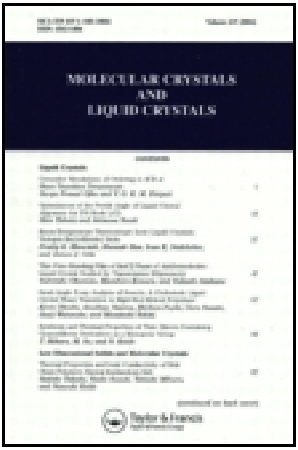

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Spectroscopy of Phase Transitions in Liquid Crystals

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Spectroscopy of Phase Transitions in Liquid Crystals

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The results of study of structural genesis of the nonoriented nematic MBBA at different temperature pre-history are reported. The temperature dependent transformations of the vibrational Raman spectra and their connection with the change of MBBA structure were investigated in the spectral region 1100-1600 cm^{-1} and in the temperature interval 163-333 K. The method to be used allows to prognosticate the structural evolution of MBBA and to identify its phase states. In particular it is found that the several coexisting fractions of different conformers may be obtained in the temperature region lower the glass transition temperature in dependence on the sample cooling rate.

Keywords: liquid crystals; Raman spectroscopy; phase transitions; conformations

INTRODUCTION

The molecular spectroscopy, particularly the vibrational Raman spectroscopy allows to obtain information on the molecular structure changes under the structural transformations in the samples. Then one can investigate the molecular processes that accompany the structural transformations as the form of molecules is connected with their packing in the condensed matter. The vibrational spectra are sensitive to the molecular transformations. Therefore, the intramolecular mechanisms of the structural changes in the samples can be manifested in these spectra. We choose the well known N-p-methoxybenzylidene p-n-butilaniline (MBBA) as a subject of our investigations. MBBA was studied in different phases before us with using the different experimental methods: neutron and X-ray analyses[1], differential scanning calorymetry[2], etc. We used the results of these investigations to establish the connection between the molecule conformational transformations and the phase transitions in MBBA.

Besides in the different papers there are the different interpretations of the sample polymorphous compositions obtained after the "shock" cooling. We make an attempt to exclude these contradictions.

Molecule of MBBA consists of two benzene rings connected by C=N bridge. This flexible bridge is one of the causes of the existence of the MBBA molecule different conformations. We can observe five intensive vibrational bands in the regions 1110-1200 cm^{-1} and 1500-1700 cm^{-1} (ν_a=1574 cm^{-1}, ν_b =1596 cm^{-1}, ν_c =1625 cm^{-1}, ν_d = 1164 cm^{-1}, ν_e = 1192 cm^{-1}) of the Raman spectra, which are sensitive for the molecular conformation. If the molecular form determines the molecular packing then the different molecular conformers pack in the different structural forms.

The goals of our paper are: 1) to establish the spectra-structure correlation under the phase transitions taking into account molecular conformations; 2) to analyze the phase transformations dynamics and the structural peculiarities of MBBA in the different phase states using the molecular spectroscopy methods.

EXPERIMENTAL METHODS

We used the microprocessing system to stabilize and control the sample temperature. The system allowed us to support the sample temperature with an accuracy 0.05 K and to control the temperature change rate in the range 150 - 300 K with an accuracy 0.1 K .

The Ar-laser with the wavelength 488 nm and the power 0.1W was used as a source of radiation. The radiation did not influence practically the sample temperature. The spectral-digital complex which includes the double monochromator, the photon counting system and PC-controller was used to record the Raman spectra (RS). Spectral width of apparatus function did not exceed 1 cm^{-1} for all experiments.

The unaligned MBBA bestowed in a sealed ampoule of 0.5 cm in diameter was the object of study at the different rates of its cooling.

In each cycle of the slow cooling (the cooling rate V = 1.5 K/min) from the temperature of phase transition into isotropic liquid (T=328 K) to the temperature 163 K the sample was annealed before RS registration at the constant temperature for 20 minutes. The analogous procedure was carried out also at the slow heating cycle of a sample.

In other experiment an ampoule with isotropic MBBA (T=328K) was placed in a vessel containing liquid nitrogen for 20 minutes. After this "shock" cooling the heating cycle was carried out (V=2K/min). In this cycle the sample was also annealed before RS registration at each temperature point for 20 minutes.

RESULTS AND DISCUSSION

Shape of Raman Bands and Dynamics of Structural Transformations

The phase transitions S (stable crystal) - N (nematics) in the case of "shock" cooling and S_2 (stable crystal modification) - N in the case of slow cooling are observed at the temperatures 291 K and 293 K correspondingly. These phase transitions are accompanied by the displacement of vibrational bands and their broadening[3]. It is the transition of type "order - disorder". The dominating mechanism of the vibrational band broadening at this transition is the heterogeneous broadening. As it is seen from paper[3] the corresponding contribution to the broadening is approximately 50%.

We try to find out the connection between the vibrational bands shape and the structural peculiarities of MBBA in the stable crystal phase as well as the dynamics of structural transformations which take place at the process of transition S - N for the case of "shock" cooling.

The stable crystal S is a mixture of two fractions of conformers with the twist angles $\theta = 43.3°$ ($\nu = 1159$ cm^{-1}) and $\theta = 82.7°$ ($\nu = 1172$ cm^{-1}). As one can see from the paper[3] the bands ν_a and ν_c in the S-phase of crystal are broadened in a comparison with the case of metastable crystal (M). Vergoten connects the bands ν_a and ν_c with the bending vibrations of C=N bridge[4]. The frequencies of bridge vibrations depend on the twist angle due to the presence of hydrogen atom linked with nitrogen atom. However this dependence is weak as compare with analogous dependence of the deformational CCH - vibrations of benzene ring. Therefore the broadening of ν_a and ν_c bands can be connected with the increasing in the S-phase of fractions of the conformers with twist angles $\theta = 43.3°$ and $\theta = 82.7°$ which gives small low-frequency and high-frequency displacement of these bands according to band observed in M-phase at $\theta = 50.2°$. Therefore we did not observe asymmetry band connected with predominating of the conformers with twist angle $\theta = 43.3°$ over the conformers with $\theta=82.7°$. A small broadening of the bands is connected with practically non-displaced their frequencies[3].

The band ν_b=1594 cm^{-1} is more sensitive to the conformational transformations. At T=251 K under phase transition M - S this band is displaced in low-frequency region. It can be connected with strong increasing of fraction of the conformers with $\theta = 43.3°$ ($\nu_d = 1159$ cm^{-1})[3]. Furthermore, at T>251 K the band ν_b becomes asymmetrical in high-frequency side[3] due to the presence of the conformers with $\theta = 82.7°$ and $\theta = 50.2°$ which quantity is approximately twice less then that of conformers with $\theta = 43.3°$. The observed behavior of band ν_b (displacement in low-frequency region, the asymmetry and correlation with transformation of band ν_d) confirms the assumption about its connection with deformational vibrations of benzene ring.

Under phase transition S - N the asymmetry of band ν_b=1592 cm^{-1} increases simultaneously with the transformation of the band ν_d[3]. One can see that this asymmetry appears at T=289 K due to the arising of new band ν_{b1}=1597 cm^{-1}. Under this phase transition one can see the strong broadening of the component 1171 cm^{-1} of band ν_d which is connected with conformers θ=82.7° , its smooth displacement in the low-frequency region by the value 3 cm^{-1} (in nematics this band has the frequency 1168cm^{-1}) as well as the large increasing of the integral intensity[3]. The individual bands with frequencies ν_b=1597cm^{-1} and ν_d=1168cm^{-1} were observed in S_1 and S_2 phases under the slow cooling too. It says about their full correlation.

When new band ν_{b1}=1597 cm^{-1}[3] attains the integral intensity maximum in N-phase, we observe[3] the single symmetrical broadened band ν_b displaced to high-frequency region (the quantity of conformers with ν=1168 cm^{-1} is practically equal to the quantity of conformers with ν=1160 cm^{-1}).

Therefore, the broadening of symmetrical band ν_b=1594 cm^{-1} in N-phase is connected not only with transition to more disordered phase (the mechanism of heterogeneous broadening), but also with complex conformational composition of MBBA (broadening of bands connected with three conformers in N-phase). Broadening of bands can lead both to symmetric band (ν_b, for example) and to manifestly asymmetric bands (ν_d, for example).

Phase Transition: Supercooled Nematics - Glass

The type of structure of the sample of MBBA after "shock" cooling was discussed in literature. Some authors asserted that a glass structure(G) arises after "shock" cooling[5-7], others supposed that there is a mixture of supercooled nematics (s/c N) and glass[2,8]. In paper[2] it was shown that relative proportions of glass and s/c nematics depend on the cooling rate. Under annealing of the supercooled sample at T=190 K the s/c N - phase transforms in solid glass. At further heating the fraction of metastable crystal increases and the fraction of stable crystal decreases[2]. Therefore, it was concluded that a glass transforms in a metastable fraction and s/c nematics transforms in a stable crystal[2].

As one can see from paper[9] all bands are narrowed and frequencies of the bands ν_d and ν_e are changed in the temperature interval 190-193 K. Obviously, it can be interpreted as the transformation of the part of s/cN-phase into a glass[9,10].

Narrowing of all bands at the phase transition s/c N - G is connected with more ordering of a glass in comparison with s/c nematics. In supercooled nematics a disordering of the mass centers is frozen. But the glass has two types of ordering regions: metastable liquid ("Islands of mobility") and crystal[11]. Note that sizes of these regions can be from 10 Å to 100 Å. Consequently, the vibrational bands get to be more narrow due to the partial disappearance of heterogeneous broadening by the value approximately of 2 cm^{-1}. Assumption that we deal here with the phase transition s/c N - G at T≈193 K is confirmed by the data of widths from Table I.

TABLE I The data of Raman bands widths in various phases of MBBA.

δ, cm^{-1} ν	$\delta_{S/C\ N}$	δ_G	$\delta_{V=35}$ T<203K	$\delta_{V=25}$ T<203K	δ_N	δ_I ISOTROPIC
ν_a	7.5	6.5	6.1	6.3	7.5	8..0
ν_b	13.3	12.0	11.4	10.4	13.0	13.2
ν_c	11.2	9.0	9.0	8.5	11.0	11.0
ν_d	15.8	14.5	-	14.5	-	-
ν_e	10.5	8.5	-	9.0	10.0	10.0

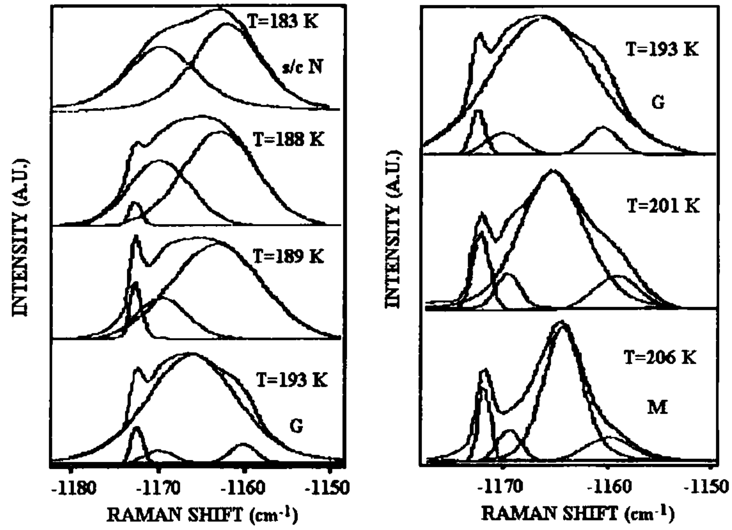
Equality of widths $\delta_{s/cN}$ (at T<193 K) and δ_N (at T=313 K) for all bands at "shock" cooling gives us grounds to conclude that practically whole nematics is supercooled. Thus at T < 190-193 K we deal with supercooled phase. From the equality of widths δ_G (in the temperature interval 190-193 K) and $\delta_{V_{cool}=25\ K/min}$ (at T<203 K and V_{cool}=25 K/min) (Table I) one can conclude that in temperature region 193-198 K we deal with the glass phase at the "shock" cooling as well as at the cooling with rate V_{cool}=25 K/min. Actually, at decreasing of the cooling rate the predomination of G-fraction over s/c N - fraction is observed[2].

The dynamics of conformational transformations at transition s/cN - G is observed for deformational CCH-vibration (ν_d) and is shown in Fig.1(a)[12,13,14]. As one can see the shape of vibrational band ν_d at T=183 K is the same as in N-phase[3].

The band ν_d is observed in Raman spectra for different conformers with good repetitionality in the wide temperature region. In the N-phase as well as in s/cN-phase one can observe the vibrational bands which correspond two main conformers with twist angles 44.4° (ν_{d1}=1160 cm^{-1}) and 59° (ν_{d2}=1168 cm^{-1}). The angles were calculated using the results of paper[2]. Note that the relative quantity of these conformers is the same in both N and s/c N phases. This fact confirms the idea that at "shock" cooling the amorphous phase is s/c nematics and the glass phase has no time to be formed. At the slow heating (V_{heat}=1.5 K/min) and twenty minutes of annealing at every temperature point the supercooled nematics gradually transforms into a glass (Fig.1(a)). It is manifested in the decreasing of a fraction of the conformers with θ=59°(1168 cm^{-1}), in the smooth increasing of a twist angle from 44.4°(1160 cm^{-1}) to 53°(1165.5 cm^{-1}), displacement of band ν_{d1}[9] and in the appearance of the new fractions of conformers with θ=82.7° and θ=43.3°(1172 cm^{-1} and 1159 cm^{-1}). Note that an integral intensity of the band ν_d is constant in the temperature region from 180 K to 213K. Therefore, it can be supposed that the appearance and increasing of the new fractions takes place mainly due to the decreasing of a fraction of the conformers with θ=59°. Hence, the relaxation transitions between various conformational states of molecules take place in s/c nematics.

The increasing of the twist angle in a glass phase on the value 9°(θ_G=53°) in comparison with its value in supercooled nematics leads to the less dense molecular packing in G-phase and to the weakening of the intermolecular interactions. Obviously, the narrowing of all five investigated bands at the phase transition s/c N - G (T=291 K) can also be explained by the weakening of the intermolecular interaction. In glass phase the band ν_d can be divided on four components which are well observed in spectrum at the narrowing of band ν_{d1} (Fig.1(a,b)). In the region of existing of G-phase

(T=193-198K) the vibrational bands shape does not change and the transitions between the various conformational molecular states are not observed.



a) b)

FIGURE 1 The temperature dynamics of conformational transformations at phase transitions **s/c N - G** (a) and **G - M** (b) of benzene ring deformational (CCH) vibration.

In G-phase on the background of wide band ν_{dl}=1165.5 cm^{-1} the new weak bands are observed. These bands are typical for the fraction of a stable crystal S (1172 cm^{-1} and 1159 cm^{-1}) and for the crystal S_2 obtained under crystallization of nematics at slow cooling (1168 cm^{-1} and 1172 cm^{-1})[3]. Therefore, it can be concluded that only the part of the s/c nematics was transformed in a glass at T=193 K. At the same temperature which corresponds to the appearance of the band 1159 cm^{-1} the rest part of s/c nematics was transformed in a stable crystal S. This transition (s/c N - S) was also observed on DSC-curve in paper[2] where it was shown that just s/c is responsible for the stable crystal fraction/ The appearance of bands 1168 cm^{-1} and 1172 cm^{-1} at T<193 K says that even at "shock" cooling the nematic sample is particularly crystallized (phase S_2). The relative quantity of these fractions can be determined from the ratio of integral intensities of the corresponding vibrational bands. This composition depends on the temperature pre-history of the sample. After the "shock" cooling we obtain in the temperature region 193 K - 198 K (the region of existing of G-phase) the next phase composition: 88% of glass, 4% of crystalline phase S and 8% of S_2-phase. At T<193 K we deal with s/c nematics where the relaxation transitions take place between the different conformational molecular states.

Phase Transition: Glass - Metastable Crystal

As one can see from the results of paper[9] the widths of all bands have a minimum at T=203 K. They are approximately equal to the band widths in the crystalline phases obtained at slow cooling[3]. Consequently, we can say that the crystalline phase (identified as M-phase) has been formed already at T=203 K. Therefore, the assertion that in the case of "shock" cooling the two amorphous mesophases and M-phase are formed at T=230 K[1,5,15] contradicts with our results. At T=203 K the phase transition G - M takes place. But the displacement of the vibrational bands ν_a, ν_b and ν_{d1} in the low-frequency region at T=201 K points out on the glass transition.

As it is seen from Fig.1(b) the glass phase is characterized by the presence of the conformers with the twist angle θ_G =53° (ν_{d1} =1165.5 cm^{-1}). In the process of the phase transition glass - metastable crystal the narrowing of the band ν_{d1} is accompanied by the development of the weak bands which are typical for the S_2 and S phases. It indicates on the correct division of band ν_d on four components in a glass phase.

From the calculation of relative integral intensities it is seen that relative amount of S and S_2 phases are not changed under phase transition. Since amount of S_2-phase is constant, the amount of S-phase to which s/c nematics transforms is not changed too. Therefore, one can conclude that in the temperature region 193 K - 198 K the fraction of s/c N-phase does not exist and just the glass phase transforms in the M-phase leaving the fractions of S and S_2 to be unchanged. This conclusion does not contradict the results of paper[2].

At T>203 K the M-phase coexists with the S and S_2 phases. Using the equations of paper[16] the twist angle typical for M-phase can be calculated. Its value is equal θ_M=50.2°(1164 cm^{-1}) that contradicts the results obtained in paper[16]. Obviously, the electronic and Raman spectra in this paper were obtained for some intermediate state with ν_d=1170 cm^{-1} which the authors identificated as M-phase.

The smooth narrowing of the bands which takes place in the temperature range 198 K - 203 K[9] most likely can be connected with the crystallization which has the character of smooth gradual ordering of the molecules throughout the volume (not the nucleus formation). Thus, the smooth disappearance of the heterogeneous broadening occurs. Using the X-ray investigations, it has been found that a transition to the solid crystal ordering realizes through the smooth reconstruction of the short-range ordering.

So for as the region of the correlated positions of the molecule centers of mass in the plane perpendicular to the director grows from the value 40Å in the initial amorphous state to the value 150Å in the crystal state (25-40 intermolecular distances) the orientational ordering of the molecules increases gradually.

Structure and Memory of Thermal Pre-History of the Nematic Phase

As it is seen from the results of paper[3] the glass and the stable crystal as well as the nematics are structurally inhomogeneous. The spectra of s/c N and N phases are the same(Fig.1(a) and paper[3]). These two phases consist of the two main fractions of conformers with twist angles 59° (1168 cm^{-1}) and 43.3°(1159 cm^{-1}). One can conclude that the packing and conformations of molecules in the amorphous phase are defined by their packing and conformations in the N-phase. Really, the length of correlated arrangement of molecules which characterizes the short-range ordering in MBBA is equal approximately 26 Å, but in the frozen sample this value is 32 Å[17]. Such change of the short-range ordering is connected, obviously, with the disappearance of molecular mobility in the process of freezing.

As it is seen from Fig. 1(a) and the results of paper[3] the molecule conformations which take place in the initial non-ordering system (N_0 or s/c N) determine the character of molecule conformations in the subsequent structural states. Such inheritance of the molecule conformations of nematics is manifested in appearance in the glass, M and S phases of the conformer fractions which are typical for the N and s/c N phases[3]. In the paper[18] it was shown that packing of nematics is inherited by these phases too.

In solid amorphous state the rearrangement of the whole disordering structural units into a crystal takes place. In the same time the appearance of the new metastable crystalline structures is possible (M and S phases). These structures can not be obtained by another method. The crystalline structures of the appearing metastable phases are closely connected with both the packing and the molecule conformations in nematic phase. So, the study of such structures gives us the information about the short-range order and conformational molecular structure of the initial non-ordering systems.

Therefore, the dissolution of complex contour of the band ν_d on three peaks is correct and monosemantic[3]. These bands are observed in all phases: s/c N, G, M, S.

Under slow cooling the inheritance of conformations and packing of the initial phase is not observed[3]. It is manifested in the disappearance of the band ν_e=1192 cm^{-1} and the wide component of band ν_a=1573 cm^{-1}. Also, as it is seen from[3] the phases S_1 and S_2 which are observed under slow cooling do not give the information about the complex conformational composition of the nematic phase. It is seen from the behavior of the band ν_d[3]. Consequently, the transition of nematics into the crystal state is connected with the essential rearrangement of the structure. Such rearrangement is possible due to the increasing of molecular mobility in the N-phase. As a result the packing and conformations of molecules of initial system are not inherited in the S_1 and S_2 phases under slow cooling unlike the ordering in frozen samples (s/c phase). Yet, the size of regions of coherent scattering (300-500 Å) in phases S_1 and S_2 is typical for cybotactic groups in liquid crystalline state. Therefore, it was assumed[18] that the macrostructure of the samples obtained after the phase transition nematics-crystal (S_1 and S_2) is determined by the macropacking of molecules in the N-phase. So, under slow cooling the macropacking is inherited in contrast to the packing.

Under slow cooling and intermediate cooling rates the initial nematic phase N_0 differs from the final N-phase in contrast to the case of "shock" cooling. The analogous situation takes place in the case of isotropic (I) phase as the I-phase differs from the I_0-phase. Fig. 2 illustrates the distinctions between N_0 and N phases at different cooling rates on the example of the band ν_d. As it is seen from Fig. 2 the conformational compositions at V_{cool}=2 K/min, 13 K/min, 25 K/min differ from those of the

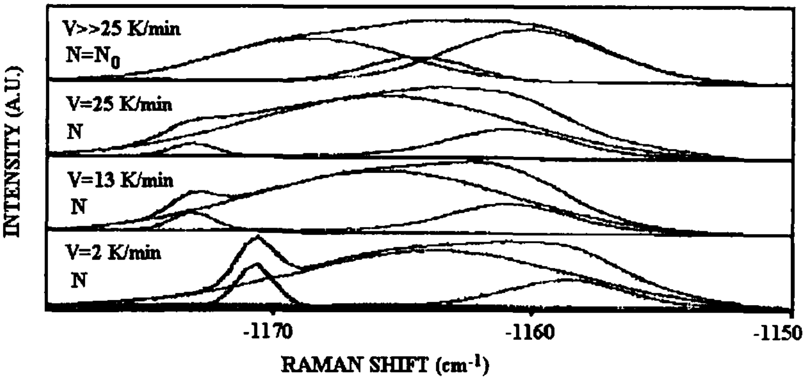


FIGURE 2 The shape of the vibrational band ν_b in the nematic phases N and N_0 at the different cooling rates.

initial phase by the relative part of conformers as well as the values of the conformer twist angles. At slow cooling and intermediate cooling rates the N-phase is a mixture of fractions of conformers with twist angles 82.7°, 52° and 44.4° as was calculated in paper[16]. The appearance of new conformers with θ=82.7°(1172cm^{-1}) which are not observed in the N_0-phase was connected with arising of cybotactic groups. These groups have the same structure as the S_2-phase. Their size is less than 500 Å. The number of these groups in the N-phase depends on the cooling rate (Fig.2). The more rate of preliminary cooling is accompanied by the appearance of more amount of crystalline phase S_2 inheriting the macropacking of N_0-phase. Consequently, at the subsequent slow cooling the number of cybotactic groups in the final N-phase is growing.

The final N-phase is sufficiently stable and the phase transition N - I during the heating cycle is reversible[3]. So, despite of the decreasing of the number of cybotactic groups in the I-phase, their number under phase transition I - N at the subsequent slow cooling is restored. Liquid crystals "remember" their pre-history of slow cooling during the several weeks. So the number of cybotactic groups and the conformational composition of the final N-phase are the indicators of the thermal pre-history of the sample. The only long annealing allows to restore the initial N_0-phase.

CONCLUSIONS

The molecular spectroscopy is a very informative method for a definition of the molecular mechanisms of the phase transitions in the mesogeneous media. It allows to study the connections between the types of molecular conformations and the character of the phase transitions in these media.

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