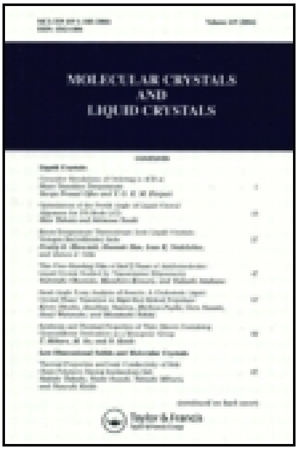

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Molecular Structure in Various Phases of Cooled Liquid Crystals

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Dynamics of polymorphous transformations in liquid crystals under different temperature conditions is studied by analysis of vibrational Raman band behavior. The correlation between bands parameters and structural especial features of different phases allows to determine the composition proportions of complex phase and detailed diagrams of phase transformations.

Keywords: liquid crystals; Raman spectroscopy; phase transitions

INTRODUCTION

The solid phase polymorphism in liquid crystals (LC) is defined mainly by structural peculiarities of molecules which can to form mesophase and by temperature pre-history of investigated samples. These two factors influence on molecular spectra cardinally. Because an analysis of positions and parameters of contours forms of vibrational bands in Raman spectra allows to obtain important information about peculiarities of structural transformations at the heating of preliminary cooled liquid crystals. Furthermore, important advantage of Raman spectroscopy in comparison with structural (X-ray investigations, neutron diffractometry) and thermal (differential scanning calorymetry (DSC), etc.) methods is possibility to trace the influence of phase transformations on individual fragments of investigated molecules and their conformations. The analysis of character of polymorphous transformations in supercooled liquid crystals was the subject of investigations in many works, for example, in[1-4]. However, often incorrect taking account of temperature pre-history of the samples (cooling rate V_{cool}, heating rate V_{heat}, annealing time at fixed temperature, etc.) leads to divergence of results.

We used Raman spectroscopy for excluding these contradictions for the solid phases identification and for analysis of the polymorphous transformations mechanisms on molecular level.

It was investigated the Raman spectra changes at "shock" cooling from isotropic phase MBBA in slow heating cycle. Then it was made same investigations at slow cooling in heating and cooling cycles[5-7]. A comparison of these results with the dates of another methods allows to trace the MBBA structural genesis at various temperature actions on it.

EXPERIMENTAL PROCEDURES

Raman spectra (RS) were obtained on automatic Raman spectrometer equipped with photon counter detector and photoelectric multiplier PEM-79. Argon laser was a source of exciting radiation (λ= 488 nm, radiation power less then 75 mW). The used slit width corresponds to 1 cm^{-1} resolution.

Automatic thermostabilization system with temperature stability 0.1 K was used. Nonoriented LC (MBBA) was included in a sealed ampoule of 0.5 cm diameter.

Variations of RS with the temperature in frequency range from 1110 cm^{-1} to 1220 cm^{-1} and from 1540 cm^{-1} to 1650 cm^{-1} at different rates of sample cooling were the subject of study in this work.

In a first experiment the sample was cooled with rate V_{cool}= 25 K/min to temperature 163 K. Then the registration of RS spectra in slow heating cycle (V_{heat}=2 K/min) from T=183 K to T=293 K was carried out. The another experiment at the rate of cooling 13 K/min in heating cycle was made.

RESULTS AND DISCUSSION

The case of cooling rate 25 K/min

The temperature dependence of widths and frequencies of investigated bands is shown on Fig. 1 and 2. The comparative data of widths and frequencies at various rates of cooling for two temperatures: T=183 K (amorphous (A) phase or crystalline phase) and T=298 K (nematic(N) phase) are presented in Table I. The temperature behavior of the vibrational bands parameters is similar to their behavior under "shock" cooling[8].

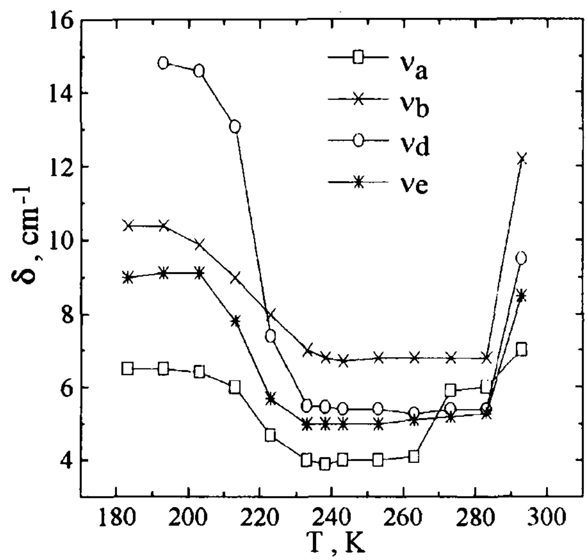


FIGURE 1 The temperature dependence of the vibrational bands widths of preliminary cooled MBBA with rate 25 K/min: ν_a=1574cm^{-1}, ν_b=1596 cm^{-1}, ν_c=1625 cm^{-1}, ν_d=1164 cm^{-1}, ν_e=1192 cm^{-1}.

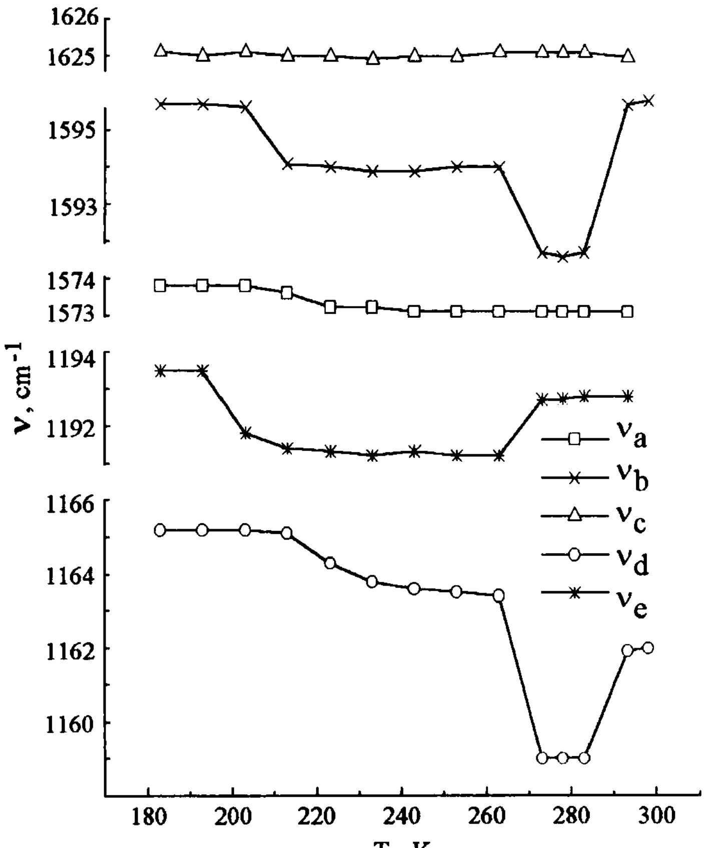


FIGURE 2 The temperature dependence of the vibrational bands frequencies of preliminary cooled MBBA with rate 25 K/min: ν_a, ν_b, ν_c, ν_d, ν_e.

But there are some distinctions. Likely to the case of "shock" cooling at T=203 K abrupt displacement of bands ν_b, ν_c and ν_d is observed. Besides widths of all bands reach of minimum at T=233 K (Fig.1) (at "shock" cooling the minimum was observed at T=213 K[8]).

So, one can conclude that the glass-transition occurs at T=203K as in the case of "shock" cooling[8] at heating of the sample. Yet, process of forming of metastable crystal is completed at T=233 K (at "shock" cooling it was observed at T=213 K). Smooth narrowing of widths in region from T=203 K to T=233 K (Fig.1) and recrystallization peak at T=230 K on DSC-curves[9,10] can be evidence of this conclusion.

In the investigations of supercooled polymers[11] abrupt decreasing of modulus of elasticity and maximum of parameters characterizing of molecular mobility was observed at temperature of glass transition. Therefore, the glass-transition was interpreted as a transition in elastic amorphous phase in which there is fragmentary mobility.

TABLE I The comparative data of Raman bands widths and frequencies at various cooling rates of MBBA and in nematic phase

V_{cool}, K/min	2	13	25	"Shock" cooling	Nematic Phase
T, K	183	183	183	183	298
ν_b, cm^{-1}	1597	1597	1595.3	1595	1595
δ_b, cm^{-1}	6	6	10.4	13..3	12.8
ν_c, cm^{-1}	1624	1624.5	1625.3	1625	1625
δ_c, cm^{-1}	6.5	6.3	8.5	11.2	11
ν_a, cm^{-1}	-	-	1573	1573	1573
δ_a, cm^{-1}	-	-	6.3	7.5	7.5
$\nu_{a'}$, cm^{-1}	1576.5	1577	1576	1576	1576
$\delta_{a'}$, cm^{-1}	2	2	2	2	-
ν_e, cm^{-1}	-	-	1194	1193.5	1193
δ_e, cm^{-1}	-	-	9	10.5	10
ν_d, cm^{-1}	1168	1167.5	1164.5	1164.5	-
δ_d, cm^{-1}	6.8	6.5	14.5	15.8	-

The fact of displacement of bands at T=203 K in low-frequency region says about transition in elastic phase. This process corresponds to decreasing of modulus of elasticity and increasing of mobility. It is manifested in experiments on internal friction. Therefore, namely frequencies are most sensitive to glass-transition independently on cooling rate. Moreover, temperature of glass transition is not depended on cooling rate.

The vibrational bands widths (Table I) in the region of existing of amorphous phase (A-phase) (T=183 K) consisted of supercooled nematic (s/c N) and glass (G) mixture are more narrow at V_{cool}=25 K/min in comparison with the case of "shock" cooling. At the same time, under "shock" cooling the width in A-phase coincide with it in N-phase.

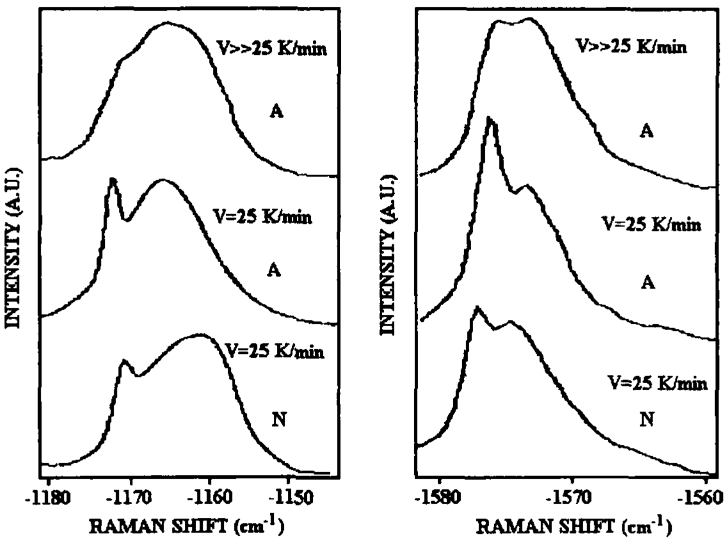


FIGURE 3 The vibrational bands shape of amorphous (A) and nematic (N) phases at various cooling rates

Therefore one can conclude that the nematic as a whole is supercooled under "shock" cooling and glass fractions in A-phase is not formed. It is known[9] that an quantity of s/c N - fraction decreases with decreasing of V_{cool} and at V_{cool} = 25 K/min the amount of glass is approximately in twice exceed amount of s/c N. Glass has more ordering structure in comparison with nematic[12].

The bands in A-phase are more narrow at V_{cool} = 25 K/min. The nematic has time in order to crystallize particularly at V_{cool}=25 K/min. The phase transition: N - S_2 (stable crystalline modification can be seen from vibrational bands shape corresponding to A and N phases (Fig.3). Presence of the strong bands 1172 cm^{-1} and 1576 cm^{-1} is typical for crystalline S_2-phase.

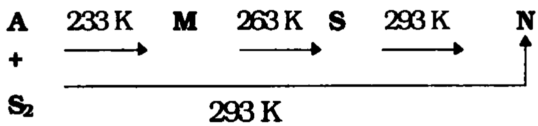
As in the case of slow cooling the sybotactic groups having the structure of S_2-phase are present in N-phase of MBBA after cycles of cooling (V_{cool}=25 K/min) and heating. Besides at temperature below T_G=203 K the phases s/c N, G, S_2 coexist.

At T=263 K the bands ν_b, ν_e, ν_d are abruptly displaced and the band ν_a, ν_c are broadened (See Fig. 1 and 2). Such transformations took place in the case of "shock" cooling at T=253 K at phase transition: metastable (M) - stable (S) crystals. In this case the frequencies was smoothly shifted at temperatures above T=253 K. Such situation is different from the case of cooling with rate V_{cool}=25 K/min where frequencies are abruptly changed at T=263 K (Fig. 2).

Obviously, it is connected with the nature of this phase transition which depends on thermal pre-history. The M-phase can be formed even at temperature T=203 K. It must be mentioned that in work[9] the M - S phase transition was not observed due to a very high heating rate (V_{heat}=8 K/min). This transition had been observed under annealing at T=273 K only. The dependence of this phase transition on thermal pre-history proves that we deal with crystalline M-phase.

The phase transition S - N is observed at the temperature T=293 K in the case of slow cooling as well as at "shock" cooling. It is manifested in the broadening and shifting of all bands to high-frequency region (Fig. 1, 2).

As result, we have obtained the following phase transitions diagram at the heating cycle of MBBA preliminary cooled with rate V_{cool}=25 K/min.



The case of cooling rate 13 K/min

The Raman spectra obtained in heating cycle of preliminary cooled MBBA with V_{cool}=13 K/min are presented in Fig. 4[13,14]. The heating cycles were similar to the case of cooling with rate V_{cool}=25 K/min.

The widths and frequencies temperature dependencies are presented in Tables II and III. As it follows from the Table I the widths and frequencies of all bands at V_{cool}=2 K/min and V_{cool}=13 K/min have the same values at $T<T_G$. They are strongly different from vibrational bands parameters obtained at "shock" cooling or at V_{cool}=25 K/min.

Hence the crystalline S_2-phase obtained at slow cooling is observed also at V_{cool}=13 K/min. Indeed the comparison of the spectra at cooling cycle with V_{cool}=2 K/min[8] at the temperature region from T=263 K to T=203 K (the S_2-phase forming region) with the spectra obtained at V_{cool}=13 K/min (Fig. 4) in region T=188-203K shows that these spectra have the same widths and frequencies.

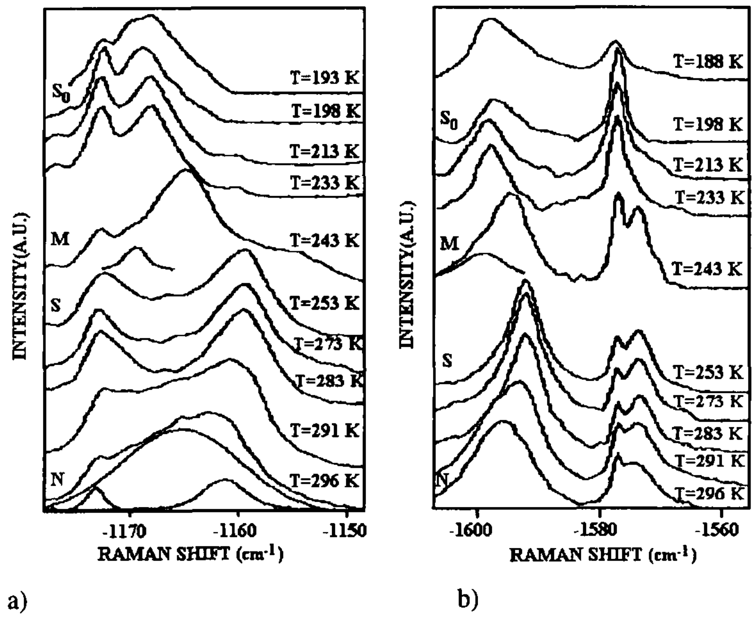


FIGURE 4 The vibrational bands changes of preliminary cooled with rate 13 K/min in heating cycle in frequency regions 1140-1180 cm^{-1}(a) and 1550-1610 cm^{-1} (b).

The S_2-phase exists until the temperature T=233 K (Fig. 4). It is known[9] that even at V_{cool}=8 K/min approximately 11% of glass phase is forming at T<203 K. The glass fraction is not manifested in widths and frequencies because this fraction is very small. Therefore it was obtained the narrow bands.

As one may see from Fig. 4, Tables II and III the new phase transition is going on at T=243 K. The widths, frequencies and relative intensities of vibrational bands at T=243 K are absolutely identical with analogous parameters observed at "shock" cooling or at V_{cool}=25 K/min in M-phase[8]. As it was shown in Ref.[9] the presence of G-phase leads to forming of M-phase. Probably the small fraction of glass transforms in metastable crystal and provokes S_2 - M phase transition at T=243 K which was not observed earlier.

Another phase transition: M - S is going on at T=253 K (Fig. 4). Analogous transformation of vibrational bands took place under this phase transition at T=253K for cases of "shock" cooling and cooling with rate V_{cool}=25 K/min.

Phase transition: S - N was observed at temperature T≈293K. As in the case of slow cooling the obtained nematic phase is different from initial N_0-phase (Fig. 3, 4a and Ref. [8]). It is manifested in changing of shape of bands ν_a and ν_d.

TABLE II The temperature dependencies of Raman bands widths of MBBA in heating cycle for the case of V_{cool}=13 K/min.

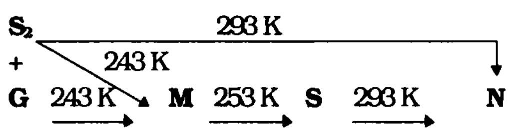
δ, cm^{-1} / T, K	δ_a	$\delta_{a'}$	δ_b	δ_c	δ_d	δ_e
183	-	2.0	5.7	6.3	-	-
188	-	1.8	-	-	-	-
193	-	2.1	5.6	6.3	-	-
198	-	1.9	-	-	6.1	-
203	-	2.0	5.2	6.1	6.5	-
208	-	2.0	5.8	6.3	-	-
213	-	2.0	6.0	-	5.6	-
223	-	2.0	6.0	6.6	-	-
233	-	1.9	6.5	6.0	-	-
243	5.0	1.8	7.0	7.0	5.1	-
253	5.6	1.8	6.2	6.7	5.2	6.7
258	-	-	6.3	6.4	-	-
263	5.8	1.8	6.4	6.4	5.9	5.9
273	5.4	1.7	6.5	6.1	6.0	6.6
283	5.7	1.7	6.6	7.0	6.1	6.7
291	7.8	1.7	7.9	9.0	15.0	8.0
296	8.0	1.7	13.3	9.8	15.5	8.6
300	8.0	1.7	13.3	10.0	15.0	8.7

TABLE III The temperature dependencies of Raman bands frequencies of MBBA in heating cycle for the case of V_{cool}=13 K/min.

ν, cm^{-1} / T, K	ν_a	$\nu_{a'}$	ν_b	ν_c	ν_d	ν_e
188	-	1577.1	1596.7	1625.1	1167.5	-
193	-	1577.2	1597.2	1624.8	1167.7	-
198	-	1576.7	1596.6	1624.8	1167.9	-
203	-	1576.7	1597.0	1625.2	1167.6	-
213	-	1577.2	1596.7	1624.8	1167.6	-
223	-	1576.7	1597.3	1625.0	1167.5	-
233	-	1576.7	-	1625.0	1167.2	-
243	1573.5	1577.1	1594.0	1625.1	1164.5	1192.0
253	1573.5	1577.2	1592.0	1625.2	1159.3	1193.8
263	1573.5	1577.2	1592.0	1625.0	1159.6	1193.8
273	1573.4	1577.0	1591.9	1625.0	1159.9	1194.0
283	1573.4	1577.0	1591.8	1624.8	1159.5	1194.0
291	1573.5	1577.0	1592.1	1625.9	1159.7	1193.9
296	1573.7	1577.0	1596.0	1626.0	-	1194.0
300	1574.0	1577.0	1596.0	1626.0	-	1194.0

The final nematic phase at V_{cool}=13 K/min coincides with N-phase obtained after slow cooling. They differ only number of sybotactic groups only. The intensities of ν_a and ν_d bands in N-phase at V_{cool}=13 K/min are smaller in comparison with slow cooling. It says about different quality of such groups in nematic phase.

Therefore, at cooling of MBBA with rate V_{cool}=13 K/min following phase transitions are going on:



CONCLUSION

It has been investigated boundary cases of cooling and analyzed the data of X-ray investigations[15,16], neutron scattering[17] about the phase states obtained for the cases of "shock" and slow cooling. It gave possibility to connect the vibrational bands shape and structural peculiarities of MBBA in various phases and to define the scheme of phase transitions more precisely.

Supercooled nematic and glass, metastable and stable crystals, S_1 and S_2 crystalline phases, initial nematic and nematic obtained after cooling and heating cycles are characterized by definite frequencies, widths, relative intensities of vibrational bands, disappearances some of them and splitting of bands. Using by these spectral characteristics it can be identify any of phases mentioned above and even coexisting some of them without difficult complex structurally-spectrally-thermodynamics investigations.

The knowledge of regularities of the structure of various phase states with spectral characteristics allows to identify the phase states and to obtain the phase diagrams for intermediate cooling rates.

The phase diagrams of predominant phases in certain temperature intervals at different cooling rate are presented in Table IV. The investigation of vibrational bands at various cooling rate allows to carry out diagnostic of phase transitions. In dependence on thermal pre-history it may be obtained a few coexisting fractions (for example, S_2, G and s/c N) at $T<203$ K. Proportional relations of these fractions are determined by cooling rate. In dependence on their correlation it is possible realization one or another of phase diagram (Table IV). The presence of even little per cent of glass in S_2-phase result in phase diagram differing from that for slow cooling. Thus they are realized following phase transitions: S_2 - M - S - N. And predominance of phase A over S_2 lead to series of transitions observed under shock cooling.

TABLE IV The phase diagrams of MBBA at various rates of cooling

"Shock" cooling	V_{cool} = 25 K/min	V_{cool} = 13 K/min	Slow cooling: Cooling cycle	Slow cooling: Heating cycle
A	A	S_2	I_0	S_1
↓ 203 K	↓ 233 K	↓ 243 K	↓317 K	↓ 203 K
M	M	M	N_0	S_2
↓ 253 K	↓ 263 K	↓ 253 K	↓263 K	↓ 293 K
S	S	S	S_2	N
↓293 K	↓ 293 K	↓ 293 K	↓203 K	↓ 317 K
N_0	N	N	S_1	I
↓317 K				
I_0				

Everything of aforesaid are correct not only for MBBA but also for others LC having benzeliden-aniline nucleus because investigated bands can be connected with vibrations of benzene rings and aniline bridge. In fact three solid modifications (A, M, S) have already found not only in gomological series of MBBA but in series of others LC too.

Thus determined spectral-structural peculiarities allows to make prognostics phase evolution and identification of phase states for wide class of LC in dependence on their thermal pre-history.

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