Dielectric studies on orientationally disordered phases of neopentylglycol $((CH_3)_2C(CH_2OH)_2)$

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Abstract. The dielectric spectra up to frequencies of 1 GHz of the substances 2,2-dimethyl-1,3-propanediol (or neopentylglycol, NPG) and 2-amino-2-(hydroxymethyl)-1,3-propanediol (or *tris*(hydroxymethyl)aminomethane, TRIS) have been determined in the orientationally disordered FCC and BCC phases respectively, in the ranges 305–353 K for NPG and 343–375 K for TRIS (in this case, in the supercooled BCC orientationally disordered phase). The dielectric relaxation of both substances has been studied by considering modified Debye theories as well as the Jonscher equation. Significant deviations from the single Debye relaxation were found in both cases. The temperature dependence of the relaxation time, assuming Arrhénius or Eyring activation models, allows one to evaluate of the activation enthalpies and entropies. Large values were obtained for both parameters, showing that there are strong intermolecular interactions via hydrogen bonds, as had been proved previously for solid phases of alicyclic and branched (tetrahedral molecules) alcohols.

1. Introduction

Globular or pseudo-globular molecules with weakly angle-dependent interactions are capable of forming orientationally disordered (ODIC) phases (plastic phases) in which positional order exists and orientational order has been lost. Such substances exhibit large entropy and volume changes at the brittle-to-plastic transition, whereas the changes in thermodynamic properties at melting are relatively small. Examples of substances displaying such a disorder are branched or tetrahedral molecules belonging to the series (CH$_3$)$_{4-n}$C(CH$_2$OH)$_n$, $n = 0, 1, \ldots 4$ and (NH$_2$)(CH$_3$)$_{3-n}$C(CH$_2$OH)$_n$, $n = 0, 1, \ldots 3$ [1–3]. Although much experimental work on the dielectric relaxation of liquid alcohols has been published, data for the mentioned series of compounds are scarce. This lack is due to two facts. On the one hand, the melting point of these compounds is relatively high, so that the brittle or orientationally disordered phases are stable at room temperature, making difficult the elimination of the holes and cracks which appear after solidification. On the other hand, the temperature range for which the ODIC phases are stable means that relaxation is observed within a relatively high frequency domain. The authors of some experimental studies (using QNS [4], IQNS [5], NMR [6, 7] and dielectric relaxation [8]) concluded that the characteristic relaxation times of the overall molecular tumbling in such plastic phases of

related alcohol compounds are considerably higher than those for similar molecules lacking groups able to form strong interactions by means of hydrogen bonds.

The purpose of the present work is then to describe the relaxation spectra of two compounds of the mentioned series in the plastic phase, in particular 2,2-dimethyl-1,3-propanediol (or neopentylglycol, NPG) $(CH_3)_2C(CH_2OH)_2$ and 2-amino-2-(hydroxymethyl)-1,3-propanediol (or *tris*(hydroxymethyl)aminomethane, TRIS) $(NH_2)C(CH_2OH)_3$.

We report measurements of the temperature and frequency dependences of the complex dielectric permittivity in the orientationally disordered phases. The results will be briefly compared with those for some related compounds.

NPG has been studied by means of calorimetry [9, 10] and x-ray diffraction techniques [11–13]. At atmospheric pressure it displays three solid phases: III and II, both of which are brittle phases, and I (a plastic phase) in addition to the liquid phase. The temperature transitions are at respectively 60 and 313.5 K. The melting point is about 400 K. Lattice symmetries and lattice parameters for phases II and I were long ago determined to be monoclinic ($P2_1/c$) and face-centered cubic respectively [12]. No work analysing the relaxation times in the orientationally disordered phase of NPG is known to us. Only one work about the dielectric dispersion of NPG at very low concentration in 1,4-dioxane has hitherto been published [14].

TRIS has been studied throughly by calorimetry [15, 16], single-crystal x-ray diffraction [17, 18], NMR [6], infrared and Raman vibrational spectroscopies [19, 20] and so on. TRIS exhibits a solid–solid transition at 407 K from an orthorhombic ($Pn2_1a$) lattice to form an orientationally disordered phase, the lattice of which is known to be body-centered cubic ($Im3m$). The results of the mentioned studies suggest that hydrogen bonds present in the ordered phase also play a dominant role in the plastic phase in spite of the orientational disorder of the molecules in such a phase.

2. Experimental details

2.1. Dielectric measurements

The complex dielectric permittivity was measured with the HP4191A impedance analyser in the 10^6–10^9 Hz frequency range. It measures the impedance of the sample from the reflection coefficient at the end of a 50 Ω co-axial transmission line. The cell consists of two gold-plated brass electrodes (diameter 5 mm) separated by two 50 μm thick silica spacers, making a plane capacitor located at the end of the line. We used as sample holder a modified HP16091A co-axial test fixture. The sample holder was held in a cryostat, which screens the system, and both temperature and dielectric measurements were fully computer-controlled [21, 22].

In order to determine the complex permittivity the materials were introduced into the dielectric cell in the liquid phase. By means of a continuous and slow cooling the measurements were started at temperatures for which the main part of the dielectric loss was enclosed within the available frequency range (up to 1 GHz).

Thus, data for NPG were measured from 353 until 305 K every 2 K, so that several measurements were carried out for the supercooled FCC plastic phase (for $T < 313.5$ K).

Concerning the TRIS compound, it was not possible to attain the dielectric loss at frequencies lower than 1 GHz in the stable temperature domain of the BCC plastic phase (407–444 K). Therefore, the orientationally disordered phase was supercooled until the dielectric spectra became well defined in order to obtain information about the

relaxation parameters. The studied temperature domain for TRIS was then 343–375 K, the measurements being performed also every 2 K.

2.2. Materials

Both NPG and TRIS were purchased from Aldrich Chemical Company with purities of 99% and 99.9+% respectively. NPG was subjected to an additional purification process through repeated vacuum sublimation at 353 K. Such a procedure provides a high-quality sample, which was indicated by the high melting temperature obtained (403.2 K) [13, 16].

3. Results

3.1. The static permittivity and Kirkwood's g factor

Figure 1 shows the static permittivity (ε') as a function of the temperature both for NPG and for TRIS. Both the FCC and the BCC plastic phases both of NPG and of TRIS revealed relatively high values for ε, identifying these phases as orientationally disordered ones. According to the general statement that the permittivity in the fully ordered phases is low, large values of such a parameter should occur at the order–disorder transition. Moreover, a decrease in the permittivity with increasing temperature, which is characteristic of the orientationally disordered phases, was observed.
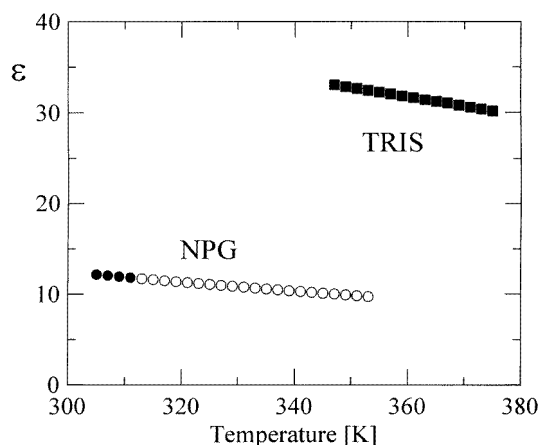

Figure 1. The static permittivity (ε) as a function of the temperature for TRIS (■) and NPG (○) in the orientationally disordered BCC and FCC phases respectively. (Full symbols indicate measurements of the supercooled state.)

From the static permittivity we could derive the Onsager dipole moment and compare its deviation from the dipole moment in the gas phase. This deviation yields the Kirkwood g factor, which, in the framework of the Kirkwood–Frölich–Onsager theory [23], can be expressed by the equation

$$g = \frac{9K_B T \varepsilon_0 V_m (\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{\varepsilon(\varepsilon_\infty + 2)^2 N_A \mu^2} \tag{1}$$

in which V_m is the molar volume, $\varepsilon_0 = 8.854 \times 10^{-12}$ C^2 J^{-1} m^{-1}, K_B Boltzmann's constant, N_A Avogadro's number, ε_∞ the high-frequency permittivity and μ the dipole

moment in the gas phase. Such parameters were obtained from the fitting of the dielectric spectra (see the dielectric relaxation section). The molar volumes for NPG and TRIS were obtained from the cell parameters previously determined by means of the x-ray diffraction measurements [10, 12, 16]. These lattice parameters are presented in figure 2 as functions of the temperature. It should be mentioned that the x-ray diffraction patterns of the orientationally disordered phases had only a very small number of reflections with considerable background scattering due to the very rapid fall-off in intensity with increasing reflection angle and to the highly disordered structure, which two phenomena contribute to increasing the Debye factor [24, 25]. In the present cases of NPG and TRIS compounds only two low-order reflections appeared. Owing to the lack of available literature data for the dipole moments, we calculated them by imposing a perfect tetrahedral symmetry of the molecule. The interatomic distances and bond angles used can be found in [2, 3]. Such a calculation provided dipole moments of 2.56 and 3.38 D for NPG and TRIS respectively. It should be mentioned that a value of 2.5 D was obtained for the dipole moment of NPG in a solution of dioxane, in good agreement with our calculated value [26].
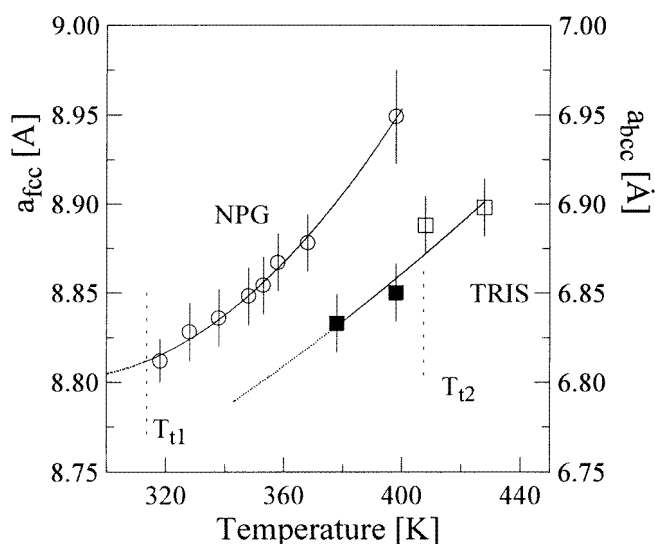

Figure 2. The lattice parameters of the FCC and BCC orientationally disordered phases of NPG (○) and TRIS (□) as functions of the temperature (full symbols correspond to measurements of the supercooled phase). T_{t1} and T_{t2} indicate the temperature transition from the brittle to the disordered phase.

The determined g factor for NPG ranged from 1.0 at 313 K to 0.7 at 353 K. For the TRIS compound the values of g were around 0.5 in the studied temperature domain. The g factor is a measure of the near-neighbour dipole–dipole correlation due to specific short-range intermolecular interactions. Thus, large values of g are found in chain [27, 28], alicyclic [29–33] and branched [34, 35] alcohols, indicating specific correlations between dipoles. Because the correlation factors of NPG and TRIS were less than unity at all studied temperatures, in spite of the relatively low relaxation frequencies that we saw in section 3.2, we attribute these effects to the formation of multimers having dipole moments smaller than those of the free monomers. Similar behaviour was found for some isomeric octyl alcohols in the liquid phase [27]. It should be mentioned that, in a recent vibrational spectroscopic

study of NPG and related compounds [36], the authors pointed out the existence of more than one spectroscopically distinguishable conformer, in agreement with the present work.

3.2. The dynamic permittivity

Figures 3 and 4 show the frequency dependences of the imaginary part of the complex permittivity at different temperatures for NPG and TRIS respectively. The plastic phases of both compounds exhibited a relatively large dielectric absorption at comparatively low frequencies. The plots of ε'' as a function of ε' (Cole–Cole plots) presented in figures 5 and 6 for NPG and TRIS respectively show skewed arcs; thus, large deviations from single Debye absorption are presented. Accordingly, the data were fitted by using the Havriliak–Negami (HN) equation:

$$\varepsilon(\omega) = \frac{\varepsilon' - \varepsilon_\infty}{[1 + (i\omega\tau)^\alpha]^\beta} - \frac{i\sigma_{dc}}{\varepsilon_0\omega} + \varepsilon_\infty \tag{2}$$

where σ_{dc} is the DC conductivity.

Table 1. Parameters of the Havriliak–Negami (α and β) and Jonscher (m and $1 - n$) equations.

	α	β	m	$1 - n$
NPG	1	0.70	1	0.70
TRIS	0.88	0.69	0.88	0.61

Equation (2) contains four adjustable parameters (ε_∞, the high-frequency permittivity; τ, the relaxation time; and the α and β exponents, see table 1) that are determined in the fitting procedure. The α and β exponents were determined to be 1 and 0.70 for NPG and 0.88 and 0.69 for TRIS respectively. The α exponent of the HN equation is unity in the case of the FCC NPG and consequently the dielectric relaxation is well represented by the Cole–Davidson equation that has often been used to describe the dielectric behaviour of other alcohols [29]. Another possible way in which to fit the loss curves is to consider the Jonscher equation [37]

$$\varepsilon''(\omega) = \frac{A}{(\omega/\omega_p)^{-m} + (\omega/\omega_p)^{1-n}} \tag{3}$$

in which there are also four adjustable parameters (A corresponding to the relaxation strength $\varepsilon - \varepsilon_\infty$; ω_p, which is related to the maximum for ε'' for a symmetrical loss curve; and the exponents m and $1 - n$). These exponents m and $1 - n$ describe the slopes of log ε'' against log ω plots in the high- and low-frequency limits respectively. Although the Jonscher equation has a better physical meaning in terms of the Dissado–Hill theory [38], the associated fitting procedure is long and tedious. A detailed comparison of the different fitting procedures and results can be found in [29, 33]. Nevertheless, it has been shown [39] that the m and $1 - n$ parameters of the Jonscher equation are related to the α and β exponents of the Havriliak–Negami function by $m = \alpha$ and $1 - n = \beta\alpha$.

The m and $1 - n$ exponents have a physical significance. The first is a measure of the exchange between neighbouring clusters in such a way that the larger $m(m \leqslant 1)$ the broader the distribution of the form and size of local cluster structures. The second ($1 - n$) has been claimed to describe intracluster vibrations, so that increasing values of $n(n \leqslant 1)$ increase the order of the local structure. The results we obtained for these parameters (see table 1) can be compared with the previous ones for related branched and alicyclic alcohols. For
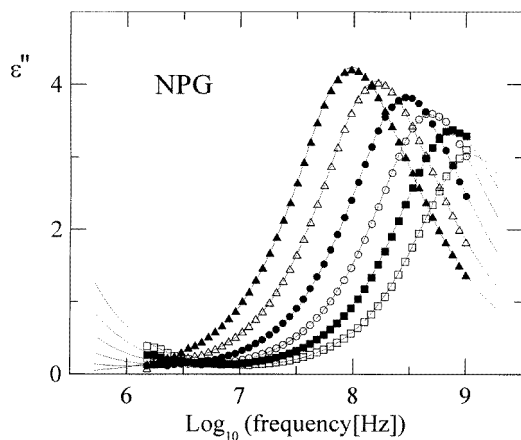
Figure 3. Dielectric losses versus frequency for NPG at various temperatures in the orientationally disordered FCC phase: (□), 353 K; (■), 343 K; (○), 333 K; (●), 323 K; (△), 313 K; and (▲), 305 K (the supercooled phase). The full lines are fits to equation (2).
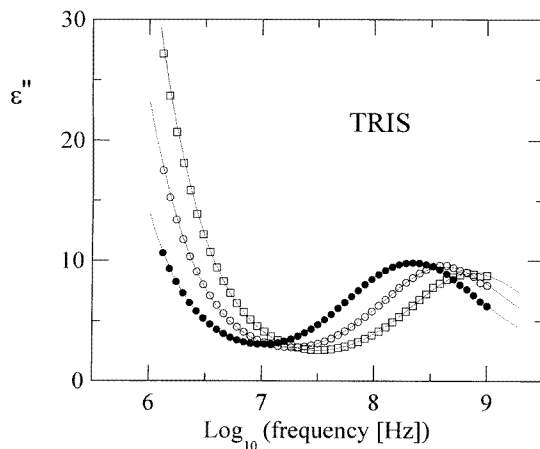

Figure 4. Dielectric losses versus frequency for TRIS at various temperatures in the supercooled orientationally disordered BCC phase: (□), 367 K; (○), 357 K; and (●), 347 K. Full lines are fits to equation (2).

branched alcohols, such as neohexanol (($C_2 H_5$)(CH_3)$_2$C(CH_2OH) [34]) and neopentanol ((CH_3)$_3$C(CH_2OH) [35]), m was determined to be close to unity, whereas it was clearly lower for alicyclic alcohols [29]. This difference was assumed to be probably associated with the different intramolecular motions observed for the flexible molecules in branched compounds. Nevertheless, in the present case the m value of TRIS is relatively far from the unity, whereas NPG behaves normally for the family compounds to which it belongs. So then, such an m value for TRIS might reveal a rigid behaviour of the branched molecule due to a highly ordered local structure produced by a large number of hydrogen bonds. Such an assumption is reinforced by the large value of the activation enthalpy, as we will see later.
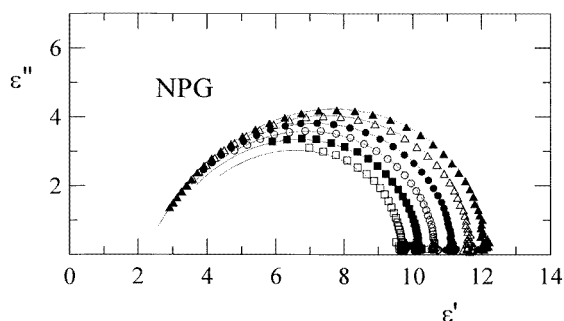
Figure 5. Cole–Cole plots for NPG at various temperatures in the orientationally disordered FCC phase: (□), 353 K; (■), 343 K; (○), 333 K; (●), 323 K; (△), 313 K; and (▲), 305 K (the supercooled phase). Full lines are fits to equation (2).
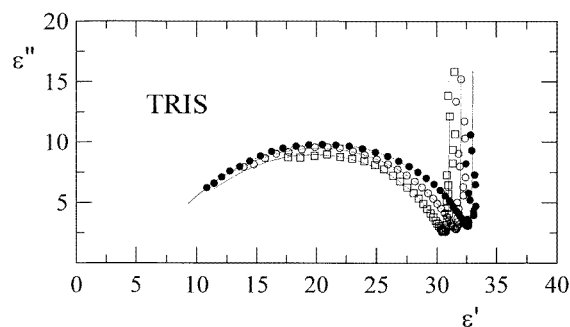

Figure 6. Cole–Cole plots for TRIS at various temperatures in the supercooled orientationally disordered BCC phase: (□), 367 K; (○), 357 K; and (●), 347 K. Full lines are fits to equation (2).

In relation to the $1 - n$ exponent, the determined values for the FCC and BCC plastic phases of NPG and TRIS are closer to those for the alicyclic alcohols than they are to those for the branched alcohols that have so far been studied in their plastic phases. The considerably low values of $1 - n$ indicate that there is a high degree of order in the local cluster structure. These facts reflect again that the dielectric relaxation of NPG and TRIS is much less Debye-like than is that of the hitherto-studied branched alcohols.

It should be mentioned that $\beta = 0.72$ was obtained for a solution of NPG in dioxane at very low concentration in a previous study [14], confirming a Cole–Davidson dispersion. Such behaviour was explained by assuming that the dissolved solid in the nearly non-polar solvent (dioxane) relaxes in a cooperative manner as it does in the pure solid. Nevertheless, this situation, in which an asymmetrical behaviour is observed in a low-concentration solution (0.333) with a non-polar solvent, is quite unexpected.

3.3. The relaxation time and activation parameters

Relaxation times for NPG were in the range 2×10^{-9} to 2×10^{-10} s in the analysed temperature range (305–353 K). For the TRIS compound similar values were obtained, namely 1×10^{-9} s at 347 K and 3×10^{-10} s at 373 K. In both cases the relaxation times were two decades lower than the corresponding literature values for other branched [34, 35]
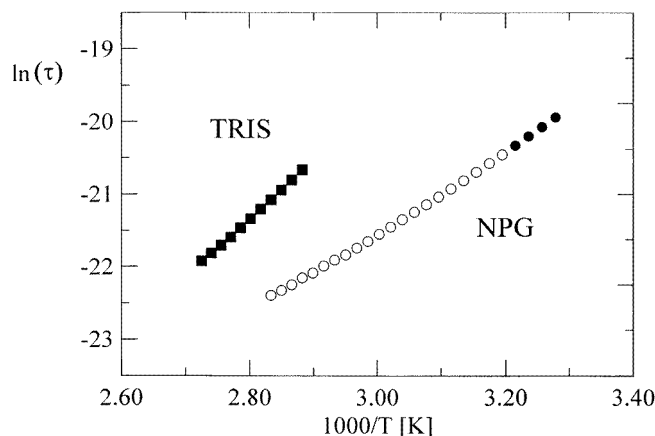
Figure 7. The dielectric relaxation time as a function of the temperature for TRIS (■) and NPG (○) (full symbols indicate measurements in the supercooled orientationally disordered phases).

and alicyclic alcohols [29–33] in their plastic phases and chain alcohols [27, 28] in the liquid phase.

The relaxation times derived from the fittings of the HN equation (2) for NPG and TRIS are plotted in figure 7 as functions of the temperature. The temperature dependence of the relaxation time can be described by an Arrhénius law; thus, the activation enthalpy is calculated from the equation

$$\tau = \tau_0 \exp\left(\frac{\Delta H}{RT}\right) \tag{4}$$

where τ_0 is a pre-exponential factor and R is the gas constant. Such a procedure gives activation enthalpies of 45.9 and 67.1 kJ mol^{-1} for NPG and TRIS respectively. These high activation enthalpies reveal that the molecules of NPG and TRIS must expend considerable energy in the plastic phases in reorienting owing to the strong intermolecular association by means of hydrogen bonds. Moreover, the existence of a higher number of hydroxyl groups in TRIS (in addition to the amine group) than in NPG makes evident the difference in the determined activation enthalpies. Similar values of activation enthalpies have been obtained for orientationally disordered phases of alicyclic alcohols (cyclohexanol, cyclopentanol and cyclooctanol [29–33]) and branched alcohols (neopentanol and neohexanol [34, 35]). At this point we want to mention that, in order to verify or to discard the hypothesis of the existence of bulky associates, the determination of the activation volume of the reorientation would be interesting.

By assuming the Eyring model, τ_0 can be interpreted in terms of an activation entropy; in such a way, the τ_0 value of the Arrhénius law of equation (4) is described by $[h/(K_B T)]\exp(-\Delta S_E/R)$, where h is Planck's constant and ΔS_E is the activation entropy. By using the Eyring model, the new activation enthalpies (ΔH_E) and the activation entropies (ΔS_E) were obtained.

Referring to the activation enthalpies, the values are obviously not too much different from the previous ones, namely 43.1 and 64.2 kJ mol^{-1} for NPG and TRIS respectively. The obtained activation entropies were 57.9 and 110.6 J mol^{-1} K^{-1} respectively. These very large values (we can only compare them with those obtained for some hydrocarbon

chain alcohols [40] and some *tert*-butyl compounds [41]) reveal that the reorientation of the dipole moment of an alcohol molecule of NPG or TRIS requires the rupture of hydrogen bonds and also the rearrangement of the surroundings of the dipole.

From a dynamic point of view, it is known that the quenching of so-called plastic phases gives rise to a glassy state [42]. The glass transition, which appears to be closely related to the freezing of well-defined large-amplitude motions, occurs when the characteristic time of the isotropic reorientational motion reaches 10^3 s [43], whereas other possible anisotropic large-amplitude motions continue to exist within the glassy state. Therefore, we can estimate the glass-transition temperatures of the studied compounds by means of the extrapolation of the relaxation time versus temperature. Such a calculation provides temperatures of about 120 and 160 K for NPG and TRIS respectively. In spite of the small temperature domains for which the relaxation times have been obtained (it must be borne in mind that, in the neighbourhood of the glass transition, non-Arrhénius behaviour might occur), the calculated glass-transition temperatures should have a realistic and physical meaning.

4. Conclusion

The results of dielectric relaxation studies of NPG and TRIS in their orientationally disordered phases have been interpreted in terms of the Dissado–Hill theory by means of the Jonscher and Havriliak–Negami equations because of the large deviations from single Debye behaviour. The low values of the near-neighbour dipole–dipole correlation (the *g* factor) have been attributed to the formation of multimers. Finally, the analysis of the relaxation times as a function of the temperature by means of the Arrhénius equation has allowed us to obtain the activation enthalpies (45.9 and 67.1 kJ mol^{-1} for NPG and TRIS respectively). Such values reveal that strong intermolecular association by means of hydrogen bonds occurs in the orientationally disordered phases.

Acknowledgments

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