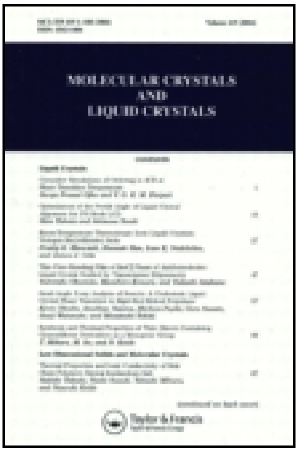

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Structural Peculiarities and Phase Transitions of MBBA with Different Thermal Pre-History

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STRUCTURAL PECULIARITIES AND PHASE TRANSITIONS OF MBBA WITH DIFFERENT THERMAL PRE-HISTORY.

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Abstract The temperature dependencies of widths and frequencies of vibrational bands in MBBA (N-p-methoxybenzylidene p-n-butylaniline) corresponding to intramolecular vibrations (1100 - 1700 cm^{-1}) were investigated in various thermal regimes. Regularities connecting frequencies and shape parameters with structural peculiarities of MBBA in different phases under fast and slow cooling were found. Besides it was obtained additional information about mechanisms of vibrational band formation in molecular spectra.

INTRODUCTION

Phase transitions investigation for supercooled liquid crystals (LC) has been performed by various methods : neutron diffractometry[1], small angle neutron scattering[2], X-ray investigation[3], differential scanning calorimetry (DSC)[4], differential thermal analysis (DTA)[5]. These methods yield contradictory results. Main discrepancies involve number and nature of detected solid phases, their identification, distinction metastable crystal (M) from stable crystal (S) recieved under slow heating supercooled LC (hypothesizes of Andrews[6] and Mizuno[7]).

The molecular spectroscopy is very effective and convenient method to investigate supercooled LC polymorphism, to attest solid phases, to trace their structural evolution and its accompanying conformational changes of molecule.

A number of works completed using vibrational spectroscopy technique have allowed to establish a correlation between liquid-crystalline material structure in different phases and vibrational bands frequencies corresponding predominantly to external degrees of freedom (up to 150 cm^{-1})[1,5,8,9]. Yet, there are a limited amount of works on investigation of solid-phase polymorphism manifestation in shift of vibrational bands corresponding to intramolecular vibrations[5,7,10] and practically there are no detailed investigations of their manifestation in broadening of high-frequency vibrational bands[11]. But just intramolecular vibrations feel both a change of molecule packing and a modification of her conformations. Different conformations ares typical for various solid phase of LC[6,7].

Lately we presented a detailed Raman study of solid phase polymorphism of MBBA under fast cooling[12]. Regularities connecting frequencies and shape parameters with structural peculiarities of LC under phase transition glass - metastable crystal were found. Therefore, it seems appropriate to investigate temperature transformations of widths (δ) and vibrational bands positions (ν) for accurate definition (in case it is a moot point) of structural peculiarities of MBBA in various thermal regimes and for receipt additional information about mechanisms of vibrational band formation under phase transitions M-S, S-nematic (N).

EXPERIMENTAL PROCEDURES

Raman spectra (RS) were obtained with the use of automated spectrometer and automatic thermostabilization system. The complex comprised a photon counter, photoelectric multiplier PEM-79. Radiation source was Ar-laser. Wave length of exciting radiation was λ=488 nm, power on sample was limited to 75 mW. Computer exercised control over spectrometer and processed spectral information. To provide temperature stabilization for the sample under study with an accuracy of 0.01 K, computer used a program which yielded temperature oscillation damping in the process of establishment of temperature in LC. Spectral width of apparatus function did not exceed 1 cm^{-1} for all experiments. Unaligned LC (MBBA) was inclosed in a sealed ampoule 0.5 cm in diameter and studied experimentally.

Variation 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 was the subject of study in this work. In each cycle of slow cooling (rate of cooling being V_{cool}=1.5 K/min) from isotropic liquid (T=328 K) to temperature of 163 K the sample was kept at each temperature point for 20 minutes before RS registration. Then, slow heating cycle (V_{heat}=2 K/min) was carried out with similar RS registration and sample annealing.

In other experiment an ampoule with isotropic MBBA was placed in a vessel containing liquid nitrogen and held there for 20 minutes. Following this "shock" cooling, the above described heating cycle was conducted.

METASTABLE - STABLE CRYSTAL PHASE TRANSITION

Let "shock" cooling, as such, be our initial concern. Phase transition occurring at

T=263 K in supercooled MBBA under slow heating is interpreted has a transformation from a metastable crystal to a stable one in works[1,7,8,13-15]. In other experiment[4] the transformation of this kind as been observed on annealing of a sample in metastable phase. Clearly defined phase transition has likewise shown itself at T=263 K in RS taken every 10 K [12] and at T=253 K in RS taken every 0.5-1 K (Figure 1, 2) in our investigations. Shifts of bands, broadening of two of five bands and splitting of the band ν=1164 cm^{-1} are quite identical at T=263 K[12] as well as at T=253 K (Table 1). Dependence of temperature of the phase transition on thermal pre-history or duration of stay at a given state for substance confirm the fact that we are dealing with metastable crystalline phase and its transition to stable crystal.

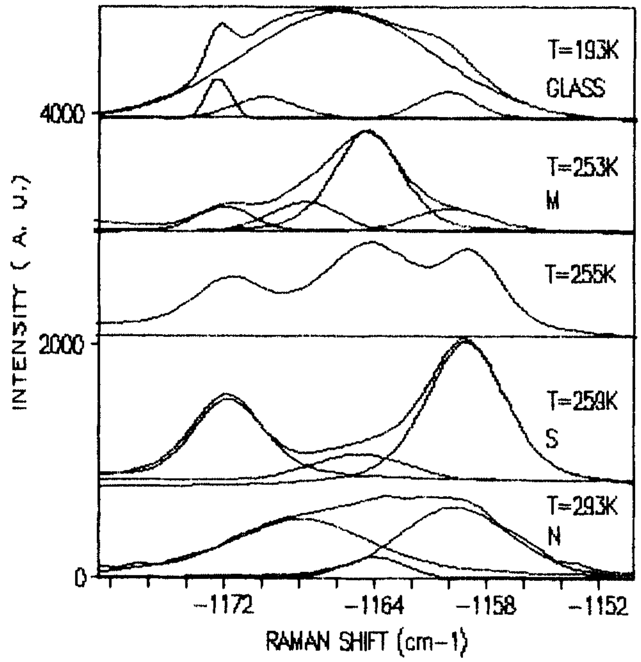

FIGURE 1 The temperature variations of the vibrational bands (1110 cm^{-1} - 1200 cm^{-1}) of MBBA under "shock" cooling.

Many papers[6,7,10,13,16] discuss structural distinctions between metastable and stable crystalline phases. The hypothesis suggested by Andrews asserts that the main distinction between these phases is manifested in different structure of butyl-chains and methoxy-group position with reference to benzene ring[6]. Besides that, the theoretical calculation performed by Mizuno[7] exists making it possible to estimate twist angles θ of aniline ring with respect to C=N-plane, in particular, for this two phases. It was revealed that stable modification consists of mixture of two molecular conformations with $\theta=44.4^0$ and 82.7^0, while metastable modification being characterized by the presence of conformer with $\theta=66.3^0$. Obtained RS validated this assumption. Particularly striking was the acute sensitivity to metastable-stable crystal transition expressed by the band of $\nu_d=1164$ cm^{-1} which splited in stable crystal. This band can be interpreted in the context of CCH deformational vibration of benzene ring[17]. And once, $\nu_{CCH}=1164$ cm^{-1} is dependent on the interatomic distance of H-atoms (possessed by aniline ring and C=N-bond). This spacing is altered when the aniline ring rotates about C=N-C plane, i.e. is a function of θ.

To obtain more detailed information on dynamics of polymorphous and conformational transformations, measurements were taken with a step of 1 K in the region of metastable-stable crystal transition and spectra were registered at 0.25 cm^{-1} intervals. This enabled us to trace kinetics of conformers transformations for various θ.

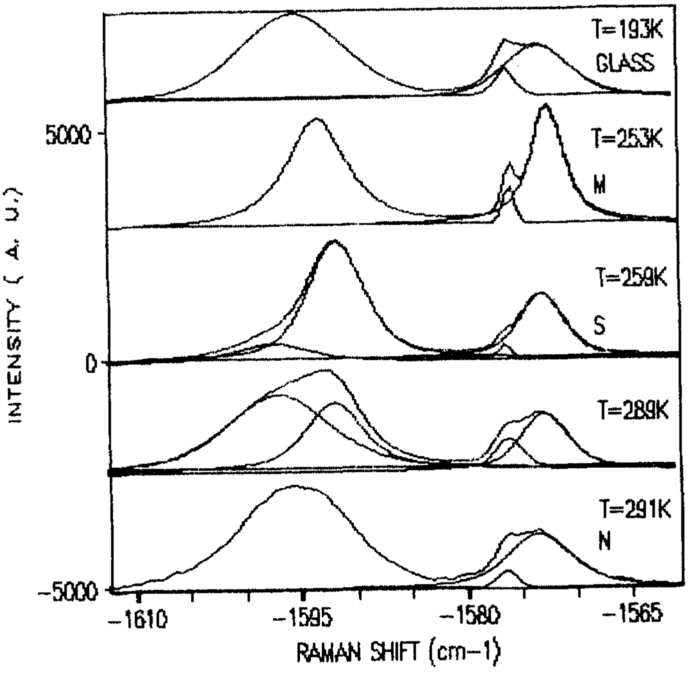

FIGURE 2 The temperature variations of the vibrational bands (1540 cm^{-1} - 1640 cm^{-1}) of MBBA under "shock" cooling.

The results are presented in Figure 1, 2 and Table 1. As Figure 1 suggests, ν_{CCH} band is divisible into four components : ν_1=1172 cm^{-1}, ν_2=1168 cm^{-1}, ν_3=1164 cm^{-1} and ν_4=1159 cm^{-1}, corresponding to four conformers with twist angles: θ_1=812.7^0, θ_2=59^0, θ_3=52^0, θ_4=44.4^0. These angles were calculated using the formula suggested in work[7]. The band ν_{CCH} was parted into 4 components to a good replication over the temperature region between 190 K and 251 K (region of glass, supercooled nematic and metastable crystal existence) (Figure 1). During the process of going from metastable to stable crystal certain part of MBBA molecules with θ_3=52^0 (1164 cm^{-1}) transform into conformers with θ_1=82.7^0 (1172 cm^{-1}) and θ_4=44.4^0 (1159 cm^{-1}) at T=251 K. This fact is corroborated by the increase in integrated intensity of ν_4 and ν_1 bands at the expense of ν_3 and by the constancy of integrated intensity for four bands over the temperature region from 210 K to 285 K.

TABLE 1 Temperature dependence of the widths (δ) and frequencies(ν) vibrational bands of MBBA: 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}.

T (K)	δ_d (cm^{-1})	ν_d (cm^{-1})	δ_e (cm^{-1})	ν_e (cm^{-1})	δ_a (cm^{-1})	δ_b (cm^{-1})	ν_b (cm^{-1})	δ_c (cm^{-1})
213	-	1164.5	6.0	1191.2	4.0	7.3	1594.0	6.6
251	5.0	1164.6	6.0	1191.2	4.0	7.6	1593.8	6.0
253	5.0	1164.6	6.2	1191.7	5.5	7.6	1592.2	7.5
255	5.0	1159.0	6.1	1193.2	5.5	7.6	1591.9	7.1
257	5.0	1159.2	6.1	1193.2	5.5	7.6	1591.9	7.5
259	5.1	1159.2	6.1	1193.1	5.5	7.1	1591.9	7.5
265	5.1	1159.2	6.1	1193.5	5.5	7.1	1692.0	7.6
269	4.6	1159.2	6.1	1193.1	5.5	7.1	1591.8	7.0
275	5.3	1159.2	6.5	1193.5	6.0	7.1	1591.8	7.0
278	5.0	1159.2	6.5	1193.3	5.5	7.1	1591.8	7.6
283	6.1	1159.2	7.1	1193.3	6.0	7.6	1591.8	8.0
285	7.1	1159.7	7.6	1193.3	6.3	7.0	1591.8	8.0
287	8.1	1159.6	-	1193.1	6.3	7.5	1591.8	8.6
289	9.0	1161.0	8.5	1193.5	6.5	7.0	1591.8	9.3
291	8.7	1161.0	9.1	1193.6	7.5	12.6	1595.7	9.6

Consequently, stable crystal consists of mixture of two conformers with twist angles of 82.7^0 and 44.4^0. The fact that there is the band of ν_3=1164 cm^{-1} at T>251 K indicates the availability of conformers with θ_3=52^0 typical for metastable crystal (Figure 1 shows ν_3=1164 cm^{-1} to be the most intensive band at T<251 K). Thus, it may be safely suggested that not the whole of metastable fraction turns into stable one and that the presence of conformers with $\theta=52^{0}$, in contrast to $\theta=66.3^{0}$ proposed by Mizuno[7], is intrinsic to the former. Besides, as evident from Figure 2 phase transition from stable crystal to nematic is observed at T=291 K. This temperature corresponds to endothermic peak of DSC experiment[4], which is associated with metastable crystal melting to nematic. However, stable crystal melts to nematic at T=295 K. Therefore, metastable fraction bears the responsibility for premature broadening of bands correlated with transition to higher-disordered medium (nematic). In all likelihood, wider bands in nematic (nearly in twice greater than in crystal)· are characterized by heterogeneous broadening. High sensitivity of intramolecular vibrations to any transition "disorder-order" type has been likewise corroborated in paper[11,12].

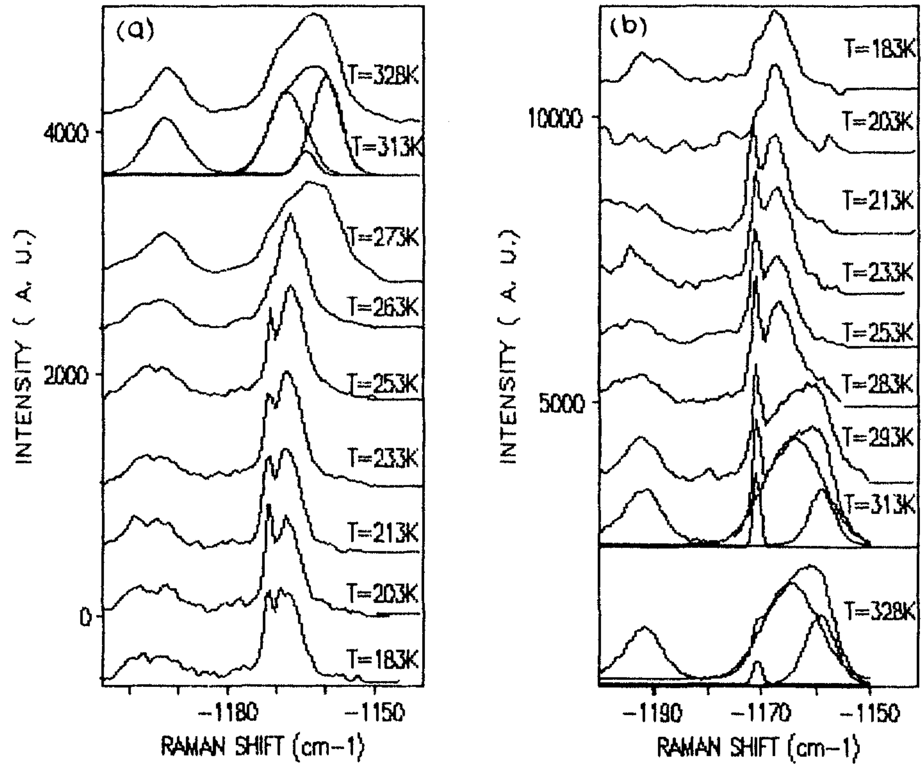

FIGURE 3 The temperature variations of the vibrational bands (1110 cm^{-1} - 1200 cm^{-1}) of MBBA under slow cooling. (a) Cooling cycle (V_{cool}=1.5 K/min). (b) Heating cycle (V_{heat}=2 K/min).

Low intensity bands, which are typical for stable fraction (ν_1=1172 cm^{-1} (82.7^0) and ν_4=1159 cm^{-1} (44.4^0)) and for crystal obtained by crystallization of nematic under slow cooling (Figure 3) (ν_2=1168 cm^{-1} (59^0)), are visible over the temperature region of 193-251 (Figure 1,2) werein metastable fraction and glass exist. Consequently, we might reason that not the whole of supercooled nematic will turn into glass at T=190 K[12]. The rest of it will transform to stable crystal (presence ν_4=1159 cm^{-1} and ν_1=1172 cm^{-1} at T=193-253 K). This transition has also been reflected in DSC curve [4]. The authors have shown that exactly the supercooled nematic is responsible for existence of stable crystal fraction. And the presence of 1168 cm^{-1} band indicates that nematic manages to crystallize out partly even on shock cooling.

In all likelihood, there are conformers distinct from each other not only by twist angle θ, but also by CH=N-group orientation[18]. This conclusion is confirmed by splitting of the band which Vergoten relates to C=N stretching vibrations[17] at ν=1573 cm^{-1} and ν=1575 cm^{-1} on rapid cooling (Figure 2). As illustrated in this figure, all phase states experienced by the supercooled MBBA constitute a mixture of conformers with two predominant orientations of C=N-groups in various proportions for different phase. Relative proportions of these conformers being equal for glass and nematic.

It would be incorrect to associate distinctions between metastable and stable phases solely with conformational changes. Investigations of low-frequency RS[1] and reduced spectra of inelastic incoherent neutron scattering[8] have demonstrated that transitions between these two phases are accompanied not only by conformational changes, but also by changes in packing of molecules. It is impossible to explain the transformations of RS occurred under phase transitions from metastable to stable crystal only by changes of twist angles. Thus, for example, it is hard to explain high-frequency shift of the band for ν_e=1192 cm^{-1} (Table 1) at T=253 K, associated with combinations of benzene-ring vibrations [17], in terms of drastic gain in fraction of conformers with θ=44.4^0 (ν_4=1159 cm^{-1}) at a sacrifice in conformers with θ=52^0 (ν_3=1164 cm^{-1}) during phase transition. The matter is that the spacing between the two H-atoms mentioned above decreases with diminution of twist angle under phase transition M-S. Consequently, benzene-ring vibrations become "loosened" and low-frequency shift is to be observed. Taking into account the factors of change in molecular packing could be helpful for interpretation of drastic fall of band intensity at ν=1573 cm^{-1} (Figure 2) in the present phase transition too.

Such a sophisticated treatment of conformational transformation dynamics for MBBA with its structure changing has demonstrated the validity of the hypothesis suggested by Mizuno[7] and the possibility of coexistence for different fractions (glass and supercooled nematic or metastable, stable crystal and crystal routinely obtained in crystallization of nematic, etc.). Depending on sample thermal pre-history (V_{cool}, V_{heat}, annealing time at different temperatures), various fractions in various proportions are obtainable within certain temperature intervals.

CRYSTAL-NEMATIC PHASE TRANSITION

The phase transition from crystal (mixture of metastable and stable crystal) to nematic occurs at T=291 K. This process manifests itself in shift of some of bands towards a high-frequency region and in theirs substantial broadening (Figure 1, 2 and Table 1). The transition is one of type "order-disorder" in which heterogeneous widening is a dominating mechanism of vibrational band forming.

Let us make an effort to correlate the shape of vibrational bands with the structural peculiarities of MBBA in stable crystal state and the dynamics of structural transformations occurring in the course of transition to nematic from stable crystal. Since Vergoten[17] relates the bands of 1573 cm^{-1} and 1625 cm^{-1} to different combinations of benzene ring, then their broadening in stable crystal at T>253 K (Table 1) can be correlated with increase of conformers fractions corresponding to $\theta=44.4^{o}$ and $\theta=82.7^{o}$, causing small low-frequency and high-frequency shifts of these bands in reference to the bands observed for metastable crystal at $\theta=52^{o}$. However, it is not inconceivable that their broadening may be provoked by a change of intermolecular interaction due to another packing of molecules in stable crystal.

The band of ν_b=1594 cm^{-1} is the most sensitive to conformational transformations. Though rather contradictory interpreted[17,19,20], this band is most likely to be related to a certain deformational vibration of benzene ring. Actually, it shifts to low-frequency region at T>251 K (Table 1), what can be related to substantial buildup of conformers fractions with $\theta=44.4^{o}$ (ν_4=1159 cm^{-1}) (Figure 1). Furthermore,. at T>251 K the band of ν_b=1594 cm^{-1} becomes asymmetric on its high-frequency side (Figure 2) due to the presence of conformers with 82.7° and 52° (their in twice smaller than conformers with $\theta=44.4^{o}$). As ν_{CCH} band transformation (Figure 1) the asymmetry grows for the band of ν_b=1594 cm^{-1}. At T=289 K it is already evident that the asymmetry marks the beginning of grows for a new band, just as expected (Figure 2). At T=291 K new band reach maximum of intensity and therefore single symmetric, widened band shifted to high-frequency region is observed experimentally (proportion of conformers with ν=1168 cm^{-1} is practically equal to that with $\nu=1160$ cm^{-1} (Figure 1)). Therefore, the broadening of the band of $\nu_b=1594$ cm^{-1} is correlated not only with transition to more disordered medium (nematic), but also with complex conformational structure of MBBA (overlap of bands connected with the presence of three conformers in nematic phase).

It has been believed previously that only glass has several conformers[13]. This hypothesis has been confirmed by the results of work[21], wherein quasi-elastic scattering in glass has been associated with relaxational transitions between different conformational states of molecules. As evident from Figures 1, 2 , not only glass, but stable crystal and nematic as well comprises a mixture of various conformers. Spectra of glass and nematic are similar . An assumption can be made that packing and conformation of molecules in glass are determined by their packing and conformation in nematic phase. The inheritance of nematic conformation likewise manifests itself in the presence of conformers with $\theta=44.4°$ and $\theta=52°$, typical for nematic phase, in stable and metastable crystal respectively. In addition, the results of work[1] have evidenced the inheritance of nematic packing for these two phases.

SLOW COOLING

Temperature dynamics of spectrograms for cooling and heating cycles and temperature dependence of width of vibrational band 1594 cm^{-1} are presented in Figure 3, 4, 5. As indicated by figures , certain transformations of bands occur at T=203 K. The bands of 1594 cm^{-1} and 1625 cm^{-1} are slightly narrowed in cooling run and widened to the same extent in heating run. Besides, relative proportions of two conformers with $\theta=82.7°$ (1172 cm^{-1}) and $\theta=59°$ (1167 cm^{-1}) change in heating run at T=203 K (Figure 3b), and intensity of band of 1576 cm^{-1} is diminished (Figure 4b). Glass transition is not noted at given temperature as in work[12] (bands are critically narrowed in contradistinction to spectra at T=193 K in Figure 1, 2). This temperature can be interpreted as the one of phase transition between two crystalline states. The conclusion drawn provides support for results obtained in work[8].

The inheritance of nematic conformation and molecular packing is not observed on slow cooling. Essential structural rebuilding is involved in nematic-crystal transition. In fact, the band of 1573 cm^{-1} vanishes on slow cooling, indicating the presence of conformers with the same C=N-group orientation. ν_{CCH} band splitting into 1172 cm^{-1} and 1167 cm^{-1} corresponds to mixture of two conformers with $\theta=82.7^0$ and $\theta=59^0$ (Figure 3). Thus, crystalline phases obtained on slow and on rapid cooling differ not only in molecular packing [8], but in conformations as well. And crystalline phases, turning into each other in reversible manner at T=203 K on slow cooling, are distinguished by proportional relationship between the two conformers having twist angles of 82.7^0 and 59^0 and bearing the same orientation of C=N-group.

On slow cooling hysteresis was noted. So, nematic-crystal transition was observed at T=263 K in cooling run and at T=293 K in heating run (Figure 3, 4, 5). Under phase transition of crystal-nematic large fraction of conformers with $\theta=82.7^0$ (1172 cm^{-1}) and distinguished orientation of C=N- (ν=1576 cm^{-1}) exist in nematic and even in isotropic liquid (spectra at T=328 K in Figure 3,4). Nothing of the kind was noted for shock cooling (see spectra at T=293 K in Figure 1, 2). These conformers were existing during a few days until nematic forgot its thermal pre-history.

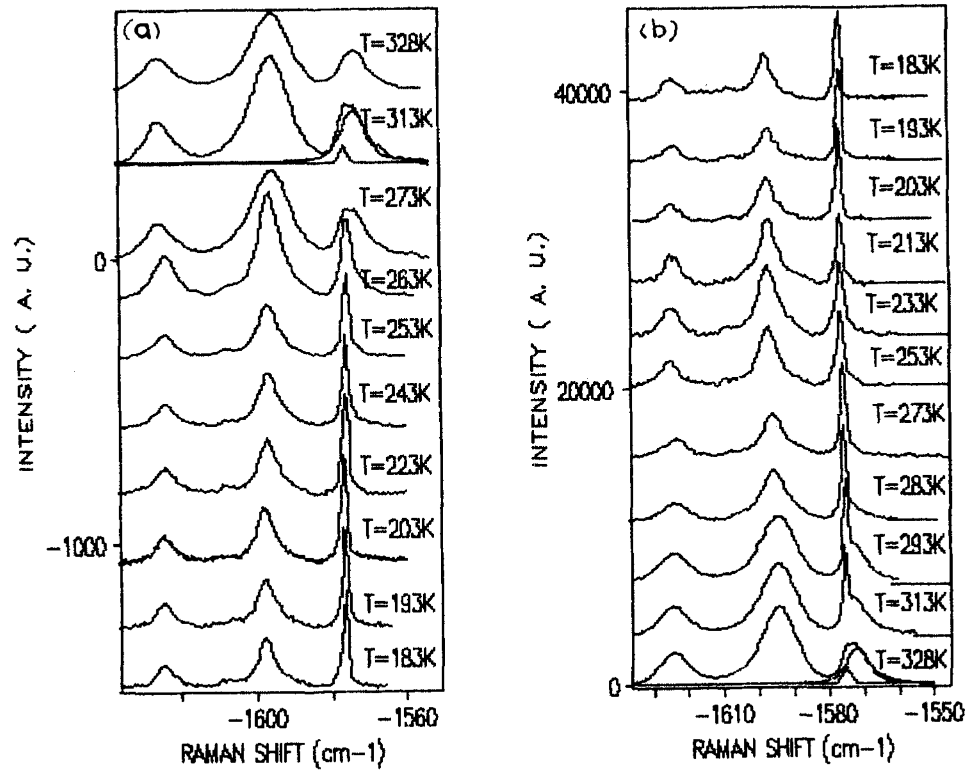

FIGURE 4 The temperature variations of the vibrational bands (1540 cm^{-1}- 1640 cm^{-1}) of MBBA under slow cooling. (a) Cooling cycle (V_{cool}=1.5 K/min). (b) Heating cycle (V_{heat}=2 K/min)

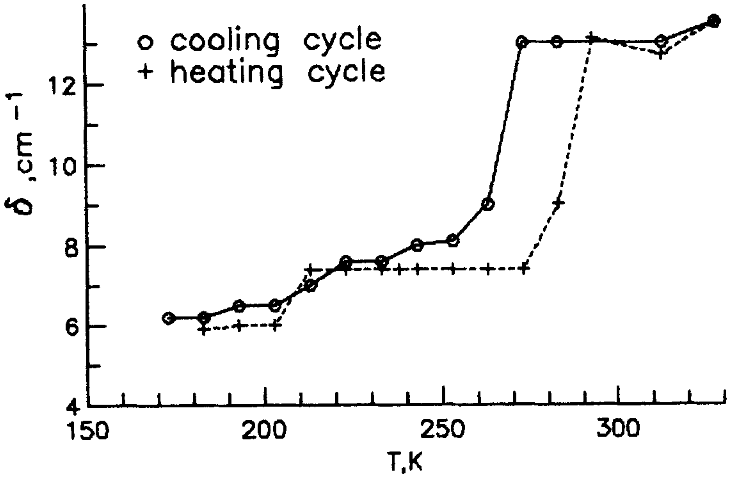

FIGURE 5 Temperature dependence of the width (δ) vibrational band 1594 cm^{-1} of MBBA in cycles of slow cooling and heating.

CONCLUSIONS

Clearly defined correlation between shape parameter (width), vibrational band position in RS and structural transformations taking place on heating slowly and rapidly cooled LC is established. It was found that crystalline phases obtained on slow cooling constitute a mixture of two conformers with $\theta=82.7^{\circ}$, $\theta=59^{\circ}$ and the same orientation of C=N-group and nematic phase comprises a mixture of three conformers, twist angles and proportions of conformers being dependent on sample thermal history (Figure 1, 2 and 3, 4).

We suppose that dominating mechanisms for vibrational band forming (50%) is heterogeneous broadening, connected with disorder in location of centers of mass, and broadening stemming from complex conformational composition for different phases of MBBA.

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