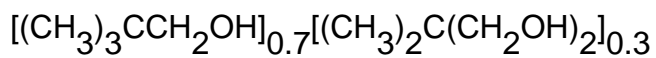


Relaxation dynamics in orientationally disordered molecular mixed crystal



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Relaxation dynamics in orientationally disordered molecular mixed crystal $[(\text{CH}_3)_3\text{CCH}_2\text{OH}]_{0.7}[(\text{CH}_3)_2\text{C}(\text{CH}_2\text{OH})_2]_{0.3}$

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Abstract. The complex dielectric function of the orientationally disordered molecular mixed crystal $[(\text{CH}_3)_3\text{CCH}_2\text{OH}]_{0.7}[(\text{CH}_3)_2\text{C}(\text{CH}_2\text{OH})_2]_{0.3}$ (NPA_{0.7}NPG_{0.3}) covering 11 decades in frequency (10^{-2} – 10^9 Hz) is measured over a broad and continuous temperature range (163–333 K) which is close to the orientational glass transition (160.9 K). For the first time, the dynamics of the orientationally disordered (OD), the supercooled orientationally disordered and the orientational disordered glass is studied without a temperature breakdown as usually occurs due to the catastrophe of the crystallization. The orientational glass transition in the OD phase exhibits the essential features of the structural glass transition, a non-Arrhenius behaviour for the temperature variation of the relaxation time and a broadening of the width of the relaxation with decreasing temperature. The temperature dependence of the relaxation time is analysed by the empirical Vogel–Fulcher–Tammann law as well as the more recent mode-coupling theory. The suggested increase of the ratio between the crossover temperature T_c and glass transition temperature T_g with decrease of fragility of the system is in accordance with the present observation for this mixed crystal ($T_c/T_g \geq 1.45$).

1. Introduction

For orientationally disordered crystals (ODICs) the translational order is always close to the ideal completely ordered structure, the difference from the local minimum of the potential energy being due to the thermal excitation of phonon vibrational modes. The translational order displays a rather symmetrical lattice structure, usually cubic or rhombohedral, although lattices with lower symmetry can be also found [1, 2]. As the molecules usually display lower symmetry, the compatibility with the highest symmetry is produced by the loss of the orientational order [1, 2]. When the reorienting molecules freeze into random configurations an orientational glass (OG) state occurs [3, 4]. The transition between the OG and its ergodic state (orientationally disordered, OD, or plastic or rotator phase) exhibits all the characteristics observed in the structural glass transition, i.e. an increasingly non-Debye relaxation and faster than Arrhenius behaviour in the relaxation time as the glass transition is approached [5–12]. Thus the OG to supercooled OD phase transition would involve only the liberation of rotational degrees of freedom, while in the structural glass to supercooled liquid transition rotational as

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well as translational degrees of freedom are certainly involved. Moreover, it has been recently shown that the rotational degrees of freedom are the dominant (dynamical) contribution to the structural relaxation general processes [9, 13, 14]. This reduction of the structural complexity should facilitate the understanding and the modelling of the glass state and transition. Thus, OGs are today the subject of intense research activity.

An additional attraction is due to the appearance, a few years ago, of new theoretical approaches such as the mode-coupling theory (MCT) [6]. Experimental works covering very a wide relaxation time range have indicated the existence of two relaxation temperature domains of the α -relaxation process (related to the flip-flop of the molecular dipoles). The temperature where qualitative changes in the dynamics occur is the crossover temperature T_c [15]. This temperature has been determined through the analysis of the temperature variations of the relaxation time in spite of the non-existence of a critical behaviour for the relaxation time itself [16]. Nevertheless, values of T_c around 1.15 – $1.2 T_g$ are reported mainly for glass-forming liquids that, according to the Angell classification [7], are generally fragile glasses. A very recent analysis of a strong network glass former (B_2O_3) has evidenced the existence of this dynamical transition at a temperature well above the glass-transition temperature ($T_c = 1.5 T_g$) [17, 18]. Then, it is interesting to investigate whether the T_c temperature defined in the MCT scenario can be determined for materials displaying non-far-from-Arrhenius behaviour, i.e. strong glasses from the Angell classification.

In this work the OG glass transition for the orientationally disordered molecular mixed crystal $[(CH_3)_3CCH_2OH]_{0.7}[(CH_3)_2C(CH_2OH)_2]_{0.3}$ (NPA_{0.7}NPG_{0.3} for short), for which T_g is 160.9 K, has been dynamically characterized. It is important to realize that the (catastrophic) recrystallization from the supercooled (metastable) OD phase after the glass transition has occurred does not exist, in contrast to the usual behaviour in many ODICs for which the lifetime metastability is relatively small. Moreover, the OG state is obtained whatever the cooling rate is, the glass transition being obtained at approximately the same temperature. This finding can be associated with the lowering of the degrees of freedom when compared to the structural glasses.

This paper is organized as follows. The experimental procedure is briefly explained in section 2. Section 3 presents the polymorphism of pure compounds and the two-component phase diagram. Section 4 describes the results for the complex dielectric permittivity and discusses the variation of the relaxation time with temperature confirming the non-Arrhenius behaviour and the broadening of the relaxation width when temperature approaches T_g . The relation between fragility and non-exponentiality together with the ratio between the crossover temperature T_c , provided by the MCT, and T_g temperature is also analysed. Conclusions are gathered in section 5.

2. Experiment

2.1. Materials

The pure materials were purchased from Aldrich Chemical Company with a purity of 99%. They were submitted to an additional purification process consisting of a vacuum sublimation at 313 K and 343 for NPA and NPG, respectively. The purity was checked by means of differential scanning calorimetry (Perkin–Elmer DSC-7). Mixed crystals were prepared from the melt of the pure materials in the selected molar composition by slow cooling to room temperature. Pure materials as well as mixed crystals were invariably treated under a controlled Ar atmosphere.

2.2. Dielectric measurements

The frequency and temperature dependence of the complex dielectric permittivity $\varepsilon^*(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu)$ was measured using a gain phase (Solartron Schlumberger 1260 with a Novocontrol BDC) from 10^{-2} to 10^6 Hz, an impedance analyser (HP-4192A) from 10^2 to 10^7 Hz and a coaxial line reflectometer (HP-4191A) from 10^6 to 10^9 Hz on the same planar cell consisting of two planar gold-plated brass electrodes (diameter 5 mm) separated by $50 \mu\text{m}$ thick silica spacers. The sample temperature is controlled by a temperature controller cryostat (Quatro, Novocontrol) using a heated N_2 gas stream. Additional details can be found elsewhere [19]. The mixed crystal material was introduced into the dielectric cell in liquid state. To prevent the possibility of hole formation in the inner-electrode space a mechanical device, which enables us to keep the electrode gap constant for the whole temperature range, was used. Likewise, the sample capacity was always checked before the measurements. Data acquisition was performed in the temperature domain ranging between 163 K and 333 K (i.e. from the glass transition temperature to the melting point) for three independent samples of the above-mentioned mixed crystal. All the measurements were made on slow cooling and stabilization at different temperature steps (± 0.2 K) to avoid undesirable changes in the kinetics of cooling.

2.3. X-ray diffraction and calorimetric measurements

X-ray diffraction measurements were performed by means of an INEL CPS120 high-resolution diffractometer (Debye–Scherrer geometry, transmission mode) and using the $\text{Cu K}\alpha_1$ ($\lambda = 1.5406 \text{ \AA}$) radiation. The apparatus is equipped with a liquid-nitrogen INEL CRY950 cryostat working in the 90–353 K range. Sample powders were introduced into Lindemann glass capillaries (0.5 mm diameter). Acquisition times of 30 min for the patterns and 10 min of stabilization time were used, the slewing speed being 1 K min^{-1} . Additional details can be found elsewhere [20, 21].

The C_p measurements were performed with a commercial modulated thermal analyser TA2910 system from TA Instruments Inc. A heating rate of 2 K min^{-1} and sample masses of about 5–10 mg were typically used. Standard DSC measurements on the same samples were performed with heating rates ranging between 2 and 5 K min^{-1} . The details of these measurements have been given elsewhere [20].

It must be pointed out that partial crystallization of the sample was never found, the x-ray diffraction, specific heat and dielectric measurements being reproducible on cooling and warming measurements.

3. Essential features of the pure compounds and of the two-component system

Pure compounds NPA ($(\text{CH}_3)_3\text{CCH}_2\text{OH}$) and NPG ($(\text{CH}_3)_2\text{C}(\text{CH}_2\text{OH})_2$) belong to a group of substances of common chemical structure $(\text{CH}_3)_{4-n}\text{C}(\text{CH}_2\text{OH})_n$, all of them displaying a face centred cubic OD phase. The low-temperature phase of NPA (triclinic) [22] transforms to the OD phase at 235.4 K, the latter being stable up to 329.8 K [20]. The brittle phase of NPG (monoclinic) transforms at 314.4 K to the OD phase and melts at 402.8 K [20]. Although the non-ergodic state corresponding to the OD phase of the pure compounds should be experimentally available, by means of a rapid and deep enough temperature quench, up to now, this state has been only reached for NPA by means of x-ray diffraction experiments [20]. The use of an ‘impurity’ to suppress crystallization has been already used in the study of structural glasses in the case of α -phenyl-*o*-cresol and *o*-terphenyl [23, 24]. In the present

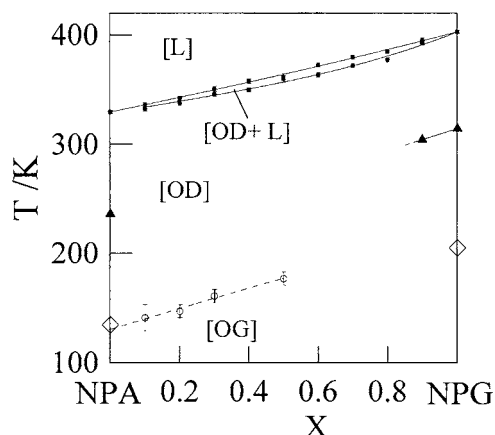


Figure 1. NPA/NPG two-component equilibrium phase diagram (●, two-phase OD + Liquid (L) equilibrium temperatures and ▲, low-temperature ordered to OD phase transition). Non-equilibrium glass transition temperatures T_g as a function of composition obtained by calorimetry (○) and by superimposing $\tau = 10^2$ s in the fits of the relaxation times (◇) for the pure components from [21] are also included.

case, the addition of a chemically and structurally similar kind of ‘guest’ molecule (NPG) into the ‘host’ lattice of NPA, gives rise to a continuous series of mixed crystals. Thus, pure components are completely miscible in the OD phase [20].

Figure 1 depicts the more significant results concerning the two-component equilibrium phase diagram as well as the non-equilibrium temperatures corresponding to the glass transition obtained by means of x-ray diffraction and specific heat measurements. Such a figure combines the glass transition temperatures measured experimentally for the mixed crystals together with those of the pure compounds obtained by assuming the characteristic relaxation time at T_g ($\tau = 10^2$ s) previously determined by dielectric spectroscopy [21]. As found a long time ago for normal alcohols [25], T_g is found to scale almost linearly with mole fraction. The mixed crystals with a high concentration of the component NPG do not undergo the glass transition and probably they partially crystallize into an orientationally ordered phase. The existence of a critical concentration ($X_c \approx 0.5$ in our case) below which long-range orientational order is lost has been widely obtained in solid solutions between a component with a multipolar moment and a non-polar component [26–29] as well as in mixtures between ferroelectric and antiferroelectric compounds [30–32]. It clearly follows from figure 1 that the decrease of T_g for the mixed crystals when the mole fraction goes to pure NPA is a direct consequence of the shorter time scale of the dynamics, which can be associated with a decrease of the intermolecular interactions as it has been inferred from thermodynamic analysis of such a two-component system [33, 34].

Figure 2(a) depicts the specific heat (C_p) anomaly as a function of temperature characterizing the typical relaxation process from the glassy state to the supercooled OD phase for the mixed crystal NPA_{0.7}NPG_{0.3}. Figures 2(b) and 2(c) show the molar volume and the volume expansivity variations as a function of temperature for the mixed crystal NPA_{0.7}NPG_{0.3} and for the NPA compound [20], respectively. The volume expansivity α_V , defined by the relationship

$$\alpha_V = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p \quad (1)$$

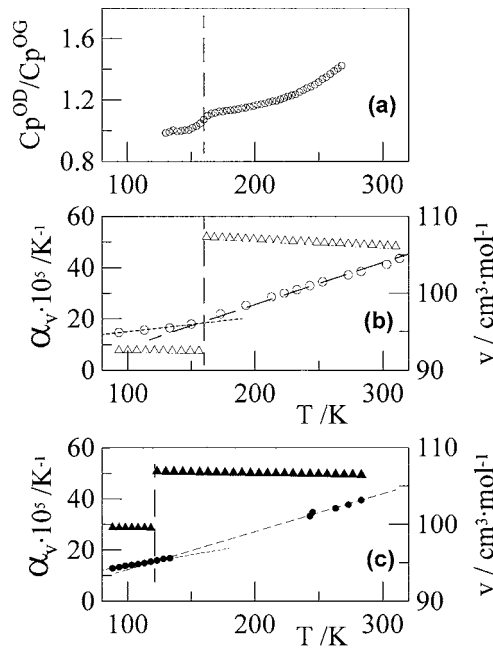


Figure 2. (a) Specific heat relation for the molecular mixed crystal $\text{NPA}_{0.7}\text{NPG}_{0.3}$ as a function of temperature. (b) and (c) Volume expansivity (Δ , \blacktriangle) and molar volume (\circ , \bullet) for the molecular mixed crystal $\text{NPA}_{0.7}\text{NPG}_{0.3}$ (b, open symbols) and for NPA (c, full symbols), as a function of temperature.

where v is the molar volume, has been calculated at each temperature. The continuous variation of the molar volume against temperature as well as the discontinuity in the volume expansivity are irrefutable signatures of the existence of the glassy state. It may be underlined that there are no available measurements of specific heat for the pure NPA compound through the glass transition. For orientational glasses belonging to the class of the strong glasses, according to the classification of Angell [7], the specific heat anomaly is usually more pronounced than expected. The same result comes out from figure 2(a). It is to be noticed from this figure that the specific heat, as well as the volume expansivity for the mixed crystal (figure 2(b)), can be measured from the OG state until the temperature stable domain corresponding to the high-temperature OD phase without the appearance of the transformation to the stable ordered low-temperature phase or to a metastable intermediate phase.

4. Results and discussion

4.1. Data analysis

As usual, the dielectric losses $\varepsilon''(\nu)$ were found to be asymmetrically broadened with respect to simple Debye behaviour and can be accounted for by using the empirical formula as a function of the frequency (ν) given by Havriliak–Negami (HN) [35]:

$$\varepsilon^*(\nu) = \varepsilon_\infty + \frac{\Delta\varepsilon}{[1 + (i2\pi\nu\tau)^\alpha]^\beta} \quad (2)$$

where ε_∞ stands for the dielectric high-frequency limit, $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ for the dielectric strength, α and β parameters determine the spectral shape and τ is the characteristic

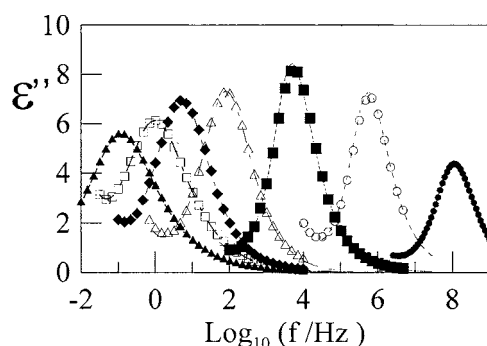


Figure 3. Imaginary ε'' part of the dielectric permittivity for various selected temperatures for the molecular mixed crystal $\text{NPA}_{0.7}\text{NPG}_{0.3}$: (▲) 163.2 K; (□) 168.2 K; (◆) 173.2 K; (△) 183.2 K; (■) 203.2 K; (○) 238.2 K; (●) 303.2 K. Continuous lines correspond to the Havriliak–Negami fits.

relaxation time. The four adjustable parameters ε_∞ , α , β and τ were simultaneously determined at each temperature in a fitting procedure of the H–N formula. As it has been observed elsewhere for other materials [10], ε_∞ is linearly dependent on temperature, the slope of which is about 0.002 K^{-1} for the temperature range studied. Such a result clearly points out the negligible effect of temperature on the value of this parameter. So, fixing the value of ε_∞ has no observable effect on the other three parameters over most of the temperature range. It is important to realize that for the high-temperature domain (from 313 to 333 K), information at frequencies well above the relaxation phenomena is rather scarce and there exist some difficulties in obtaining good fits of ε_∞ . In such a situation, the possibility of fixing ε_∞ reduces the scatter on the other three parameters and, of course, on the determination of the dielectric strength.

Figure 3 shows the frequency dependence of the imaginary part ε'' of the complex dielectric permittivity for various selected temperatures as well as the HN fits. The contribution of the DC conductivity to the response, which is mainly due to the known hydrogen bond effects, has been previously subtracted. The possible secondary relaxation peaks, i.e. the Johari–Goldstein relaxation processes [36], which in the present case could be associated with conformational disorder, did not appear in the measured frequency range providing an additional facility to analyse the mean (primary) α -relaxation.

The relaxation strength as a function of inverse temperature as determined from the fit of the HN function is shown in figure 4. According to the Onsager equation [37], the strength should be proportional to the inverse of the temperature. Nevertheless, such a fitting gave rise to a linear relation that does not pass through the origin, showing that this deviation indicates the existence of a co-operative behaviour that discards the possibility of the molecules rotating as free dipoles. Moreover, from the data represented in figure 4, it could be deduced that the strength does not follow the temperature variation expected from the MCT [6], for which $T\Delta\varepsilon \approx \text{const}$ at temperatures $T > T_c$ and $T\Delta\varepsilon \approx (T_c - T)^{1/2}$ at $T < T_c$ (see table 1). At a temperature around 220 K (which is close to the crossover temperature T_c as we will show below) the strength changes in its temperature dependence.

Also from the fit of HN function the shape parameters α and β have been determined (the $\alpha\beta$ product is plotted in figure 5). The former is close to 1 in the high-temperature domain ($T \geq 210 \text{ K}$), which means, as observed in other OD compounds, that the Cole–Davison (CD) function can accurately describe the non-Debye relaxation process. The temperature independent behaviour of β in the high-temperature region is in agreement with the MCT [6], for which the independent behaviour is predicted at temperatures above T_c . At a temperature

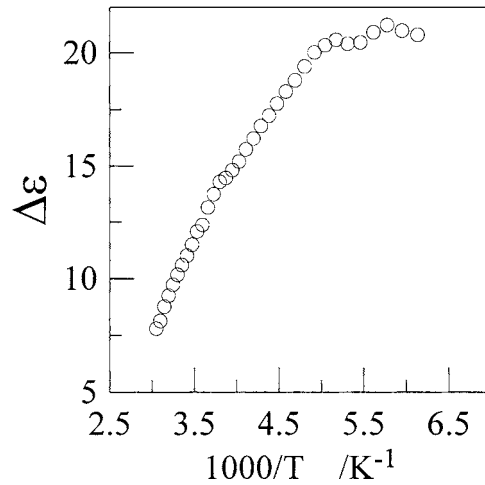


Figure 4. Dielectric strength as a function of inverse temperature as determined from the fit of the Havriliak–Negami function for the molecular mixed crystal $\text{NPA}_{0.7}\text{NPG}_{0.3}$.

Table 1. Parameters obtained from the fits of the temperature dependence of the relaxation time to the Arrhenius (A), Vogel–Fulcher–Tammann (VFT) and mode-coupling theory (MCT) equations.

Type of fit	τ_0 (s)	A (K)	T_0 (K)	T_c (K)	γ
A	$19.0 (\pm 0.3) \times 10^{-16}$	$5585 (\pm 88)$	—	—	—
VFT	$5.85 (\pm 0.2) \times 10^{-15}$	$1261 (\pm 94)$	$75.3 (\pm 2.0)$	—	—
MCT	$3.7 (\pm 0.6) \times 10^{-10}$	—	—	$226.8 (\pm 2.0)$	$4.4 (\pm 0.6)$

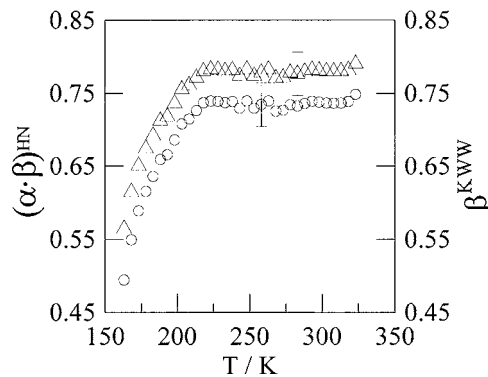


Figure 5. Shape parameters $\alpha\beta$ (○) or β^{KWW} (Δ) as a function of temperature as determined from the fit of the Havriliak–Negami function for the molecular mixed crystal $\text{NPA}_{0.7}\text{NPG}_{0.3}$.

close to the onset of the mentioned co-operative effects, it is no longer possible to fit accurately the dielectric loss by using the CD function. Approaching the glass transition temperature, the common feature of many glass-forming materials, i.e. a decrease of the shape parameters with temperature, is found, indicating the strong deviation from the Debye behaviour. If the relaxation is described by means of the Kohlrausch–Williams–Watts (KWW) stretched relaxation function [38],

$$\phi(t) \equiv \exp[-t/\tau]^{\beta^{\text{KWW}}} \quad (3)$$

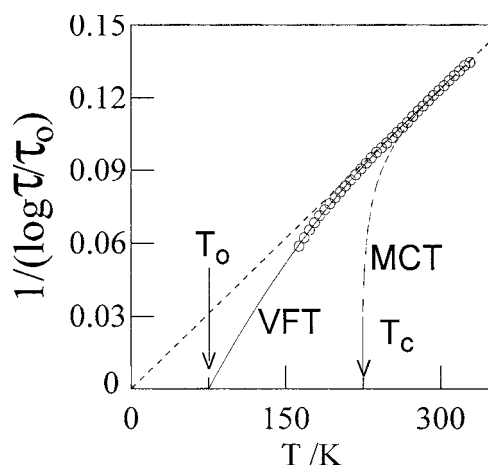


Figure 6. $1/\log(\tau/\tau_0)$ (τ_0 being the attempt time corresponding to the Arrhenius fit of the high-temperature domain) against temperature for the molecular mixed crystal $\text{NPA}_{0.7}\text{NPG}_{0.3}$. Arrows indicate characteristic temperatures (T_0 , Vogel temperature and T_c , critical or crossover temperature).

the β^{KWW} parameter, calculated by the recent established relationship ($\beta^{KWW} = ([\alpha\beta]^{HN})^{1/1.23}$) [39], follows the same variation with temperature (see figure 5).

4.2. Relaxation time

The temperature dependence of the relaxation time describing the dynamic behaviour of the α -relaxation is easily obtained from the fit of the HN function. Figure 6 shows a plot of $1/\log(\tau/\tau_0)$ against temperature for the mixed crystal, τ_0 being the attempt time corresponding to the Arrhenius fit of the high-temperature domain. The simple picture of thermal activation with temperature independent activation energy (Arrhenius law) only fits for a narrow high-temperature domain corresponding to the OD phase, particularly between 283 and 333 K. The associated activation enthalpy ($\Delta H = AR$, where R is the gas constant) is 46.4 kJ mol^{-1} . This value, which is close to those of the pure compounds NPA (49.8 kJ mol^{-1}) [21] and NPG (45.9 kJ mol^{-1}) [40], is an indication of the existence of strong intermolecular interactions due to the hydrogen bonds. Similar values of activation enthalpies have been obtained for OD phases of alicyclic alcohols and branched alcohols [41].

The observed trend to increase the activation energy when approaching the glass transition gives rise to the fit of the empirical law established by Vogel–Fulcher–Tammann (VFT) [42]

$$\tau = \tau_0 \exp \left[\frac{A}{T - T_0} \right] \quad (4)$$

where τ_0 is an attempt time and T_0 ($T_0 < T_g$) is the divergence temperature (Vogel temperature) for the relaxation time. This VFT law, which is known to fit the relaxation time as the temperature approaches T_g as a consequence of the enhanced co-operative motions, gives rise to a strong consistency with the experimental data. The T_0 temperature is found to be 75.3 K (see table 1) which is certainly far away from the T_g temperature. As we will indicate later, such an effect is a direct consequence of the low fragility of this material.

According to the MCT [6], the temperature dependence of the relaxation dynamics follows a power law as

$$\tau = \tau_0 ((T - T_c)/T_c)^{-\gamma} \quad (5)$$

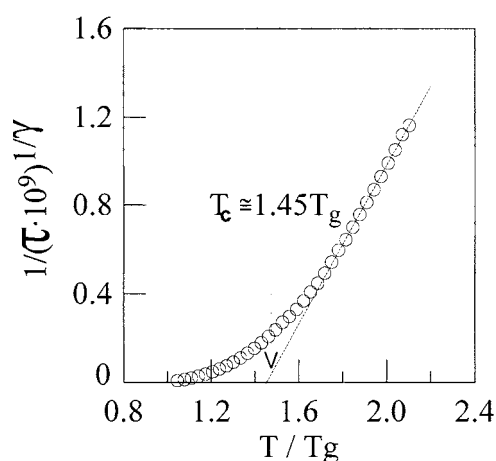


Figure 7. $1/(\tau \times 10^9)^{1/\gamma}$ as a function of T/T_g for the molecular mixed crystal $NPA_{0.7}NPG_{0.3}$. The arrow indicates the characteristic T_c critical temperature.

for $T > T_c$. One of the most recent important findings is the existence of a crossover or critical temperature (around $1.2 T_g$) where qualitative dynamical changes take place [15, 16]. Following a very recent procedure to determine T_c [43], the temperature dependence of $1/(\tau \times 10^9)^{1/\gamma}$ as a function of T/T_g , where T_g was taken as the temperature at which $\tau = 10^2$ s, has been plotted (figure 7). By means of such a procedure $T_c \approx 1.45 T_g \approx 226$ K is found, which is certainly close to the temperature where both shape parameter $[\alpha\beta]^{HN}$ (or β^{KWW}) and the relaxation strength display the strongest temperature changes. It may be underlined that certainly, an *exact* determination of T_c would need higher-frequency data and, therefore, the above determination must be assumed as a low limit for T_c . The resulting crossover temperature is quite different when compared to the values found for structural glasses [43]. Until now, many of the MCT predictions have been compared to experimental data for fragile systems. Recent studies for the strong structural glass B_2O_3 [17, 18] have shown that the existence of strong directional bonds influences the dynamics, particularly, the vibrational contribution to the dynamic structure factor in the low-temperature region. Thus, the crossover temperature, which was settled at about $1.2 T_g$ for fragile glasses [15], was enlarged to $1.6 T_g$ [17] or $1.5 T_g$ [18] for the strong glass former B_2O_3 . The exponent γ obtained from the fit of our data was $4.4 (\pm 0.6)$, which is certainly higher than previous reported values (between 2 and 4) for relatively fragile structural glasses [43].

It has been pointed out that when an MCT is applied to diluted orientational glasses two contributions to the rotation–translation coupling should be present, i.e. between the centre-of-mass displacements and the orientational motions and between these orientational motions and the random strain fields produced by the substitutional disorder [24, 28]. In the present case, the implication of this chemical disorder would seem to be negligible as can be inferred from the non-variation of the Bragg peak's width with temperature. Although such a result must be cautiously considered due to the used powdered samples, previous works have shown the same conclusions in single crystal studies [24, 44]. In contrast, for quadrupolar glasses the broadening of the width of the Bragg peaks has been clearly observed [45]. Nevertheless, figure 2(b) shows that the discontinuity jump in the volume expansivity takes place at a temperature close to the C_p anomaly. This means that the structural and the orientational relaxation processes freeze together and, then, a coupling between orientation and translation

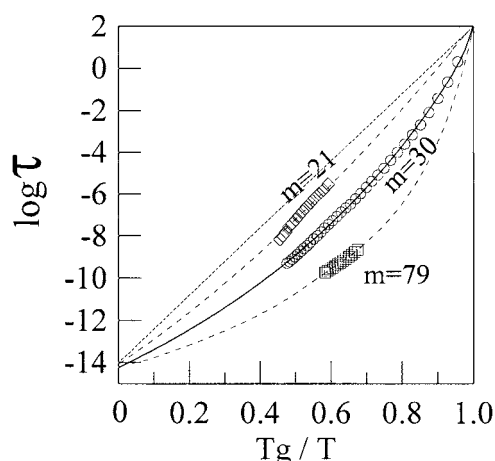


Figure 8. $\log \tau$ against T_g/T (Angell plot) for the NPA (\diamond), NPG (\square) and molecular mixed crystal $\text{NPA}_{0.7}\text{NPG}_{0.3}$ (\circ). The value of the fragility coefficient m is also included.

takes place. For NPA the situation is quite different because the T_g temperature obtained by superimposing $\tau = 10^2$ s ($T_g = 135$ K) is relatively far away from that obtained by x-ray diffraction data ($T_g = 123$ K) [20]. Moreover, the volume expansivity jump at the transition is smaller for the NPA than for the mixed crystal. In contrast, the volume expansivity value in the OG state for the mixed crystal is smaller than that of the pure material. In addition, the lattice parameters of the fcc lattice for the NPA and the mixed crystal at their respective glass transition temperatures are equal (8.60 \AA) [20]. Considering the molecular van der Waals volumes of NPA and NPG (102.6 and 108.9 \AA^3 respectively) it is quite evident that a higher packing is present in the OG phase of the mixed crystal and can be assumed as the reason for the orientational–translational coupling in the mixed crystal. This maybe the explanation why the quench is easier in the mixed crystals than in pure NPA and thus the measurements can be made in real time at low temperature. In spite of the lack of the structures for NPA and for the mixed crystal, these steric considerations can be made in order to analyse the existence of a higher number on unfavourable energetically dipole orientations due to such a coupling. Although the partial contribution to the C_p anomaly of the freezing of the translational degrees of freedom is known to be small, the contribution of the coupling to the orientational relaxation process remains an overwhelming research subject.

4.3. Fragility

The sketch of the relaxation time for NPA, NPG and the molecular mixed crystal $\text{NPA}_{0.7}\text{NPG}_{0.3}$ describing the strong/fragile behaviour is displayed in an Angell plot (figure 8). Such a plot indexes the temperature dependence of the relaxation time of glass formers by means of the fragility parameter, which is defined [46] by the equation

$$m = \left. \frac{d \log \tau}{d(T_g/T)} \right|_{T=T_g} . \quad (6)$$

The fragility of pure materials NPA and NPG has been recently published [21]. NPA is an example of strong behaviour ($m = 21$) which is usually found in simple planar compounds such as thiophene [47]. In contrast, NPG displays a fragile behaviour ($m = 79$). The increase

of the fragility in OG has been suggested [48] as a consequence of an increase of the lattice disturbance due to the molecular reorientation; this reasoning matches up with the packing coefficient of the NPA (0.59) and NPG (0.64), both at 313.2 K. The mixed crystal displays a slightly higher fragility ($m = 30$), as cyclohexanol [47] ($m = 40$), cyclooctanol ($m = 33$) [10], and cyanoadamantane ($m = 35$) [49].

A tentative and phenomenological relation between the fragility and the stretched exponential relaxation was proposed by Böhmer *et al* [48] as the linear relationship:

$$m = 250 - \beta^{KWW}(T_g)320 \quad (7)$$

where $\beta^{KWW}(T_g)$ is the Kohlrausch–Williams–Watts (KWW) width parameter at the glass transition temperature.

For the mixed crystal, the strong decrease of the shape parameter with decreasing temperature moves away the calculated fragility with the Böhmer equation from the real value determined from the Angell plot. Thus, at T_g , the β^{KWW} value is around 0.55, which provides a fragility value of 74 by using equation (7), while that calculated from the Angell plot (i.e. equation (6)) is determined to be 30. The chemical disorder, which is thought to introduce additional anisotropy in the molecular interactions [48], can be used as an argument for this behaviour. In addition, it should be noticed that orientationally disordered mixed crystals are known to be notable exceptions from the general trend given by equation (7) [48].

5. Conclusions

The results of the complex dielectric permittivity for the molecular mixed crystal $[(CH_3)_3CCH_2OH]_{0.7}[(CH_3)_2C(CH_2OH)_2]_{0.3}$ in the orientationally disordered, the supercooled orientationally disordered and the orientationally glass phases have been reported at frequencies from 10^{-2} to 10^9 Hz and temperatures from 163 to 333 K.

The analysis of the dielectric spectrum of this molecular mixed crystal exhibits an increasingly non-Debye relaxation, a decrease of the shape parameters and a faster than Arrhenius behaviour in the relaxation time as the glass transition temperature is approached.

The scaling of the α relaxation has been characterized by two characteristic temperatures, the Vogel temperature T_0 and the critical or crossover temperature T_c . In relation to the critical temperature ($T_c \geq 1.45 T_g \approx 226$ K), it is certainly close to the temperature where both shape parameter $[\alpha\beta]^{HN}$ (or β^{KWW}) and the relaxation strength display the strongest changes. This behaviour is markedly different when compared to those found for structural glasses [43]. We have also shown that the empirical VFT law gives an accurate description of the temperature dependence of the relaxation time in the whole temperature range from the OG to the OD phases. This fact agrees to the low fragility displayed for the studied molecular mixed crystal.

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