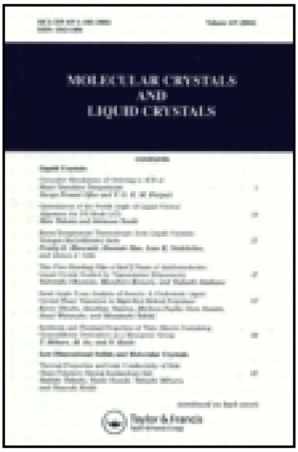

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Short and Long-Range Correlations of N- (4′-n-pentyloxy benzylidene)-4-n-butylaniline (PBBA) Molecules in Smectic G and Glass of Smectic G Phases

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Short and Long-Range Correlations of N-(4'-*n*-pentyloxy benzylidene)-4-*n*-butylaniline (PBBA) Molecules in Smectic G and Glass of Smectic G Phases

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The literature dielectric data of Johari and Goodby on the main relaxation in smectic G phase and on secondary relaxation in the glass of smectic G phase of PBBA has been analyzed to estimate and compare the local and long-range correlation parameters describing the molecular reorientations.

Keywords: Liquid crystals, glass, correlation parameters, dielectric relaxation

1. INTRODUCTION

In liquid phases, in the vicinity of the temperature T_g of the transition from the liquid phase into the glass phase, two non-Debye relaxation processes are detected.[1,2] The main relaxation of the electric permittivity $\varepsilon(\nu) = \varepsilon' - i\varepsilon''$ occurs in the kHz frequency range and reveals high magnitude. On cooling, the approaching of the glass transition temperature is detected by dramatical slowing down of the main relaxation. The non-Arrhenius temperature dependence of characteristic time scale $1/\nu_{\max}$ is described by the Vogel-Tamman-Fulcher expression[3,4] basing on the free volume model (the $\nu_{\max}$ is the frequency at the maximum of loss). For description of the asymmetric shape of $\varepsilon(\nu)$ the standard phenomenological expressions like Cole-Davidson or Kolhrausch-Williams-Watts[5] have been used so far. Nagel and co-workers[6] has recently developed the interesting scaling relationship: When presenting the dielectric data in form $w^{-1}\log(\nu_{\max}\varepsilon''/\nu\Delta\varepsilon)$ versus $w^{-1}\log(\nu/\nu_{\max})$ the experimental points from various temperatures collapse into the single curve (w is the half-maximum width of the loss peak normalized with the corresponding width $w_D = 1.14$ of the Debye peak, $\Delta\varepsilon = \varepsilon(0) - \varepsilon'(\infty)$, i.e. the difference between electric permittivity in the limits of low and high frequency, respectively). The number of cases for which the dielectric data obey the scaling grows up and embraces various kinds of glass-forming materials.[7] There is still search for interpretation of that unique behavior covering the frequency range of more than 10 decades. The secondary relaxation occurs at the higher frequencies and is characterized by much smaller asymmetric loss peak, of amplitude rapidly decreasing with temperature. The secondary relaxation survives T_g with unchanged rate and gives the Arrhenius activation energy. There is evidence that in higher temperatures of the liquid phase both types of relaxations merge.[1] This relaxational behaviour seems common to various molecular, ionic and atomic glass formers as well as to liquid crystals and some orientationally disordered crystals.[8]

The substances for which the relaxation processes have been studied in both liquid and glass phases are rather rare. It seems interesting to analyze them and to compare their shapes to understand the influence of the glass transition on the dynamics of the reorienting molecules. Useful tools for comparising the dynamics in various phases give us Jonscher observation of the universal response:[9] In various types of disordered materials he has found that the power-law frequency dependence of electric permittivity

$$\varepsilon''(\nu) \sim (\varepsilon'(\nu) - \varepsilon(\infty)) \sim (\nu/\nu_{\max})^{n-1} \qquad \nu > \nu_{\max} \tag{1}$$

$$\varepsilon''(\nu) \sim (\varepsilon(0) - \varepsilon'(\nu)) \sim (\nu/\nu_{\max})^{m} \qquad \nu < \nu_{\max} \tag{2}$$

is generally observed. For materials in the thermodynamically stable phases the fractional exponents n and m are independent of the temperature. The Dissado-Hill many-body cluster model[10] leading to the relations (1) and (2) explains the non-Debye behaviour of $\varepsilon(\nu)$ by the presence of interactions between entities of the medium. The n and $1 - m$ parameters could be regarded as a measure of the size of the local correlations of reorienting molecules and as a measure of the size of the long-range correlations in the medium, respectively. The Debye model, relevant for systems of non-interacting materials, is characterized by n and $1 - m$ equal zero. The correlation parameters seem also to be the measures of degree of spatial order on local and long-range levels of the sample morphology.

The purpose of the paper is to analyze and compare the relaxation processes observed by Johari and Goodby:[1] the main one in low temperatures of the smectic G phase of N-(4′-*n*-pentyloxy benzylidene)-4-*n*-butylaniline molecule (PBBA) and the secondary one in the glass phase obtained by rapid cooling of the smectic G phase. Figure 1 presents the schematic structure of the PBBA molecule and the phase sequence determined by optical microscopy.[1] The smectic A phase of PBBA reveals the

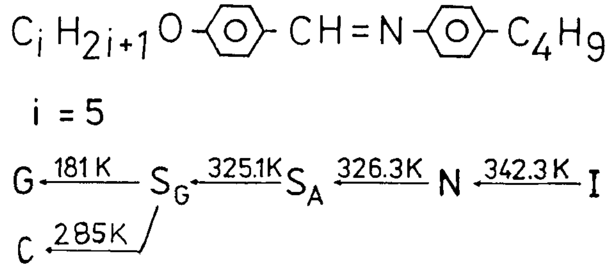

FIGURE 1 Molecular structure of PBBA and the phase sequence.

focal-conic texture. While cooling the transition to the smectic G phase is marked by dendritic growth of mosaic areas. The smectic G phase is one of the most ordered liquid crystalline phases like the hexagonally packed smectic B but with additional tilt of the molecules with respect to the layer plane. Neutron scattering measurements[11] support the statement about the extention of the inter-layers correlations over at least 1000 layers and the in-plane correlations of the molecules to at least 1000 Å. However, the X-ray diffraction investigations[12] have not confirmed the long-range order of the true crystalline phase . Such sample in the smectic G phase is frozen into the glassy phase. Thus, the parameters of local and long-range correlations obtained by the analysis of the dielectric data in the smectic G and the glass phase of smectic G seem to be a good supplement.

For the smectic G phase the relaxational changes have been detected by measuring the dielectric loss $\varepsilon'' C_p$ ($C_p = 11.6$ pF is the geometrical electric capacity of the empty vessel) with the accuracy 0.1 pF in the frequencies ranging from 50 Hz to about 100 kHz. In the glass phase the $\tan \delta(\nu) = \varepsilon''(\nu)/\varepsilon'$ has been measured with 1% accuracy in the frequency range from 120 Hz to 100 kHz. In these frequencies the decrease of the real part of electric permittivity has been lower than 2%. No prefered alignment of the molecules has been induced in the samples. The analysis has been performed to check the size of deviation of the dielectric loss from the Debye model. From the shape of absorption curves the local and long-range correlation parameters have been evaluated for both phases of PBBA. Next, they were compared with the parameters estimated for the cases of relaxation observed in liquid crystalline and glass phases of similarly shaped molecules. Finally, suggestions on the interpretation of the power-law frequency dependence of the relaxation in glasses were presented.

2. RESULTS AND DISCUSSION

The main relaxation observed in the smectic G phase is presented in Figure 2 in the form of the single master curve $\log(\varepsilon'' C_p)$ vs $\log \nu$ scaled at 205 K. The scaling procedure bases on appropriate shifting of the $\log(\varepsilon'' C_p)$ vs $\log \nu$ curves going through the experimental points measured in various temperatures along both coordinates to coincide with the curve for the temperature chosen as the scaling one (here 205 K). The slopes of two straight lines drawn through the points measured at several temperatures above 200 K enable us to estimate $n = 0.7 \pm 0.05$ and $1 - m = 0.2 \pm 0.05$. The experimental points measured at the temperatures close to T_g deviate from the master curve: The closer the temperature of the experimental points to the transition, the larger the 1-m value. In Figure 3 the secondary relaxation observed in the glass of smectic G phase is presented. The loss are so low that $\tan \delta(\nu) = \varepsilon''(\nu)/\varepsilon'$ reflects the dielectric loss $\varepsilon''(\nu)$ frequency dependence, since the dispersion of ε' is negligible.[5] In the temperature range under consideration the long-range correlations are described by $1 - m = 0.88 \pm 0.05$ and seem to be temperature independent. The local order ($n \sim 0.85$) decreases slightly with increasing temperature. The freezing of the smectic G phase into the glass phase causes moderate enlargement of the degree of local order and a dramatic jump of the degree of long-range order. The main and the secondary relaxation processes differ significantly from the Debye behaviour.

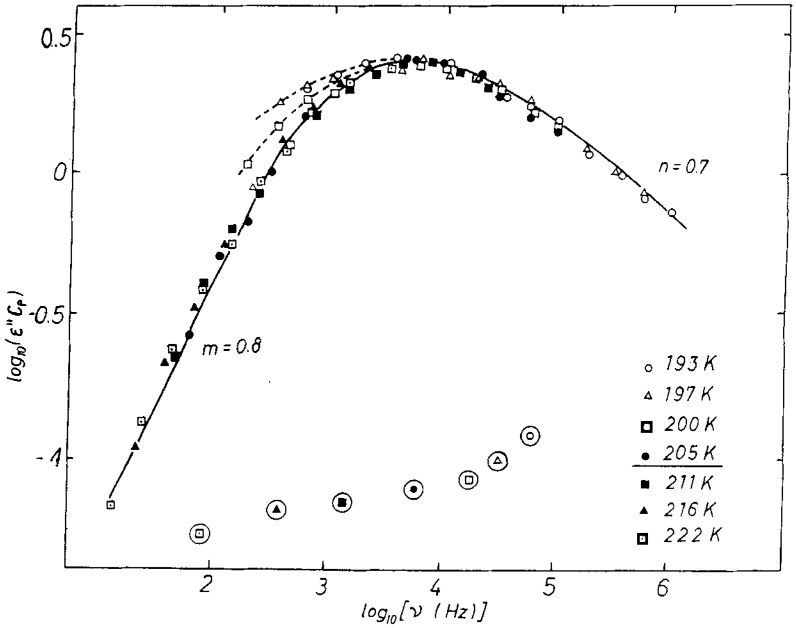

FIGURE 2 The master curve log ($\varepsilon'' C_p$) vs log ν scaled at 205 K for PBBA in smectic G phase. $C_p = 11.6$ pC is the geometric capacitance of the sample. The encircled points are the traces of the reference point, the dot in the circle, created in shifting of the log $\varepsilon'' C_p$(log ν) curves for various temperature along both coordinate to superimpose them with the curve in scaling temperature.

The Table I presents the correlation parameters describing the above examples of relaxation. For comparison, there are collected the n and $1 - m$ values for the nematic of 5OAOB,[13] for MBBA[14] in slowly cooled and quenched nematic phases and for glass of the cholesteric phase of cholesteryl hydrogen phthalate.[15] For MBBA, the n and $1 - m$ have been evaluated earlier by Pathmanathan.[14] The MBBA has been chosen for comparison as it is the first member of the same homologous series as PBBA . In turn, the molecule of 5OAOB with N_2O bridging group, is of the similar length and molecular structure as PBBA: One heptyloxy chain in 5OAOB is replaced by butyl chain in PBBA. The examples of relaxations are ordered starting from that of the highest degree of disorder in the sample ($1 - m$, $n \sim 0$). It is worth noting that in the smectic G phase of PBBA (No. 2), the long-range structural order of elongated molecules is only slightly higher than in the nematic phase of 5OAOB and in high temperature liquid crystalline phases of many other substances.[13] Instead, the local order varies essentially from $n = 0.1$ for nematic of 5OAOB to $n = 0.7$ for smectic G phase of PBBA. The small long-range correlation parameter ($1 - m = 0.2$) confirms that the smectic G phase is a liquid phase. The next examples in the Table, Nos. 3 and 4, show that for solid phases of MBBA only the degrees of long-range order are larger than for smectic G phase of PBBA. It seems interesting that the degree of local order in smectic G phase is higher than in the soild phases of MBBA. Nos. 5 and 6 in the Table represent the glasses of the smectic G and cholesteric[15] phases. Despite different shapes of the molecules as well as structural properties of the original liquid crystalline phases (smectic G and cholesteric,

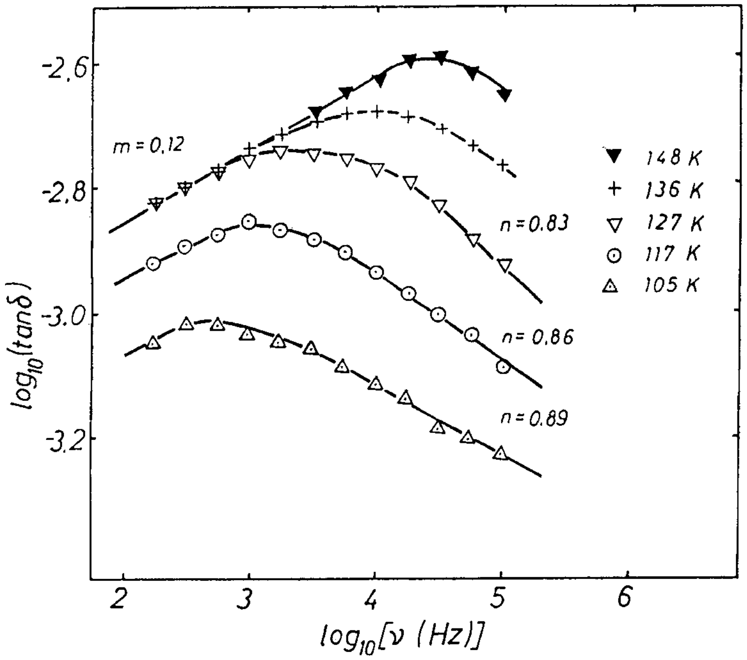

FIGURE 3 The log tanδ vs log ν plot for various temperatures of the glass of smectic G phase of PBBA.

TABLE I

Correlation parameters for liquid crystalline materials in liquid, solid and glass phases

No.	Substance	Phase	Correlation parameters $n \pm 0.05$	$1 - m \pm 0.05$	Relaxation rate $\omega_{\max}$ in kHz
1	5OAOB*	nematic	0.22	0.09	$2*10^3$ (350K)
2	PBBA	smectic G	0.7	0.2	60(205K)
3	MBBA** (slowly cooled nematic)	solid	0.53	0.55	0.15(188K)
4	MBBA	quench N	0.82	0.6	0.12(150K)
5	PBBA $T_g = 181$K	glass S_G	0.89	0.88	2.5(105K)
6	chol*** $T_g = 297$K	glass Ch	0.87	0.82	6(150K)

* N-(4'-di pentyloxy azoxybenzene)
** N-(4'-*n*-methyloxybenzylidene) 4'-*n*'-butylaniline
*** cholesteryl hydrogen phthalate

respectively) the correlational behaviour is similar in both glass phases. The n and $1 - m$ values point to a high dynamical order in both short and long ranges (n, $1 - m > 0.8$). In spite of the presence of long-range orientational order in liquid crystalline phases the process of relaxation in the glassy state of liquid crystals is characterized by the same size of correlations as in the glass obtained from the liquid phase.[16]

The fact that the scaling procedure turns out to be non-applicable for glasses confirms the hypothesis as to the origin of the relaxational process.[1] Johari[2] proposed that the above relaxations seem to be coming from two effects: the main one from the hindered rearrangement of the molecules and the secondary from the translational or rotational diffusional motions of molecules and/or their segments. In the course of lowering the temperature towards T_g the medium starts to differentiate into more flexible and more rigid regions.[4,17,18] Thus, motions within those regions are characterized by different time scales. While approaching temperature T_g the free volume becomes so small that the rate of the molecular rearrangements goes to zero. However, the small-step diffusion is still possible in the flexible regions that decrease with decreasing temperature. The decrease of temperature reduces the regions of the sample where the molecules and/or their segments still reorient even in the glass phase. Thus, the number of dipoles which take part in the process of relaxation is temperature dependent and causes the temperature dependence of shape of the dielectric loss curve. With decreases of temperature the intensity of the loss curve diminishes, while the degree of local correlations of motions increases as the dielectric increment grows.

The significant broadening of $\varepsilon''(\nu)$ and the power-law behaviour with n and $1-m$ tending to unity show that in glasses one deals not with intrinsic time scale but with a continuum of scales from microscopic (corresponding to fast motions) to mesoscopic (corresponding to very slow motions). Glasses are the freezing liquid phases, so they are solid states with many locally stable configurations. The comb-like potential barrier seems to be appropriate as a model of a barrier for dipolar reorientations which is rough on many scales of energy.[17,18] This hierarchical structure of the free energy surface reflects the complexity of microscopic features of the glass phase. Rapid cooling results in some constraints[8] in spatially disordered system. The degrees of freedom characterized by larger time constants can be regarded as constraints for the degrees of smaller time constants.

3. SUMMARY

The power-law frequency dependence of dielectric loss have been proved for the smectic G and the glass of smectic G phases of PBBA. The analysis of the literature dielectric relaxation data show a high degree of local correlations in both phases ($n > 0.7$). In glass transition temperature the large jump of the value of long-range correlation parameter has been found from the value $1-m$ equal 0.2 (typical for high temperature liquid crystalline phases) to $1-m$ equal 0.88.

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References

1. G. Johari and J. W. Goodby, *J. Chem. Phys.*, 77, 5165 (1982).
2. G. P. Johari, *J. Chem. Phys.*, **82**, 283 (1985).

3. G. S. Fulcher, *J. Am. Ceram. Soc.*, **6**, 339 (1925); H. Vogel, *Phys. Z.*, **22**, 645 (1921).
4. M. H. Cohen and G. S. Grest, *Phys. Rev. B*, **20**, 1077 (1977).
5. A. K. Jonscher, Dielectric Relaxation in Solids, Chelsea Dielectric Press, London, 1983, p.66.
6. P.Dixon, L. Wu, S. R. Nagel and B. D. Williams and J. Carini, *Phys. Rev. Lett.*, **65**, 1108 (1990).
7. D. Leslie-Pelecky and N. Birge, *Phys. Rev. Lett.*, **72**, 1232 (1994); A. Schlosser, *Phys. Rev. Lett.*, **67**, 999 (1991) and the references therein.
8. M. I. Klinger, *Physics Reports*, **165**, 276 (1988); J. C. Phillips and M. F. Thorpe, *Solid State Commun.*, **53**, 699 (1986).
9. A. K. Jonscher, *Nature*, **267**, 673 (1977).
10. L. Dissado and R. M. Hill, *Chem. Phys.*, **111**, 193 (1987); L. Dissado and R. M. Hill, *Proc R. Soc. Lond. A* **390**, 131 (1983).
11. A. J. Leadbetter, M. A. Mazid and R. M. Richardson, *Liquid Crystals*, ed. by S. Chandrasekhar, Heyden, London, 1980, p. 65.
12. J. W. Goodby and R. Pindak, *Mol. Cryst. Liq. Cryst.*, **75**, 233 (1981).
13. M. Massalska-Arodź, *Acta Physica Polonica A*, **74**, 773 (1988).
14. K. Pathmanathan, L. Dissado and R. M. Hill, *Mol. Cryst. Liq. Cryst.*, **135**, 65 (1986).
15. M. Massalska-Arodź, *Phys. Rev. B*, **47**, 14552 (1993); G. P. Johari, J. W. Goodby and G. E. Johnson, *Nature*, **297**, 315 (1982).
16. R. M. Hill, *Nature*, **275**, 96 (1978); M. Shablakh, R. M. Hill and L. Dissado, *J. Chem. Soc. Faraday Trans. 2*, **78**, 625 (1982): see β-relaxation in 44 mol% chlorobenzene in pyridine.
17. V. S. Dotsenko, *J. Phys. C: Solid State Phys.*, **18**, 6023 (1985).
18. D. E. Stein, *Chance and Matter*, North-Holland, Amsterdam, Oxford, New York, Tokyo, 1987, p. 577; R. Palmer, D. Stein, E. Abrahams and P. W. Anderson, *Phys. Rev. Lett.*, **55**, 958 (1984).