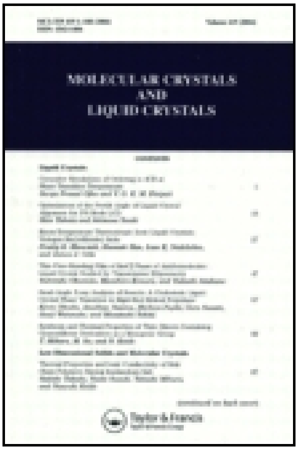


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

# Glassy Phases Formed by Fast Cooling of Mesomorphic Materials

N. Kirov [a] , M. P. Fontana [b] [a] & N. Affanassieva [c] [a]

[a] Institute of Solid State Physics, 72 Boul., Lenin-Sofia, 1184, Bulgaria

[b] Istltuto dl Fistca, Via M. D'Azeglio 85-Parma, Italy

[c] Institute of Spectroscopy, USSR Academy of Sciences, Moscow, USSR

Version of record first published: 13 Dec 2006.

To cite this article: N. Kirov , M. P. Fontana & N. Affanassieva (1982): Glassy Phases Formed by Fast Cooling of Mesomorphic Materials, Molecular Crystals and Liquid Crystals, 89:1-4, 193-215

To link to this article: http://dx.doi.org/10.1080/00268948208074478

*Mol. Cryst. Liq. Cryst.*, 1982, Vol. 89, pp. 193–215
0026-8941/82/8904-0193$06.50/0

# Glassy Phases Formed by Fast Cooling of Mesomorphic Materials

N. KIROV
*Institute of Solid State Physics, 72 Boul. Lenin-Sofia 1184 (Bulgaria)*

M. P. FONTANA
*Istituto di Fisica, Via M. D'Azeglio 85-Parma (Italy)*

*and*

N. AFFANASSIEVA
*Institute of Spectroscopy, USSR Academy of Sciences, Moscow (USSR)*

(*Received January 27, 1982; in final form May 5, 1982*)

Our studies of the phases formed by rapid cooling of mesogenic materials in the nematic and smectic phases are described. More than 40 mesogens were investigated. In many, but not all of the cases, a glassy phase was formed. This was examined with scanning calorimetry and Raman, IR and FIR spectroscopy. All of these techniques support the conclusion that the pattern of molecular disorder in the mesophase is frozen-in when the glass is formed. The relationship between molecular structure and glass-forming ability is discussed. Factors which lead to a large number of molecular conformers (such as terminal alkyl chains) favor glass formation, whereas absence of such factors and the presence of factors such as permanent dipole moments, which encourage molecular ordering, inhibit glass formation.

## INTRODUCTION

The glassy phase of a liquid crystal was first reported for cholesteryl hydrogen phthalate.[1] Later the preparation of a similar glassy state by rapid cooling of *N*-2-hydroxy-4-methoxybenzylideneaniline (2,4 OH MBBA) was described.[2] Recently Kirov *et al.*[3] reported the formation of a vitreous state by quenching the nematic and smectic A phases of azomethine derivatives. The present paper continues these investigations with an emphasis on the relationship between glass-forming tendency and the structure of the mesogen molecules.

The X-ray diffraction patterns of quenched nematic materials indicate that the cooling process actually freezes-in the molecular ordering in the nematic phase. Actually, it appears that, within experimental error the X-ray pattern of a nematic glass is the same as that of the corresponding room temperature nematic material MBBA.[10]

A comparison of the values of the orientational order parameter $S_2$ should provide strong evidence as to whether the resultant glass retains the liquid crystal alignment or not. As shown in our previous paper,[11] the degree of order in the mesophase and in the glassy liquid crystal is the same within experimental error and remains virtually unchanged as the sample is cooled. This indicates that the resultant glassy mesophase has the same alignment as the initial mesophase and demonstrates that, in spite of the thermal shock, the macroscopic alignment continues to operate effectively throughout the whole freezing process.

It is easy to demonstrate visually that the nematic or smectic A materials can be quenched-in by rapid cooling. If a microscope slide carrying a drop of such material is plunged into a bath of liquid nitrogen, held there for a few seconds, and then withdrawn for inspection, it can be seen that the material has a clear glassy appearance.[10]

In what follows, we shall discuss evidence obtained by thermodynamic and spectroscopic measurements of quenched-in glassy and metastable phases, and try to establish a connection with the structure of the corresponding mesogens; the latter is a topic which has not been previously discussed in the literature.

## EXPERIMENTAL

The experimental procedure for quenching the mesophase and the techniques used for the investigation of the vitreous phases formed were described in our previous papers.[3] More than 40 different mesogens were investigated, namely, *para*-substituted azomethines, azo and azoxybenzene derivatives, alkyl- and alkoxy-tolanes and biphenyls, alkoxybenzylideneamino esters of cinnamic, hexanoic, and other organic acids with long alkyl chains, as well as cyclohexanone derivatives. All materials were purified by recrystallization and were dried in a vacuum for 24 hours. The phase transition temperatures agreed well with the best literature data. In all cases the quenching rate was about 15-20 K min$^{-1}$.

## RESULTS AND DISCUSSION

### A. Calorimetric measurements

*Scanning calorimetry* Figure 1 gives as a typical example, the thermograms for *N*-4-ethoxybenzylidene-4-butylaniline (EBBA). Run 1 shows the heating curve of the crystalline material. Two endotherms are observed here; crystal-nematic (309 K) and nematic-isotropic liquid (350 K). Run 2 gives the cooling curve of the isotropic phase at a rate of about 15-20 K min$^{-1}$. The transition from isotropic liquid to the nematic liquid is observed at almost the same temperature as upon heating (even with cooling as fast as 50 K min$^{-1}$). However the nematic phase is easily supercooled and when the freezing rate is greater than 10 K min$^{-1}$, the nematic-crystalline solid phase transition does not

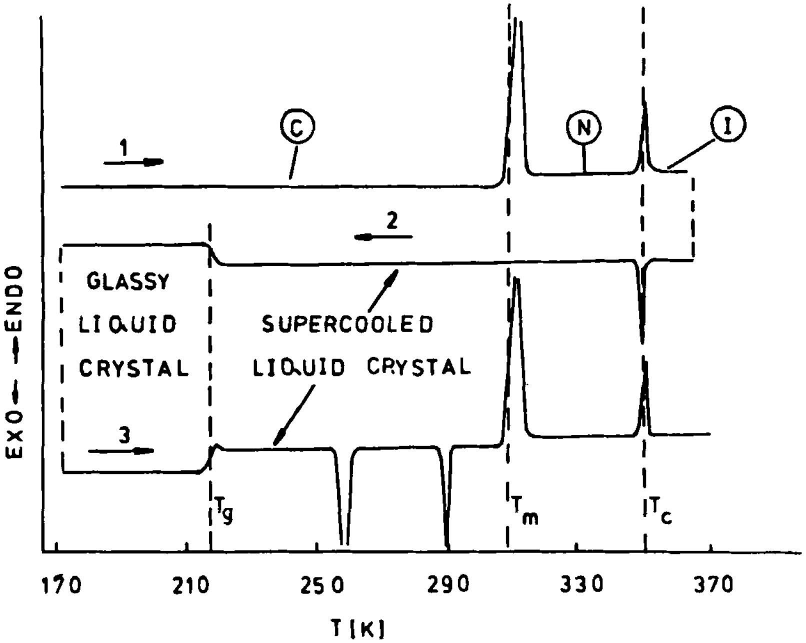


FIGURE 1 Thermograms of *N*-4-ethoxybenzylidene-4-butylaniline (EBBA); Run 1—2.5 K min$^{-1}$ (heating); Run 2—15-20 K min$^{-1}$ (quenching); Run 3—2.5 K min$^{-1}$ (heating); C—crystal phase, N—nematic phase, I—isotropic liquid.

occur. Upon further cooling the heat capacity curve shows an anomalous jump similar to that associated with a glass transition. No appreciable thermal effects were observed on further cooling down to 80 K. The glass transition usually occurs within a narrow temperature range centered on an approximate characteristic temperature known as the "glass transition temperature $T_g$". The glassy phase is stable for at least several days if it is kept at liquid nitrogen temperature. Run 3 shows a heating curve of the vitreous state at a rate of 2.5 K $\text{min}^{-1}$. A glass transition phenomenon is observed at $T_g = 219$ K. On further heating, the supercooled nematic liquid crystal is transformed into another solid phase by a broad exothermic transition. Since this phase is not a glassy one but an intermediate metastable crystalline solid we shall not discuss its structure here but the reader is referred to our previous paper[3] and the literature quoted therein. The thermograms of the other EBBA derivatives show slight changes in the transition temperatures but are otherwise similar. A linear relationship between $T_g$ and the molecular weight $M$ is observed for the homologous series of *N*-4-alkoxybenzylidene-4-alkylanilines (Figure 2).

Figure 3 shows the heating and cooling thermograms of *N*-4-pentoxybenzylidene-4-chloraniline for a similar heating, cooling, heating sequence. Three endotherms are observed upon heating the crystal phase. (Run 1)—crystal phase–smectic B ($S_B$) (332 K), smectic B–smectic

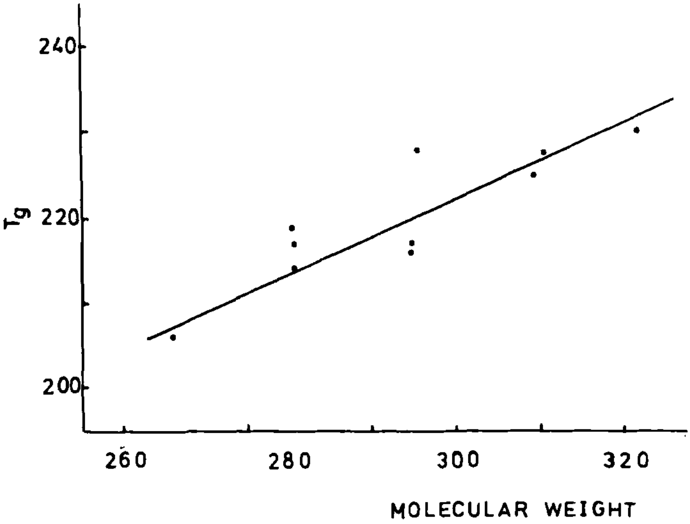


FIGURE 2 Glass transition temperature $T_g$ as a function of molecular weight $M$ for all investigated *N*-4-alkoxybenzylidene-4-alkylanilines.

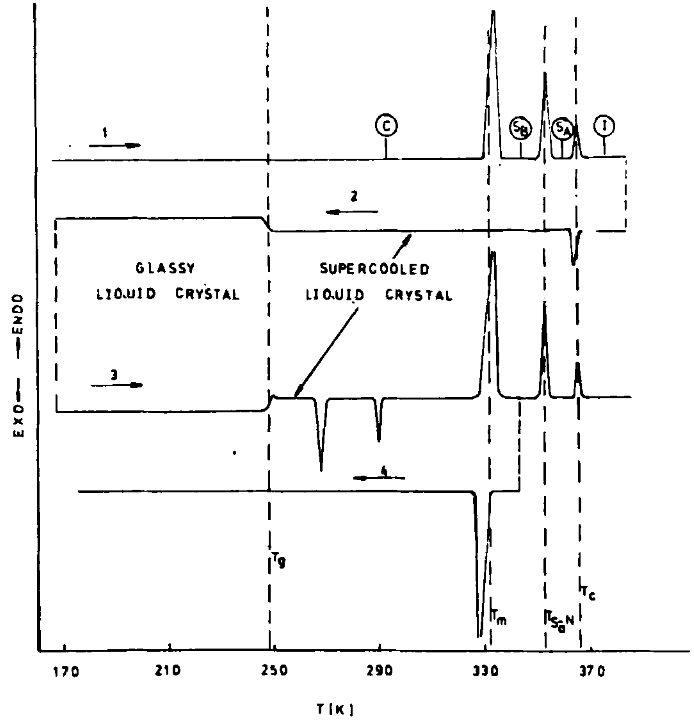


FIGURE 3 Thermograms of *N*-4-pentoxybenzylidene-4-chloraniline; Run 1—2.5 K $\mathrm{min}^{-1}$ (heating); Run 2—20 K $\mathrm{min}^{-1}$ (quenching initiated from isotropic liquid); Run 3—2.5 K $\mathrm{min}^{-1}$ (heating); Run 4—15-20 K $\mathrm{min}^{-1}$ (quenching initiated from smectic B phase); C—crystal phase, $S_{\rm B}$—smectic B phase, $S_{\rm A}$—smectic A phase, I—isotropic liquid.

A ($S_{\rm A}$) (353 K), and the last one—smectic A-isotropic liquid (366 K). Run 2 represents the cooling curve of the isotropic phase. As in the case of EBBA and its homologues, the phase transition isotropic liquid-$S_{\rm A}$ takes place reproducibly at almost the same temperature as upon heating (even for cooling rates as fast as 50 K $\mathrm{min}^{-1}$). The next phase transitions $S_{\rm B}$-$S_{\rm A}$ and $S_{\rm B}$-crystal phase do not occur and the smectic A phase is supercooled. Upon further cooling it is quenched to give a glass. As with the nematic liquid crystals, this glassy phase is stable for long periods of time at liquid nitrogen temperature. At higher temperatures, its lifetime decreases and the transition from the vitreous state to the supercooled $S_{\rm A}$ is observed at 248 K (Run 3).

On further heating, the supercooled $S_{\rm A}$ liquid crystal is transformed by broad exothermic transitions *via* an intermediate metastable solid state[3] into the stable crystal which does not change any more. Thermograms of the same form—with only the temperatures of the phase transitions slightly different—are observed for the butyl and hexyl homologues where the $S_A$ phase is also supercooled and gives a glass. However, quenching the smectic B phase even with the highest possible rate of cooling (~50 K min$^{-1}$) does not yield a glassy phase. This result can be explained in terms of the different structures of the three mesomorphic phases. The only structural restriction in the classical nematic state is that the long axes of the molecules maintain a parallel or nearly parallel orientation. The molecules are mobile in three dimensions and can rotate around their long axes. The quenching process preserves this structure and produces a metastable glassy phase. Smectic A contains unstructured layers; abrupt cooling of this mesophase preserves the existing disorder and forms a metastable vitreous state. The smectic B, however, is different. This structured smectic liquid crystal has long range order of the molecules in the layers. The X-ray investigations indicate that $S_B$ is more ordered than $S_A$ and is closer to the ordinary solid crystal. Hence rapid cooling of this phase produces a crystalline solid rather than a glassy state.

Other groups of compounds, e.g., 4-substituted alkyl and alkoxy tolanes and biphenyls, 4-nitrophenyl 4-*n*-alkoxybenzoates, etc. show a

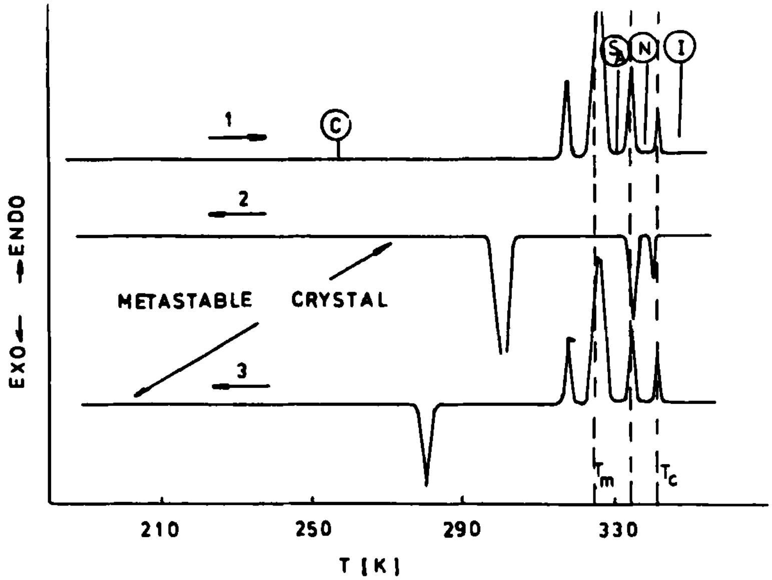


FIGURE 4 Thermograms of 4-nitrophenyl 4-*n*-octyloxybenzoate (NPOOB); Run 1—2.5 K min$^{-1}$ (heating); Run 2—15-20 K min$^{-1}$ (quenching); Run 3—2.5 K min$^{-1}$ (heating); C—crystal phase, $S_A$—smectic A phase, N—nematic phase, I—isotropic liquid.

different pattern of thermal behavior. For these, even cooling rates of up to 50 K $min^{-1}$ cannot produce a vitreous state. The stable crystal phase of 4-nitrophenyl 4-*n*-octyloxybenzoate (NPOOB) undergoes a phase transition at 318 K to give a new solid phase which melts at 324 K to give an $S_A$ phase (Figure 4). The next phase transformation to the nematic phase takes place at 335 K, and the clearing temperature $T_c$ is a little higher, namely 341 K. On cooling (Run 2) the nematic phases and smectic phases are restored at almost the same temperatures as upon heating, while the phase transition from $S_A$ into the solid phase is observed at about 30 degrees lower. No glass transition has been observed on further cooling down to 120 K. The solid phase formed upon cooling of the melt of NPOOB is also stable if it is kept at liquid nitrogen temperatures. At higher temperatures, its life-time decreases, being 15 hours at 203 K, 10 hours at 267 K and 1 hour at 260 K. At about 275 K the metastable phase passes directly into the stable crystal phase identical to that obtained by slow crystallization from the melt, with a broad, slow exothermic transition.

## RESIDUAL ENTROPY AND ENTHALPY VALUES

The most important thermodynamic properties of the glassy metastable phase are the residual entropy and enthalpy at 0 K. These are a measure of the configurational disorder. The residual entropy of the glassy state formed by 2,4-OH MBBA is reported to be $S_0$ (vit.) = 12.69 ± 0.16 $JK^{-1}$ $mol^{-1}$. The difference at 0 K between the enthalpy of the vitreous state $H_0$ vit and that of the perfectly ordered crystalline solid $H_0^0$cryst. is equal to 11.38 ± 0.04 KJ $mol^{-1}$.[2] From this and other thermodynamic data for glassy liquids and glassy crystals,[4] Sorai and Seki[2] proposed the term "glassy liquid crystal". Using the same procedure, we found that for some Schiff derivatives $H_0$–$H_0^0$ lies between 10.10 and 13.30 KJ $mol^{-1}$, e.g. 10.61 ± 0.08 (*N*-4-pentoxybenzylidene-4-chloraniline), 10.25 (*N*-4-hexoxybenzylidene-4-chloraniline), 11.03 ± 0.09 (MBBA), and 11.50 ± 0.09 (EBBA) KJ $mol^{-1}$. Further entropy and enthalpy data as well as other thermodynamic functions for different mesomorphic materials will be published separately. These results are close to Sorai and Seki's data, and we could therefore identify the metastable phase formed by rapid cooling of the azomethine mesomorphases as a glassy liquid crystalline state.

### B. Vibrational spectroscopy

Further justification for describing the solid phase formed by quenching the mesophase as a vitreous mesophase arises from the following spectroscopic and optical measurements:

i) The strong similarity between the glassy liquid crystal and the liquid crystal phase is indicated by the similarity of the frequencies of almost all bands (with a few exceptions mostly below 250 $cm^{-1}$). In fact, the low frequency Raman spectra of EBBA (Figure 5), the overall IR spectra in the region 700–1700 $cm^{-1}$(Figure 6) and the Raman spectra between 400 and 1750 $cm^{-1}$ of EBBA (Figure 7) indicate that the glassy phase is structurally very close to that of the original mesophase. In the stable solid the bands corresponding to carbon–carbon and polymethylene chain vibrations are sharp, as is typical for high purity crystals. In the vitreous state the bands assigned to the vibration of the polymethylene chain —$CH_2$ scissoring, around 1450 $cm^{-1}$, wagging and twisting modes between 1350 $cm^{-1}$ and 1200 $cm^{-1}$, carbon–carbon stretch (1050–850 $cm^{-1}$) broaden and some of them even merge. The region 2700–3000 $cm^{-1}$ where $CH_2$ and $CH_2$ symmetric and asymmetric stretching appear is also very typical. The well defined bands of the stable crystalline solid are replaced by a broad band with ill defined

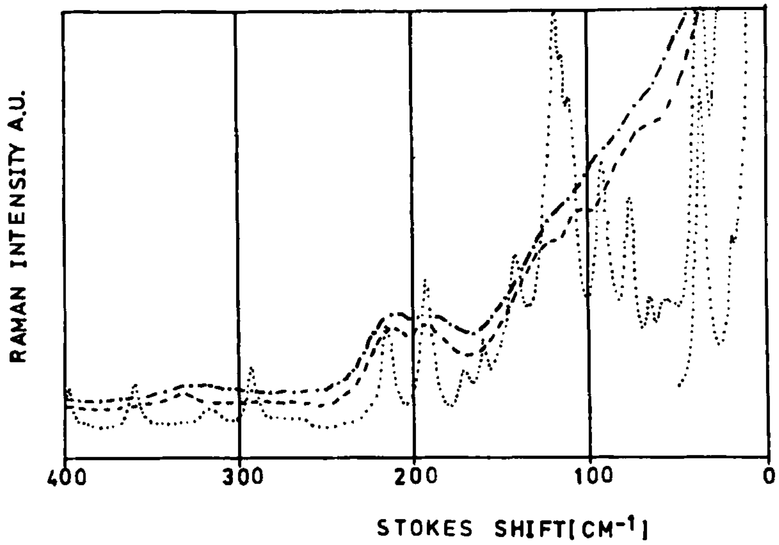


FIGURE 5 Low frequency Raman spectra of EBBA; dotted line—stable crystal phase (90 K); alternate dash-dotted line—nematic phase (310 K); dashed line—glassy phase (90 K).

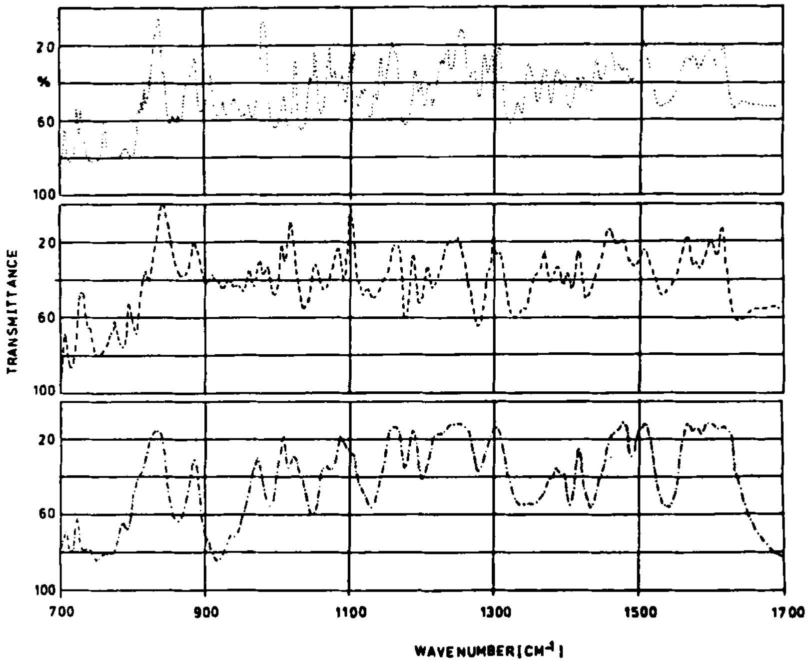
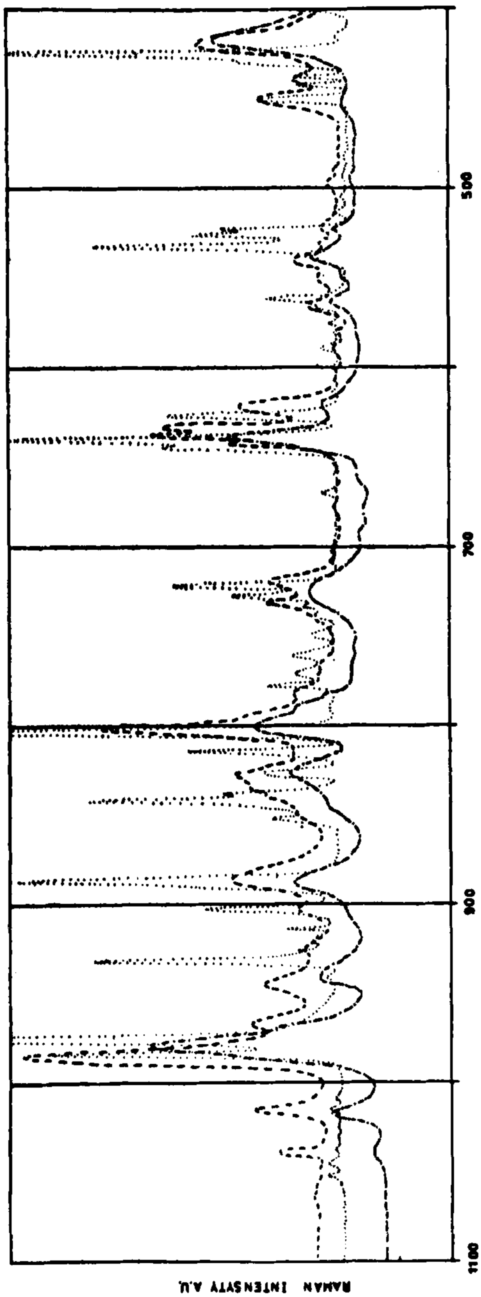


FIGURE 6 IR spectra of $P_5BCA$; dotted line—stable crystal phase (90 K); alternate dash dotted line—$S_A$ phase (360 K); dashed line—glassy phase (90 K).

shoulder.[5] In our opinion this is due to the additional rotational isomeric forms of the alkyl and alkoxy chain which occur in the mesophase and are frozen-in as the metastable glassy phase is formed. However, the structure of the glassy liquid crystalline phase is more complicated and probably the differences in the molecular core structure between the vitreous mesophase on the one band and the stable crystal on the other may be also responsible for the formation of the glassy phase. In fact, Traetteberg *et al.*[5] have demonstrated that, for the most stable conformer in the gas state of benzylideneaniline (BA), the phenyl ring bonded to the carbon end of the C═N bridge is coplanar with this bond, while the other phenyl ring is extensively rotated (52° approximately) about the *N*-link. X-ray structure determination of BA and some of its derivatives in the crystalline state verified that the aniline ring is twisted out of the C—N═C—C plane by amounts varying from 41° to 55° and that the benzal part also lies out of the plane with a smaller, and opposite, twist of 8–14°.[6] BA, therefore, can exhibit some deformations around N—$\phi$ and C—$\phi$ bonds.[7] If the N—$\phi$ dihedral angle is taken as 51°, the 90° degree barrier ΔE (min. → 90°) is very


500
700
900
1100
RAMAN INTENSYTY A.U.

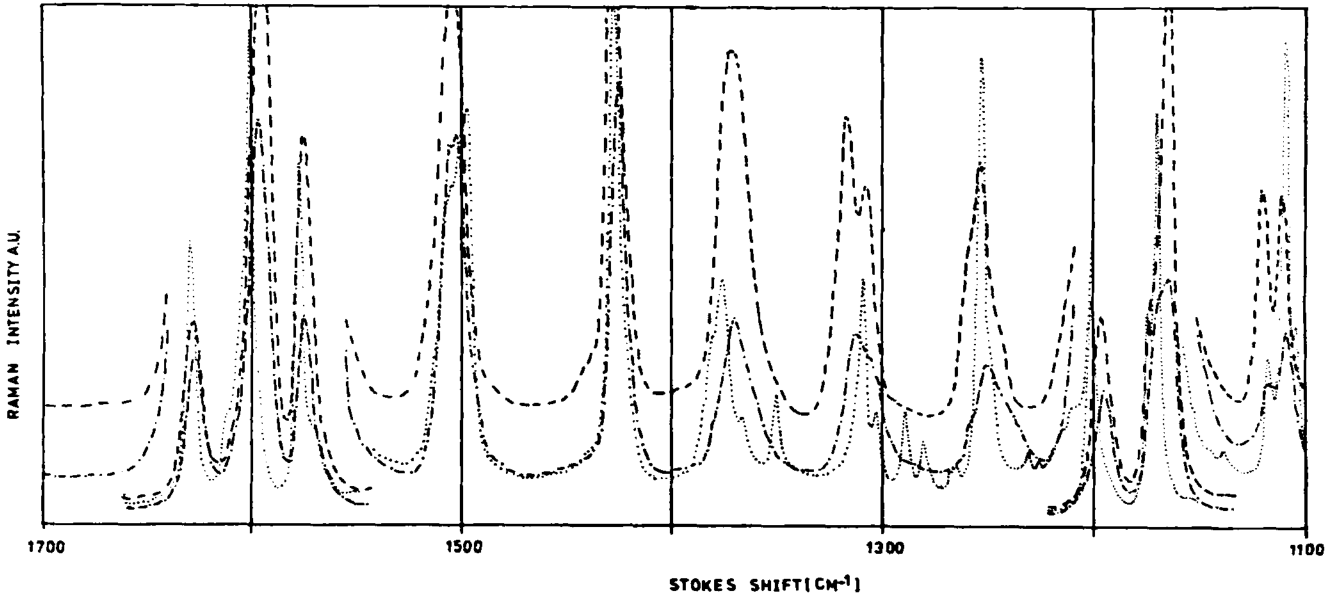


FIGURE 7 Raman spectra of EBBA; dotted line—stable crystal phase (90 K); alternate dash-dotted line—nematic phase (310 K); dashed line—glassy phase (90 K). A. 400–1100 cm$^{-1}$ region; B. 1100–1700 cm$^{-1}$.

small, namely 0.6 kcal $mol^{-1}$. In general, energies in the range 0.5–1.0 kcal $mol^{-1}$ are needed to obtain the less favorable planar form from the twisted one in the solid state. Hence, even moderate temperatures can easily create conformers with different positions of both phenyl rings with respect to the central CH═N bridge. X-ray studies[8] indicate also that in the metastable phase formed by cooling the isotropic liquid of 4-chlorobenzylidene-4′-chloraniline the two benzene rings are coplanar, whereas in the crystalline solid one is tilted toward the other. It is consequently possible that different conformers exist in the mesophase (in addition to the various rotational isomers of the end alkyl and alkoxy groups) and can be frozen-in as the glassy phase is formed. In fact the Raman bands assigned to stretching and bending vibrations of the benzene ring and CH═N bridge, e.g. 1628 $cm^{-1}$ [CH═N stretching, $\phi$—N stretching + S(8)], 1575 $cm^{-1}$ (S(8) + S(9) + S(7) + CH═N stretching), 1370 $cm^{-1}$ [S(9) + $\phi$—N stretching), 1164 and 1182 $cm^{-1}$ ($\phi$—N bending + S(9) + S(8)] have different frequencies, half-widths, shapes and are often split in the glassy phases (Figure 7). In the IR spectra, however, these changes are not very pronounced (Figure 6). Unfortunately, the information which we can derive from the Raman spectra of the polymorphic modifications is not sufficient for precise determination of the benzene ring position. Obviously, more X-ray data are needed to clarify the structure of the vitreous solid modifications formed by liquid crystalline materials.

ii) The half-width $\delta$ of the bands of the glassy phase is about two-three times bigger than that of the stable crystal if both are at liquid nitrogen temperature and is close to that of the mesomorphic state. For example $\delta$ of the EBBA Raman bands 1028, 1537 and 1575 $cm^{-1}$ is 11, 8 and 9 $cm^{-1}$ respectively for the glassy mesophase and only 5, 3 and 4 $cm^{-1}$ for the stable crystalline solid. Similar results are obtained for all other IR and Raman vibrational bands. The most drastic changes are those in the low frequency region where the band at 220 $cm^{-1}$, from the Raman spectrum of EBBA, has a half-width of 24 $cm^{-1}$ for the vitreous liquid crystalline state while the corresponding value for the crystal phase is only 9 $cm^{-1}$. This asymmetric line broadening confirms the aforementioned conclusion that many different conformers are present in the glassy phase.

Let us see now what vibrational spectroscopy can tell us about the structure of the polymorphs formed by biphenyl, tolane and alkoxybenzoate derivatives. As we already mentioned, no glass transition was observed on quenching the mesophases of these materials. Indeed, looking at Figure 8, where we report, as an example, the low-frequency Raman spectra of the stable and metastable solid modifications of NPOOB and for comparison the spectrum of smectic A, considerable differences between the two solid forms are seen. Again, as in the case of MBBA, EBBA and other *para*-substituted Schiff bases, the most ordered phase is the stable crystal modification—all peaks are sharp and the Rayleigh wing is very weak. However, the metastable phase formed by NPOOB is not a glass. Actually, it shows a well-defined low frequency Raman spectrum, deformed by a more intensive Rayleigh wing. This indicates that only a partial disorder affects the selection rules. The same results are obtained for the alkoxytolanes and cyanobiphenyls.

In the higher frequency region (Figure 9), many bands assigned to alkyl chain vibrations, benzene ring and CO stretch vibrations in the metastable solid modification are split into doublets. The half-widths $\delta$ of the bands from the metastable phase are bigger than in the stable crystal state. This is to be expected since the change from an oscillator in a perfectly ordered environment to one which is in a disordered state should be accompanied by a broadening of the band. This results from superposition of overlapping bands, shifted from the frequency of the unperturbed oscillator. However the differences between these two solid forms are not so drastic as in the case of the glassy liquid crystal.

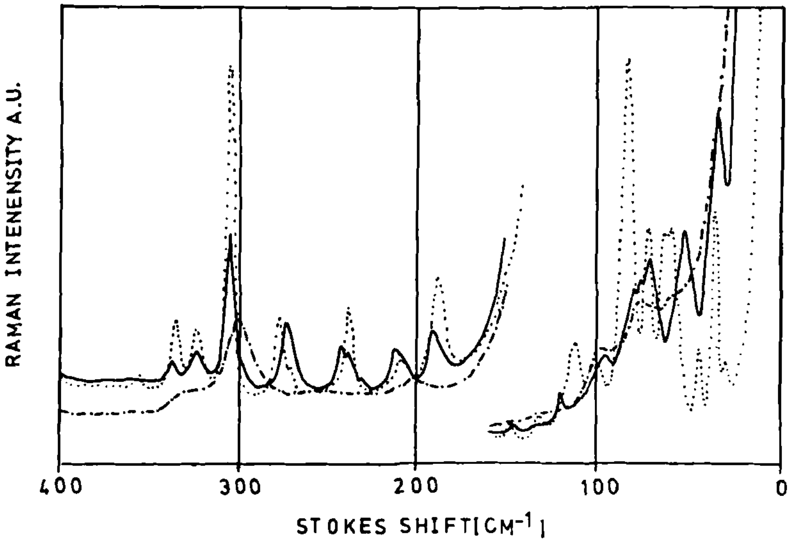
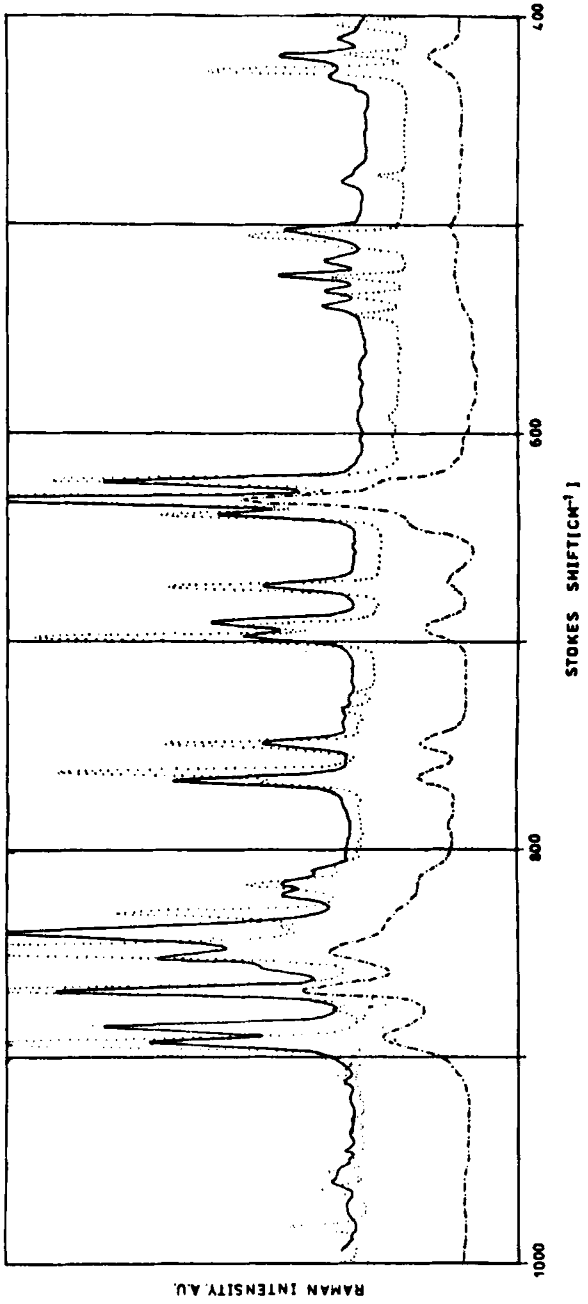


FIGURE 8 Low frequency Raman spectra of NPOOB; dotted line—stable crystal phase (90 K); alternate dash-dotted line—$S_A$ phase (330 K); full line—metastable crystal phase (90 K).


400
600
800
1000
STOKES SHIFT(CM$^{-1}$)
RAMAN INTENSITY A.U.

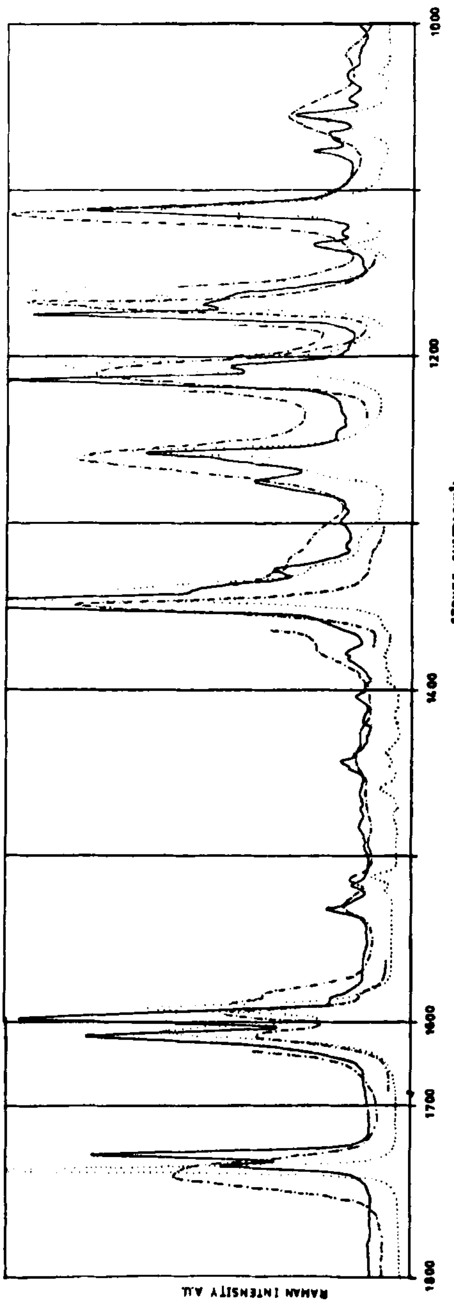


FIGURE 9 Raman spectra of NPOOB; dotted line stable crystal phase (90 K); alternate dash-dotted line—$S_A$ phase (330 K); full line—metastable crystal phase (90 K); A. 400–110 cm$^{-1}$ region; B. 1100–1700 cm$^{-1}$ region.

In general, most of the bands in the metastable crystal solid are broader by only 1–2 $cm^{-1}$, while in the glassy liquid crystal phase all modes are two–three times wider than those in the stable crystal and have values for $\delta$ close to those of the mesophase. All these results indicate that the metastable phases formed by tolane, biphenyl and alkoxybenzoate derivatives are unstable crystal modifications which contain a mixture of two different relatively rigid conformers.

It would be interesting to find a correlation between molecular structure and the glass-forming tendency. With this in mind we investigated the thermal behavior of different liquid crystalline materials as well as some similar non mesogenic compounds. The results are summarized in Table I. It has to be emphasized here that all these results are obtained with cooling rates of 15–20 K $min^{-1}$. The reader will notice first that all compounds with comparatively large dipole moments, namely cyanobiphenyls, azoxybenzenes and nitrophenyl alkoxybenzoates do not form a glassy phase. Some of them, e.g. 4-nitrophenyl 4-*n*-alkoxybenzoates, alkyl and alkoxy tolanes and cyanobiphenyls with longer alkyl chains form only different metastable crystalline phases whose structure will be a subject of separate investigation. The formation of crystalline polymorphs upon cooling of some of the 4-cyano-4′-alkoxybiphenyls has been also reported by Gray *et al.*[12] Recently Bulkin[13] has shown that 4-cyano-4′octyloxybiphenyl forms a metastable crystalline phase having an appreciably lower melting point.

Benzylideneaniline itself does not form any glassy phase and *N*-4-methoxybenzylidene-4′-propylaniline is the first derivative capable of forming a glassy nematic liquid crystal. The higher members of this homologous series give metastable glassy states readily. A vitreous mesophase is also formed by chlorine derivatives of alkyl substituted anils as well as by alkoxybenzylideneamino esters of cinnamic, hexanoic, heptanoic and other organic acids with long alkyl chains. The reader will notice also that even 4-octyloxy-4′-ethoxytolane and 4-cyano-4′-decyloxybiphenyl (i.e., the tolane and biphenyl derivatives with the longest alkyl chain studied by us so far) do not form any glassy phases.

### C. Glass forming tendency and molecular structure

The connection between the glass-forming tendency and molecular structure is closely related to the problem of whether or not a liquid crystal will crystallize before undergoing a glass transition. This will be determined by the rate at which the mesomorphic material is cooled and by the crystallization rate constants. The larger these constants,

## TABLE I

Correlation between glass-forming tendency and molecular constitution of some mesomorphic materials.

| Substance | Formation of Glassy Mesophase |
|---|---|
| 4,4'-dimethoxyazoxybenzene | no |
| 4,4'diethoxyazoxybenzene | no |
| 4,4'-dipropoxyazoxybenzene | no |
| 4,4'-dibutoxyazoxybenzene | no |
| 4,4'-dipentoxyazoxybenzene | no |
| 4,4'-dihexoxyazoxybenzene | no |
| 4-cyano-4'-pentylbiphenyl | no |
| 4-cyano-4'-heptylbiphenyl | no |
| 4-cyano-4'-octylbiphenyl | no |
| 4-cyano-4'-pentoxybiphenyl | no |
| 4-cyano-4'-hexoxybiphenyl | no |
| 4-cyano-4'-heptoxybiphenyl | no |
| 4-cyano-4'-octyloxybiphenyl | no |
| 4-cyano-4'-decyloxybiphenyl | no |
| 4-butyl-4'methoxytolane | no |
| 4-pentyl-4'-methoxytolane | no |
| 4-heptyl-4'-methoxytolane | no |
| 4-pentyl-4'-ethoxytolane | no |
| 4-hexyl-4'-ethoxytolane | no |
| 4-heptyl-4'-ethoxytolane | no |
| 4-octyl-4'-ethoxytolane | no |
| *N*-4-methoxybenzylidene-4-butylaniline | yes |
| *N*-4-ethoxybenzylidene-4-butylaniline | yes |
| *N*-4-propoxybenzilidene-4-butylaniline | yes |
| *N*-4-butoxybenzylidene-4-butylaniline | yes |
| *N*-4-pentoxybenzylidene-4-butylaniline | yes |
| *N*-4-hexoxybenzylidene-4-butylaniline | yes |
| *N*-4-propoxybenzylidene-4-propylaniline | yes |
| *N*-4-butoxybenzylidene-4-chloraniline | yes |
| *N*-4-penthoxybenzylidene-4-chloraniline | yes |
| *N*-4-hexoxybenzylidene-4-chloraniline | yes |
| *N*-4ébutoxybenzylidene-4-propylaniline | yes |
| *N*-4-ethoxybenzylidene-4-cyanoaniline | no |
| *N*-4-butoxybenzylidene-4-cyanoaniline | no |
| *N*-4-hexoxybenzylidene-4-cyanoaniline | no |
| 4-nitrophenyl 4-*n*-octyloxybenzoate | no |
| ethyl 4-ethoxybenzylidene-4'-aminocinnamate | yes |
| *n*-propyl 4-*n*-octylbenzylidene-4'-aminocinnamate | yes |
| *N*-4-ethoxybenzylideneaminophenyl hexanoate | yes |
| *N*-4-ethoxybenzylideneaminophenyl heptanoate | yes |
| *N*-4-ethoxybenzylideneaminophenyl octanoate | yes |
| 4-butyl-4'-methoxyazoxybenzene | no |
| diethyl 4,4'-azoxydibenzoate | no |
| 2,6-bis(4-*n*-butoxybenzylidene)-cylohexanone | yes |

Typical cooling rate: 15 ÷ 20°K min$^{-1}$

the more rapidly the liquid crystal has to be cooled in order to form a glass.

The crystallization of a liquid crystal or a pure liquid appears to be a process of nucleation and growth. That is, small crystals form and grow into the supercooled liquid crystal phase. All growth occurs at the mesophase–crystal interface. Thus, two parameters are involved in this process: the frequency of nucleation of crystals per unit volume $Y$ and the velocity $U$ of their growth. With the knowledge of $Y$ and $U$ one should be able to estimate the conditions for glass formation or crystallization.

According to classical nucleation theory, the steady state frequency of homogeneous nucleation (i.e. nucleation unassisted by existing interfaces) of crystals in liquids or liquid crystals should be given by:[14]

$$Y = \frac{m_v D'}{a_v^2} \exp\left(-\frac{W*}{kT}\right) \tag{1}$$

Here $m_v$ is the number of liquid crystalline molecules per unit volume; $a_0$ is the molecular diameter. $D'$ is a rate constant, having dimensions of a diffusion coefficient which governs the transport of the molecules across the liquid–nucleus interface and $W*$ is the thermodynamic barrier to nucleation originating from the work necessary to form the crystal–liquid crystal interface. For spherical nuclei

$$W* = \frac{16\pi\sigma^3}{3(\Delta G_v)^2} \tag{2}$$

where $\sigma$ is a parameter which in classical theory is identified with the liquid crystal surface tension and the free energy change per volume accompanying crystallization, $\Delta G_v$, is related to the entropy of the crystallization $\Delta S_v$ and the temperature interval of undercooling $\Delta T$ according to $\Delta G_v = \Delta S_v \Delta T$.

Because of the complications arising from the evolution of heat during crystallization, it is often difficult to interpret the phenomenon of growth of finite crystals in supercooled one component isotropic liquid or liquid crystal phases. There is therefore great uncertainty concerning the mechanism of this process. Nevertheless, for present purposes the crystal growth rate can be expressed as follows:[14]

$$U = f \frac{D''}{a_0} [1 - \exp(\theta \Delta G_v / kT)] \tag{3}$$

Here $f$ is the fraction of crystal surface sites to which molecules can be attached, $\nu$ is the molecular volume, and $D''$ is the rate constant again having the dimension of a diffusion constant which governs the transport of the molecules across the liquid crystal interface. Supposing that the rate constant $D''$ in Eq. 3 can be identified by the self-diffusion constant of the liquid or liquid crystal $D$,[14] the crystal growth velocity can be related to fluidity $\varphi$ (reciprocal viscosity) by putting in place of $D$, the expression given by the self-diffusion–fluidity equation:[15,16]

$$\varphi = \frac{4D\nu}{r^2 kT} \tag{4}$$

where $\nu$ is again the molecular volume and $r$ is the radius, thus

$$U = \frac{fkT\varphi}{3\pi a_\nu^2}\left[1 - \exp(\nu\Delta G_\nu/kT)\right] \tag{5}$$

i.e., the crystal growth rate decreases as viscosity increases and, as a result, vitrification becomes easier. Equation (5) explains the observed linear dependence of $T_g$ on molecular weight for the homologous series of *N*-4-alkoxybenzylidene-4′-alkylaniline (Figure 2): indeed such a correlation has long been known to exist for simple molecular liquids,[17] but is reported here for the first time for mesomorphic materials.

According to the formal theory outlined here, the important parameters which govern the formation of glassy phases are $\sigma$, $\Delta f_\nu$, $D'$, $D''$ and $A_s$,[19] $A_s$ being the specific area of nucleating heterogeneties. For liquids free of foreign surfaces we are not concerned with $f(\nu)$ or $A_s$. Our knowledge of the liquid crystal–crystal interfacial tension $\sigma$, of $D'$, $D'$ and of the active site fraction $f$ is very limited. Nevertheless, the following rule can be useful in this case:[14] at a given level of cohesive energy, the greater the glass forming tendency of a substance in a particular class, the less the ratio $\Delta U_m/\Delta S_m$ where $\Delta U_m$ and $\Delta S_m$ are respectively, the energy and entropy of crystallization at low pressure. This generalization can be restated as follows: the greater the glass-forming tendency of a substance in a particular class, the less the energy, at constant cohesive energy, necessary to produce a given amount of disorder. With this generalization the effect of molecular constitution on a glass forming tendency can be at least partially understood.

In the liquid crystalline and isotropic liquid phases formed by Schiff base derivatives, the two benzene rings can rotate with respect to the central bridge overcoming a low potential barrier—only 0.5–1.0 kcal $\text{mol}^{-1}$—thus creating a mixture of conformers at higher temperatures. Benzylideneaniline, however, does not form any glass phase, but its homologue MBBA forms a vitreous state. Obviously, the attachment of an alkyl chain with its different rotational isomers combined with the flexible central molecular part produces a large amount of disorder at the cost of relatively little energy. Two additional pieces of evidence can be cited here to support this assertion:

i) alkyl and alkoxy substituted tolanes even with the longest alkyl chain studied (4-*n*-octyloxy 4′-ethoxytolane) do not form any glassy modification. In fact the carbon–carbon triple bond constitutes a group which possesses rigidity and keeps the molecular linearity, thus preventing the formation of any different conformers of the molecular cores which could be frozen into the metastable vitreous state.

ii) It was found that molecular asymmetry increases the glass forming tendency of simple organic substances since it increases the entropy of the system.[14]

Mesogens with a strong dipole moment, e.g., alkoxyazoxybenzenes, nitrobenzoates, cyanobiphenyls and alkoxybenzylidene cyanoanilines do not form any glass phases. One of the reasons is probably the lack of conformers formed by these components. The alkyl chain is not long enough to create sufficient disorder and the entropy of the mesomorphic phase is very low. Hence, according to Eq. (5) nucleation will readily occur and a crystalline solid will be formed. The strong dipole moment undoubtedly leads to appreciable dipole–dipole interactions, resulting in substantial decreasing of the relaxation times for molecular reorientation during crystallization. In fact, a strong molecular association in other nitrile group-containing molecules, due to the intense dipole moment of the C—N bond ($CH_3CN$ for example) is well known.[18] This indicates that the kinetic barrier to crystal growth will be lower than that for glass formation. In order to obtain glassy modifications from these materials, either the quenching rate has to be increased by one–two orders, or the molecules have to be elongated sufficiently. It is not easy, however, to decrease the molecular reorientation time by a few orders of magnitude—alkoxyazoxybenzenes and cyanobiphenyls with hundreds of carbon atoms would have to be synthesized. It is easier to increase the cooling rate by a few orders of magnitude when the materials are condensed from the vapour on a cold substrate. In this way for example water, which is a very bad glass-former, can be vitrified.[19] It has to be pointed out here that contaminants favor the formation of the glassy mesophase by decreasing the energy differences between supercooled mesophases and the crystal phase.

## FACTORS DETERMINING THE GLASS-FORMING PROPERTIES OF MESOGENS

All results reported here allow us to formulate the following generalizations for the influence of molecular factors on the $T_g$ values and on glass-forming tendency.

i) Mesomorphic materials with stiff chain backbones and rigidly held bulky side groups do not form any glassy phases or indicate a reluctance to do so by having high $T_g$ values.

ii) Molecules with strong dipole moments, e.g. alkoxybenzylidene cyanoanilines, alkoxyazoxybenzenes and cyanobiphenyls do not form a glassy state upon quenching. This is due to the strong dipole–dipole interactions which tend to restrict the molecular motion and as a result, inhibit the formation of the partially ordered state of the glassy phase.

iii) Conversely, mesogen molecules with loosely held, dangling end groups which tend to loosen the molecular structure will exhibit a low $T_g$.

iv) For a wide variety of mesomorphic materials, the ratio $T_g/T_m$ (where $T_m$ is the melting temperature) generally falls between 0.60 and 0.75 if the temperatures compared are in °Kelvin (Table II). This is not surprising, since structural properties affecting $T_m$ are similar to those affecting $T_g$. The same result is reported also for glassification of

TABLE II

The ratio $T_g/T_m$

| Substance | $T_m$ | $T_g$ | $T_g/T_m$ |
|---|---|---|---|
| *N*-4-methoxybenzylidene-4-butylaniline (MBBA) | 293 | 206 | 0.70 |
| *N*-4-ethoxybenzylidene-4-butylaniline (EBBA) | 309 | 219 | 0.71 |
| *N*-4-propoxybenzylidene-4-butylaniline (P$_3$BBA) | 313 | 220 | 0.69 |
| *N*-4-butoxybenzylidene-4-butylaniline (BBBA) | 315 | 225 | 0.71 |
| *N*-4-pentoxybenzylidene-4-butylaniline (P$_5$BBA) | 319 | 230 | 0.72 |
| *N*-4-propoxybenzylidene-4-pentylaniline (P$_3$BPA) | 307 | 217 | 0.71 |
| *N*-4-butoxybenzylidene-4-chloraniline (BBCA) | 358 | 218 | 0.60 |
| *N*-4-pentoxybenzylidene-4-chloraniline (P$_5$BCA) | 332 | 228 | 0.69 |
| *N*-4-hexoxybenzylidene-4-chloraniline (HBCA) | 331 | 228 | 0.69 |
| *N*-4-butoxybenzylidene-4-propylaniline (BBP$_3$A) | 313 | 216 | 0.69 |
| *N*-4-ethoxybenzylideneaminophenyl heptanoate | 343 | 260 | 0.76 |
| ethyl 4-ethoxybenzylidene-4′-aminocinnamate | 358 | 270 | 0.75 |

$T_g$: glass transition temperature
$T_m$: melting point temperature

amorphous polymers.[20] With $T_m$ known, it is then possible, using the ratio discussed above to calculate the expected region where $T_g$ will fall.

In general, the structural factors increasing the stiffness and the size of the moving segments will tend to increase $T_g$. However, *a priori* prediction of $T_g$ from structural molecular information only is very difficult.

All generalizations about glass-forming tendency and its relation to molecular constitution provided here are empirical. More efforts have to be made in this direction for a complete understanding of the influence of molecular structure on vitreous state formation. It is to be expected that X-ray diffraction and neutron scattering studies will prove to be valuable techniques in these future investigations.

## Acknowledgments

One of us (N.K.) thanks Prof. M. P. Fontana and his associates from the Raman spectroscopy group, Institute of Physics, University of Parma for their cordiality and hospitality. This work is a part of the collaboration programme between the Institute of Solid State Physics at the Bulgarian Academy of Sciences and the Physics Institute, Parma University. The financial support of the Italian National Research Council is also greatly acknowledged.

## References

1. K. Tsuji, M. Sorai and S. Seki, *Bull. Chem. Soc. Japan*, **44**, 1452 (1971).
2. M. Sorai and S. Seki, *Mol. Cryst. Liq. Cryst.*, **23**, 299 (1973).
3. N. Kirov, M. P. Fontana and F. Cavatorta, *Mol. Cryst. Liq. Cryst.*, **54**, 207 (1979).
4. K. Adachi, H. Suga and S. Seki, *Bull. Chem. Soc. Japan*, (a) **41**, 1073 (1968); (b) **43**, 1916 (1970); (c) **44**, 78 (1971); (d) **45**, 1960 (1972); M. Sugisaki, H. Suga and S. Seki, *Bull. Chem. Soc. Japan*, **41**, 593 (1968); M. Sugisaki, H. Suga and S. Seki, *Bull. Chem. Soc. Japan*, **41**, 2586 (1968); S. S. Chang, J. A. Horman and A. B. Bestul, *J. Res. Nat. Bur. Stan.*, **A71**, 293 (1967); S. S. Chang and A. B. Bestul, *J. Chem. Phys.*, **56**, 503 (1972).
5. M. Traettenberg, I. Hilmo, R. L. Abraham and S. Ljunggren, *J. Mol. Structure*, **48**, 395 (1978).
6. H. D. Burgi and D. Dunitz, *Helv. Chim. Acta*, **53**, 1747 (1970); **54**, 1255 (1971); J. Bernstein and G. M. J. Schmidt, *J. Chem. Soc. Perkin Trans. 2*, 946 (1972).
7. H. Perrin and J. Berges, *Proceedings of the Conference on Liquid Crystals of One and Two-Dimensional Order and their Applications*, Garmish-Partenkirchen, Fed. Rep. of Germany, January, 21–25, 1980, (eds. W. Helfrich and G. Heppke), Springer-Verlag, Berlin, p. 89.
8. J. Bernstein and C. M. Schmidt, *J. Chem. Soc. Perkin Trans. 2*, 951 (1972).
9. G. Vergoten and G. Fleury, *Mol. Cryst. Liq. Cryst.*, **30**, 213 (1975).
10. J. E. Lydon and J. O. Kessler, *J. Phys. (Panes)*, **36**, 153 (1975).
11. M. P. Fontana and N. Kirov, *Mol. Cryst. Liq. Cryst. Lett.*, **56**, 195 (1980).

12. G. W. Gray, K. J. Harrison, J. A. Nash, J. Constant, D. S. Hulme, J. Kirton and E. P. Raynes, *Liquid Crystals and Ordered Fluids*, (eds. J. F. Porter and J. F. Johnson), Plenum Press, New York (1971), Vol. 2, 617.
13. B. J. Bulkin, K. Brezinsky and T. Kennelly, *Mol. Cryst. Liq. Cryst.*, **55**, 53 (1979).
14. D. Turnbull and N. H. Hohen, *J. Chem. Phys.*, **29**, 1049 (1958); D. Turnbull, *Solid State Physics*, Academic Press, New York (1956), Vol. 3, p. 225; see also J. H. Hollomon and D. Turnbull, *Progress in Metal Physics*, Pergamon, London (1956), Vol. 4, p. 333; M. Avrami, *J. Chem. Phys.*, 7, 1103 (1939).
15. F. R. N. Nabarro, *Report of Conference on Strength of Solids*, Physical Society, London (1948).
16. C. Herring, *J. Appl. Phys.*, **21**, 437 (1950).
17. G. Tamman, *Aggregat Zustand.*, Leipzig (1922).
18. T. B. Freedman and E. R. Nixon, *Spectrochim. Acta*, **A28**, 1375 (1972).
19. J. A. Pryde and G. O. Jones, *Nature*, **170**, 685 (1952).
20. F. E., Kazasz, H. E. Bair and J. M. O'Reilly, *J. Poly. Sci., Part A-2, Poly. Phys.*, **6**, 1141 (1968).