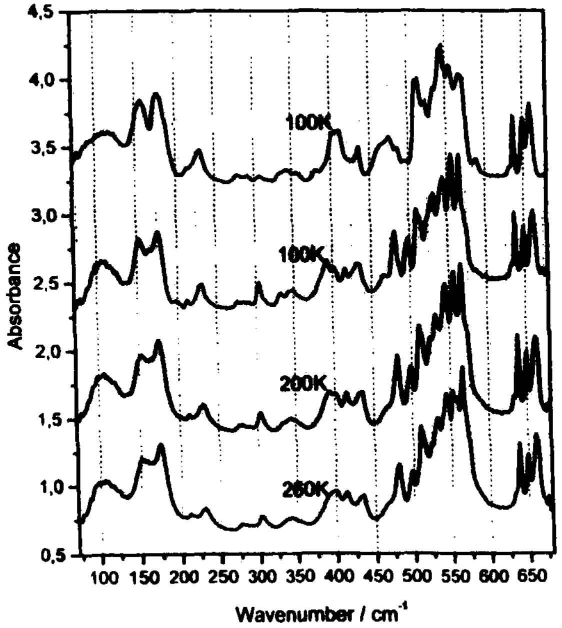

FIGURE 3 IR spectra of low temperature glass (the top curve) and of the crystal phase at various temperature.

In Fig.5 the process of the crystallization (upper curve) and the melting (lower curve) is presented in the form of the interferograms' main maxima vs. time observed as the response of the sample to the changes of temperature. One can see that there are two different crystallization rates. This process seems to be a complex and long lasting. The rate of crystallization depends on the temperature at which the process occurs which was detected and described during the dielectric studies [3]. That observation is valid for the melting as well.

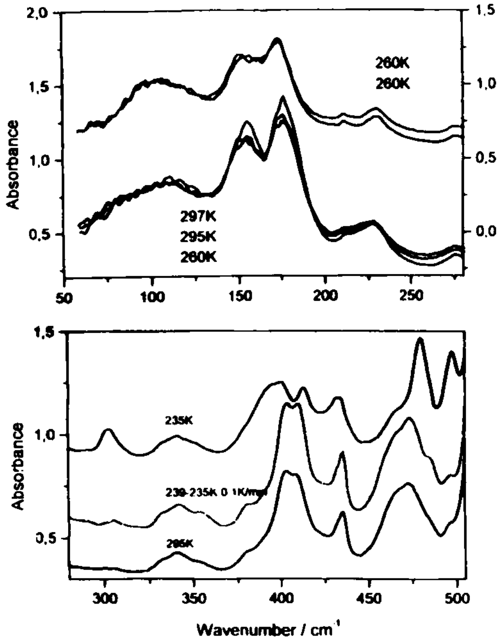

FIGURE 4 Far IR spectra from 50 - 300 cm^{-1} for the crystal phase (upper curves) and isotropic phase (lower curves). Far IR spectra from 300 - 500 cm^{-1} for the crystal, cholesteric and isotropic phases (from top to the bottom).

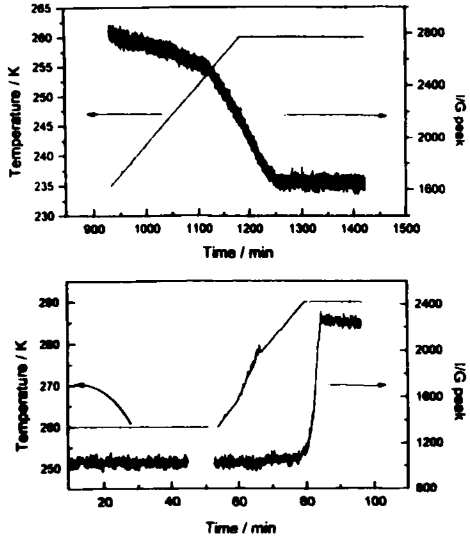

FIGURE 5 Evidence of the crystallization (upper curve) and the melting (lower curve) in the form of FIR interferograms' main maxima vs. time along the temperature changes.

CONCLUSIONS

There is no contradiction between all experimental methods about identification of phases of isopentylcyanobiphenyl. It was clarified that heating the sample succeeded by formation of a crystal phase only in case when it was proceeded by cooling below 240 K. The features of the low frequency spectrum of FIR point to conclusion that the crystalline phase is highly disordered. Searching for the smectic phase mentioned in earlier paper was unsuccessful but there are hints suggesting existence of another low temperature solid phase.

Acknowledgments

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