Dielectric study of dynamics of organic glasses

Yunlong Cui†, Javier Wu†, Natalie Kamanina†, Alfredo Pasaje†, Alexander Leyderman†§, Alfonso Barrientos†, Marcus Vlasse‡ and Benjamin G Penn‡

† Department of Physics, UPR-RUM, Puerto Rico 00680-9016, USA
‡ NASA-MSFC, Alabama 35812, USA

E-mail: `alex@feynman.upr.clu.edu`

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Abstract. The dynamics of organic compounds 2-cyclo-octylamino-5-nitropyridine (COANP), (S)-2-N-α-(methylbenzylamino)-5-nitropyridine (MBANP), 2-(N-prolinol)-5-nitropyridine (PNP), and N-(4-nitrophenyl)-(L)-prolinol (NPP) were studied by dielectric relaxation spectroscopy in the frequency range of 10 Hz–2 MHz and differential scanning calorimetry (DSC). The dielectric and DSC studies showed that COANP, MBANP and PNP underwent glass transition. However, NPP crystallized so rapidly upon cooling that the glass state could not be observed. It was found that the crystalline process of COANP did not slow the structure relaxation of COANP glass. The relaxation times fitted well to the empirical Vogel–Fulcher equation $\tau = \tau_\infty \exp[E_a/k_b(T - T_{VF})]$. The activation energies E_a and the Vogel–Fulcher temperature T_{VF} were 54.5 meV and 239 K for COANP, 86.2 meV and 249 K for MBANP and 84.9 meV and 245 K for PNP, respectively. The crystalline temperatures of COANP and MBANP were given as 300 K and 330 K, respectively. An anomalous behaviour of the dielectric permittivity of PNP glass was observed.

1. Introduction

The investigation of the relaxation dynamics of organic compounds 2-cyclo-octylamino-5-nitropyridine (COANP), (S)-2-N-α-(methylbenzylamino)-5-nitropyridine (MBANP), 2-(N-prolinol)-5-nitropyridine(PNP), and N-(4-nitrophenyl)-(L)-prolinol (NPP) is an interesting area because of the potential nonlinear applications of these compounds both in the glass and crystal states. The glass transition temperatures of these compounds are very low, thus to fabricate an electro-optic device with these organic glasses, it is necessary to curtail their crystallization rates. However, poled glass films of organic compounds such as COANP and MBANP exhibit adequate nonlinear susceptibilities [1]. On the other hand, thin single-crystal organic films grown from the melt can directly lead to waveguide applications [2, 3]. Although recrystallization of some undercooled melts are extremely slow, sudden recrystallizations may occur rapidly if the melts are cooled to glasses first and then heated again [4].

A dielectric study of the dynamics of these organic compounds is not only important to help monitor crystal growth, but also to correlate results with other dielectric investigations. Recently, real-time dielectric spectroscopy studies of the molecular dynamics of relaxation during crystallization of low-molecular-weight compounds [5] and polymers [6–9] have been reported. COANP, MBANP, PNP and NPP are low-molecular-weight compounds with anomalous solidification behaviours, which are good candidates in which to study the mechanism of the transition from glass to crystal. Eich *et al* [1] carried out dielectric relaxation measurements of COANP and MBANP and found that the loss maximum, which corresponds to the relaxation time τ, when plotted in an activation diagram shows a nonlinear Arrhenius-type dependence. Lahajnar *et al* [4], Kind *et al* [10] and Dolinsek *et al* [11] studied the dynamics of the super-cooled liquid state of COANP [4, 10, 11], MBANP, PNP and NPP [4] and found that the temperature dependence of the self-diffusion coefficients of COANP, MBANP and PNP could be well described in terms of Vogel–Fulcher (VF) behaviour, while the crystallization of NPP was too fast to measure. In this paper, the dielectric permittivity and dielectric loss of COANP, MBANP, PNP and NPP compounds were measured in the frequency range of 10 Hz to 2 MHz with a LCR meter in the temperature range from the melting point to a temperature which is much lower than the glass transition point. It was found that COANP, MBANP and PNP glasses formed at the glass transition temperatures T_g, as determined by the differential scanning calorimetry (DSC) measurements, and the relaxation times satisfied the empirical VF equation. However, NPP crystallized so rapidly upon cooling that the glass state could not be observed. The experimental results are consistent with those reported in [4]. An anomalous behaviour of dielectric permittivity of PNP glass was observed.

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§ Author to whom correspondence should be addressed.

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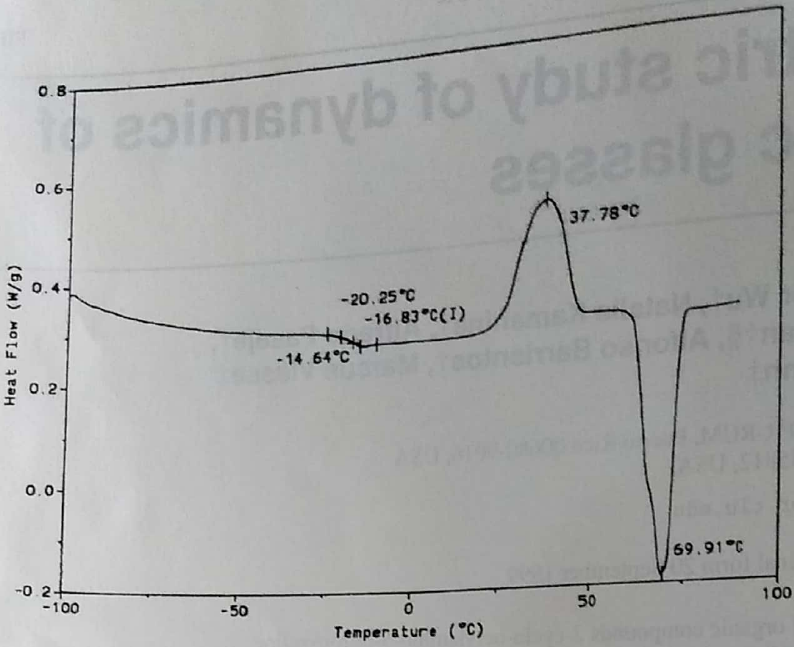


Figure 1. A typical MDSC scan on a COANP sample with heating rate of 5 K min^{-1}.

2. Experimental details

COANP, MBANP, PNP and NPP polycrystalline compounds were synthesized and purified with standard preparation procedures similar to those published [12–15]. The dielectric measurements were performed in the frequency range of 10 Hz–2 MHz with a QuadTech LCR meter (model 7600). It takes around 5 min to complete a 200 point scan from 10 Hz–2 MHz with medium accuracy. The temperature of a sample was set to a value in the range of 80–400 K by a MMR micro-miniature refrigeration system coupled to the K-20 programmable temperature controller. In the dielectric measurement, the temperature step was taken at 1–2° at $T > T_g$, and 5–10° below T_g. The refrigerator cools a sample from ambient to about 80 K in 20 min.

The measurement cell, as shown in figure 1 of [2], consists of two parallel quartz plates on which gold layers were deposited. One of the plates has a depression at its centre with the diameter of about 10 mm. Plates with depression depth of 50 μm, 100 μm and 200 μm were used. The second plate serves as a lid. The recess is surrounded by a groove. A cell filled with the powder of the compound was put onto a hot plate and heated to its melting point, then the cell was introduced into the MMR refrigerator, in which the cell was cooled with high-pressure nitrogen passing through tiny metal tubes surrounding the sample holder.

In dielectric measurements, the results could be expressed in terms of either complex permittivity or complex conductivity [16], which are mutually converted. In this experiment, the real and imaginary parts of the complex dielectric permittivity ε^* were obtained with the assumption that the cell is equivalent to a circuit consisting of an ideal capacitance C_p in parallel with a pure resistance R_p. The dielectric permittivity ε', dielectric loss ε'', and tangent dielectric loss, $\tan\delta(\varepsilon''/\varepsilon')$, of a compound are given as $\varepsilon' = C_p/C_0$, $\varepsilon'' = 1/(R_pC_0\omega)$ and $\tan\delta = 1/(R_pC_p\omega)$, respectively, where ω is the angular frequency, C_0 is the capacitance of a empty cell. The absolute value of $\tan\delta$ is independent of the geometric dimensions of the cell. For the 100 μm cell, C_0 is 6 pF, and $\tan\delta$ is very small except in the region near the high-frequency edge.

The dielectric relaxation processes are usually fitted with the phenomenological Havriliak–Negami [17] formula:

$$\varepsilon^* = \varepsilon' - \mathrm{i}\varepsilon'' = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)/[1 + (\mathrm{i}\omega\tau)^\alpha]^\nu \quad (1)$$

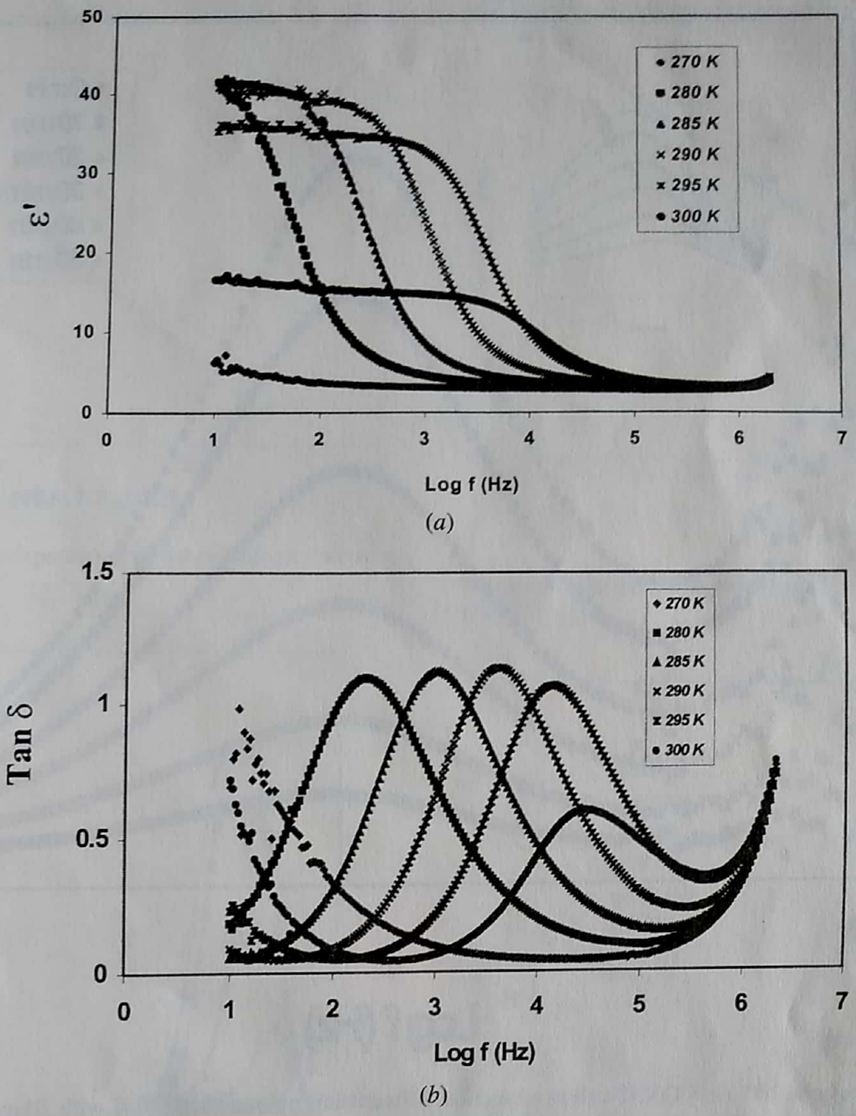
where α and ν are shape parameters. The relaxation time τ was derived from f_{max}, at which ε'' shows a maximum [18, 19]. In our experiments, all of the relaxation data of COANP, MBABP and PNP glasses fitted well with the Cole–Davidson form of (1), with $\alpha = 1$, $\nu \neq 1$. At high temperatures, the data fitted with a single-relaxation-time Debye formula, which was found to apply to the relaxation of polar liquids and plastic crystalline phases [20] with $\alpha = \nu = 1$. If the relaxation behaviour is of the Debye type, the relaxation time τ connected to the critical frequency f_m, at which $\tan\delta$ reaches its maximum A_m, is given by the equation

$$2\pi f_m\tau = A_m + (1 + A_m^2)^{1/2}. \quad (2)$$

The DSC technique provides the precise determination of the melting temperatures T_m, crystallization temperature T_c and glass transition temperature T_g. A TA instrument, model 2920 modulated differential scanning calorimeter (MDSC) was used to study the thermal characteristics of the four compounds. The samples (about 5 mg each) were encapsulated in hermetic aluminum cells and positioned in the MDSC chamber. The samples were cooled down in a home-made chamber filled with liquid nitrogen. Each sample was cycled from crystal to melt, super-cooled liquid, glass state, then to a temperature well below the glass transition, and back, to above the melting point. This was performed at least twice with heating or cooling rates of 5 K min^{-1}. An empty aluminum cup was used as the reference.

3. Results and discussion

Figure 1 shows a typical thermal behaviour of the COANP sample. The sample was previously cooled down to



(*a*)

(*b*)

Figure 2. (*a*) The dielectric permittivity and (*b*) the tangent dielectric loss of a 100 μm COANP cell as function of frequency measured at various temperatures.

−160 °C and on heating, it melted at 72 °C. A step transition upon heating from the glass to the liquid-like state on the heating cycle was clearly seen at −16.83 °C, recrystallization occurred upon heating at 37.78 °C and the crystal melted at 69.9 °C. However, the DSC experiments show that pristine, super-heated COANP melts do not crystallize upon cooling. The fact that the COANP glass crystallized on heating is important to organic crystal growth from a melt, because it took a few days to crystallize a COANP from melt confined in the Pockels cell at room temperature [2]. T_m, T_c and T_g of COANP, MBANP, PNP and NPP are given in table 1, where NPP crystallized upon cooling at 350 K from the melt, and no crystallization peaks were found for MBANP and PNP.

The melts of COANP, MBANP, PNP and NPP just below their melting points can be cooled to as low as 80 K. However, below the glass transition temperatures T_g, as determined by DSC measurements, of COANP, MBANP and PNP, the dielectric permittivity of the glasses are roughly constant irrespective of the temperature and frequency, and the tangential dielectric losses are extremely small. As the temperatures increase to those above T_g, the glasses exhibit structural relaxation. Figures 2(*a*) and 2(*b*) give the typical frequency dependence of the dielectric permittivity and the tangential dielectric loss, respectively, of a COANP glass embeded within a 100 μm cell measured at various temperatures. It can be seen from figure 2(*a*) that the curve of 270 K in the low-frequency region starts to bend at high values; a step forms in the curve of 280 K; and a plateau appears at the curve of 285 K, the plateau extends to the high-frequency region, but its height decreases as the temperature increases. The curves are well fitted with the real part of the Cole–Davidson formula. The structural relaxation of the COANP glass at 270 K can be deduced

Table 1. MDSC measurements of the glass transition temperature T_g, melting temperature T_m and crystalline temperature T_c of COANP, MBANP, PNP and NPP with cooling and heating rates of 5 K min^{-1}.

Compound	T_g (K)	T_m (K)	T_c (K)
COANP	258	345	314
MBANP	273	361	
PNP	273	365	
NPP		392	350

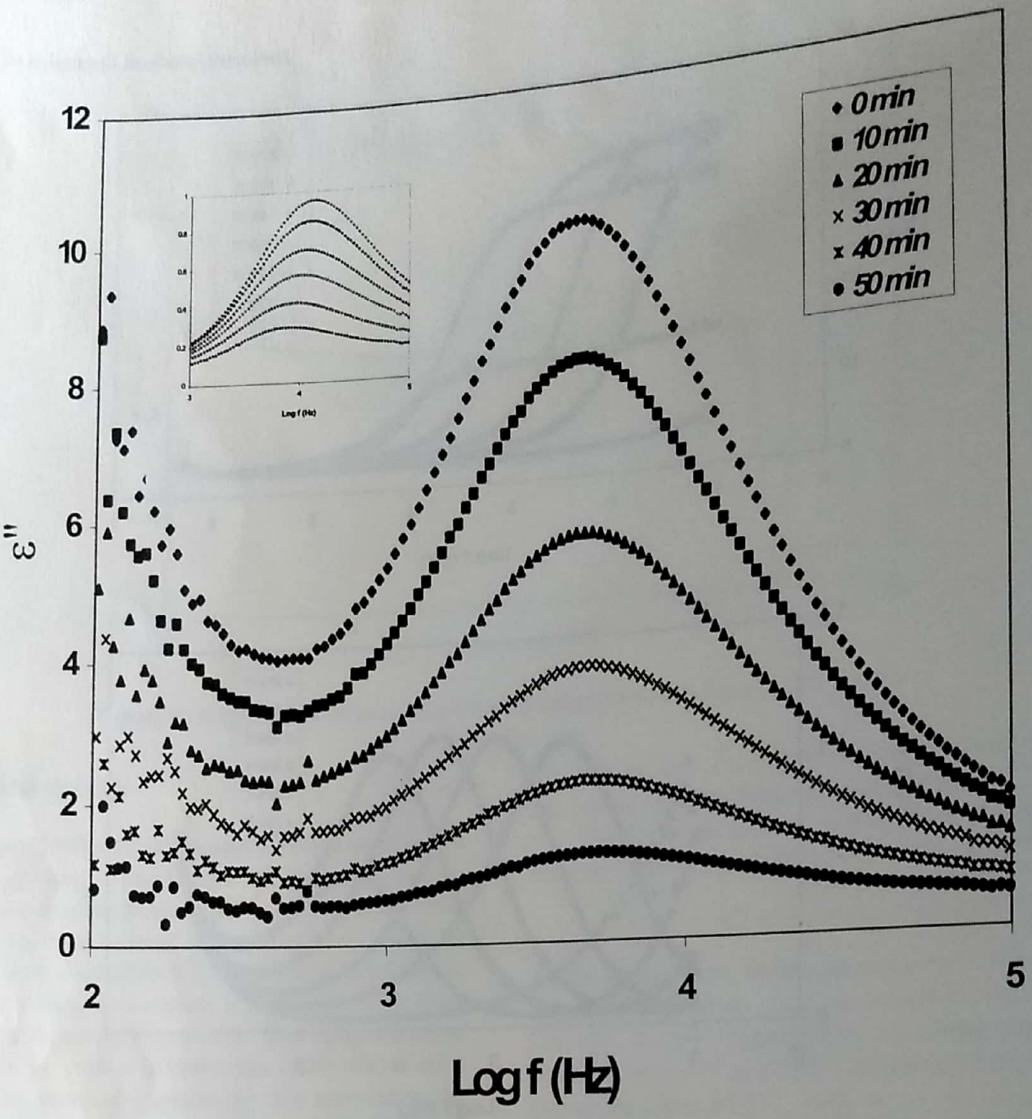
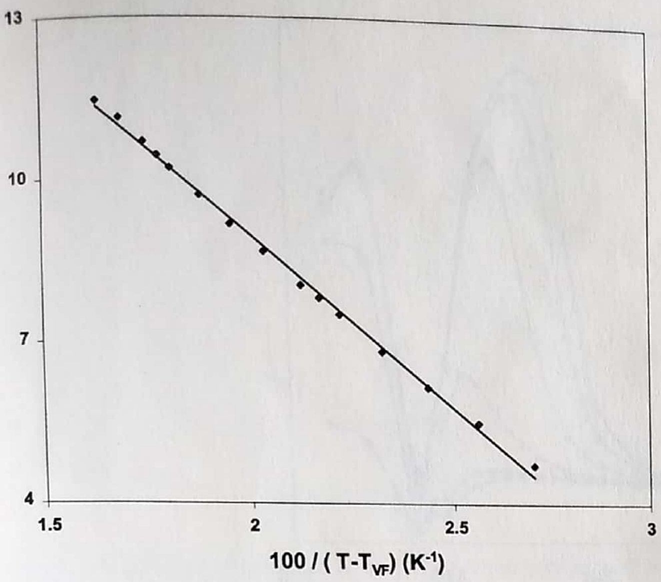


Figure 3. The dielectric loss of a 200 μm COANP cell as a function of frequency, measured at 296 K with 10 min, 20 min, 30 min, 40 min and 50 min intervals. The inset gives the corresponding tangential dielectric loss.

from figure 2(*b*), in which the dielectric loss of the COANP glass at this temperature is significantly larger in the low-frequency region. At 280 K, a well-developed peak appears and then shifts from low frequency to high frequency as the temperature increases. It is interesting to note that below 295 K, the heights of peaks are almost the same because the crystallization rates are small; and the height of the peak at 300 K is much lower than those of 280 K, 285 K, 290 K and 295 K due to an increased state of crystallization of the COANP glass. Figure 3 shows curves of the frequency dependence of the dielectric loss of a 200 μm COANP glass measured at 296 K, each one at 10 min intervals from top to bottom. It is well known that the frequency of maximum loss of a polymer glass will shift towards the lower frequency [9] due to aggregation of crystallization. However, the effect of crystallization on structure relaxation of low-molecular-weight compounds, such as COANP is not significant. It is found in figure 3 that the height of the peak decreases with time, however the peak position is not shifted. In other words, the crystallization process did not slow down the relaxation process of the COANP glass at 296 K, at least within 1 h, and thus the relaxation times extracted are reliable. The result is consistent with that in [5] in which the shift of the α-peak position of a low-molecular-weight compound started at a degree of crystallinity of above 90%. The COANP glass during the crystallization process can be regarded as a two phase system: with glass and crystal parts. The dielectric loss ε'' during crystallization can be described by a weight superposition of the two limiting spectra [6], where the dielectric loss $\varepsilon''(f,t) = (1 - N(t))\varepsilon''_{glass}(f) + N(t)\varepsilon''_{crystal}(f)$ and $N(t)$ is crystallinity. Since $\varepsilon''_{glass}(f) \gg \varepsilon''_{crystal}(f)$ and $\varepsilon''(f,t) \cong (1 - N(t))\varepsilon''_{glass}(f)$, if crystallization does not proceed too fast. The inset of figure 3 shows the tangential dielectric loss of the sample. It is worthy to note that both the position and the height of the original tangential dielectric peak are altered severely. The shape parameter ν decreases with time, but the relationship of the peak position to the peak height of each curve satisfies equation (2). The relaxation times were calculated by equation (2) in the temperature range from 278 K to 300 K during which well-developed peaks are observed. Figure 4 shows the temperature dependence of the relaxation time. The line is a fit to the empirical VF equation:

$$\tau = \tau_\infty \exp\left[E_a/k_b(T - T_{VF})\right] \qquad (3)$$

where E_a is the activation energy, τ_∞ the inverse attempt frequency and T_{VF} the VF temperature. The activation



igure 4. The temperature dependence of the relaxation time of a OANP glass.

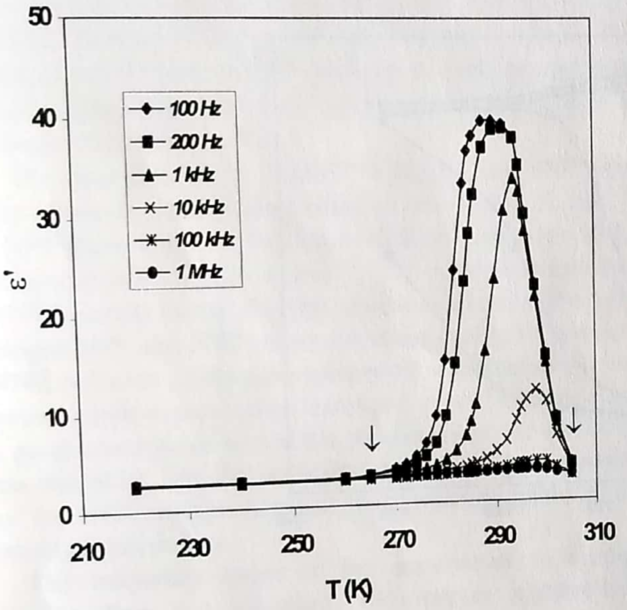


Figure 5. The dielectric permittivity of a 100 μm COANP cell measured as a function of temperature at various frequencies.

energy in the equation is different from that in the Arrhenius equation. The VF parameters are not identical, and depend a little on the fitting temperature.

The temperature dependence of the dielectric permittivity of the 100 μm COANP glass at various frequencies is given in figure 5. It is found that our results agree with those reported by Eich *et al* [1] when the temperature is less than 290 K. As the temperature increases, because the crystallization of the COANP liquid-like state accelerates, the dielectric permittivity for all frequencies decreases rapidly. One can find three different regions in figure 5 (see the two vertical arrows): the pure glass state that exists for temperatures lower than 265 K, below which the dielectric permittivity are independent of temperature and frequency; the crystal state exists at temperatures higher than 300 K; and the transition (structure relaxation process) state of glass to crystal that exists between 265 K and 300 K. The VF equation can be used to determine the glass transition temperature T_g by setting $\tau(T_g) = 100$ s [21]. For COANP, T_g is calculated as 263 K.

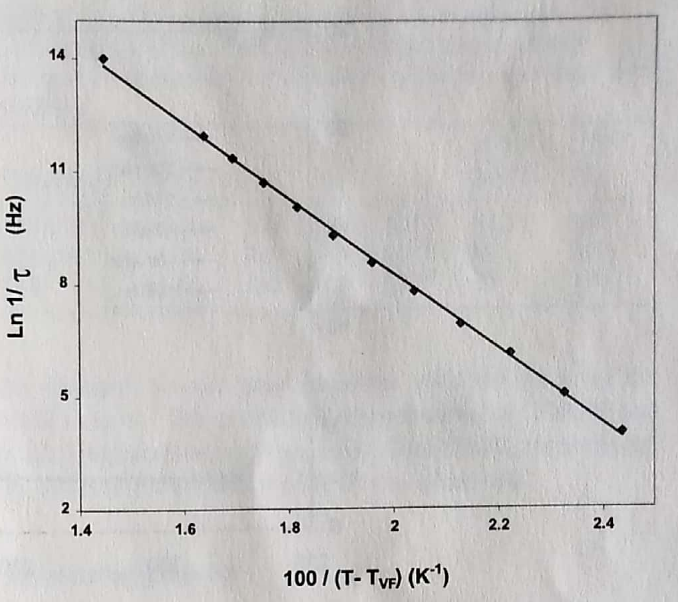


Figure 6. The temperature dependence of the relaxation time of a MBANP glass.

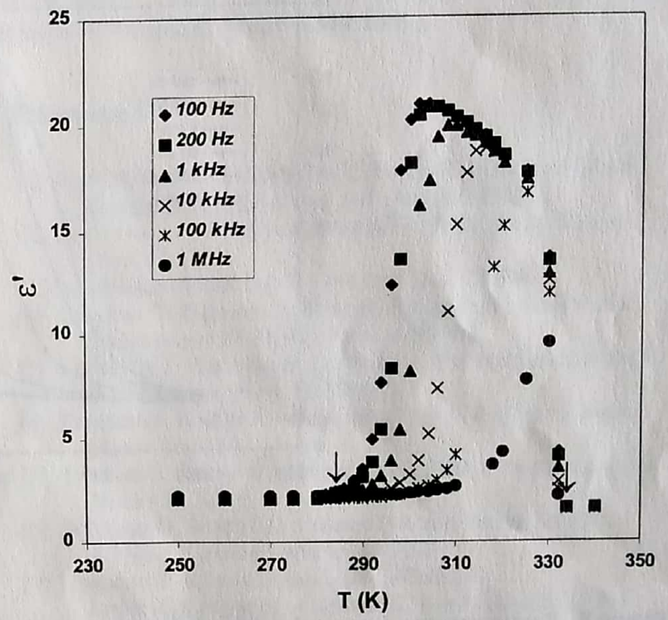
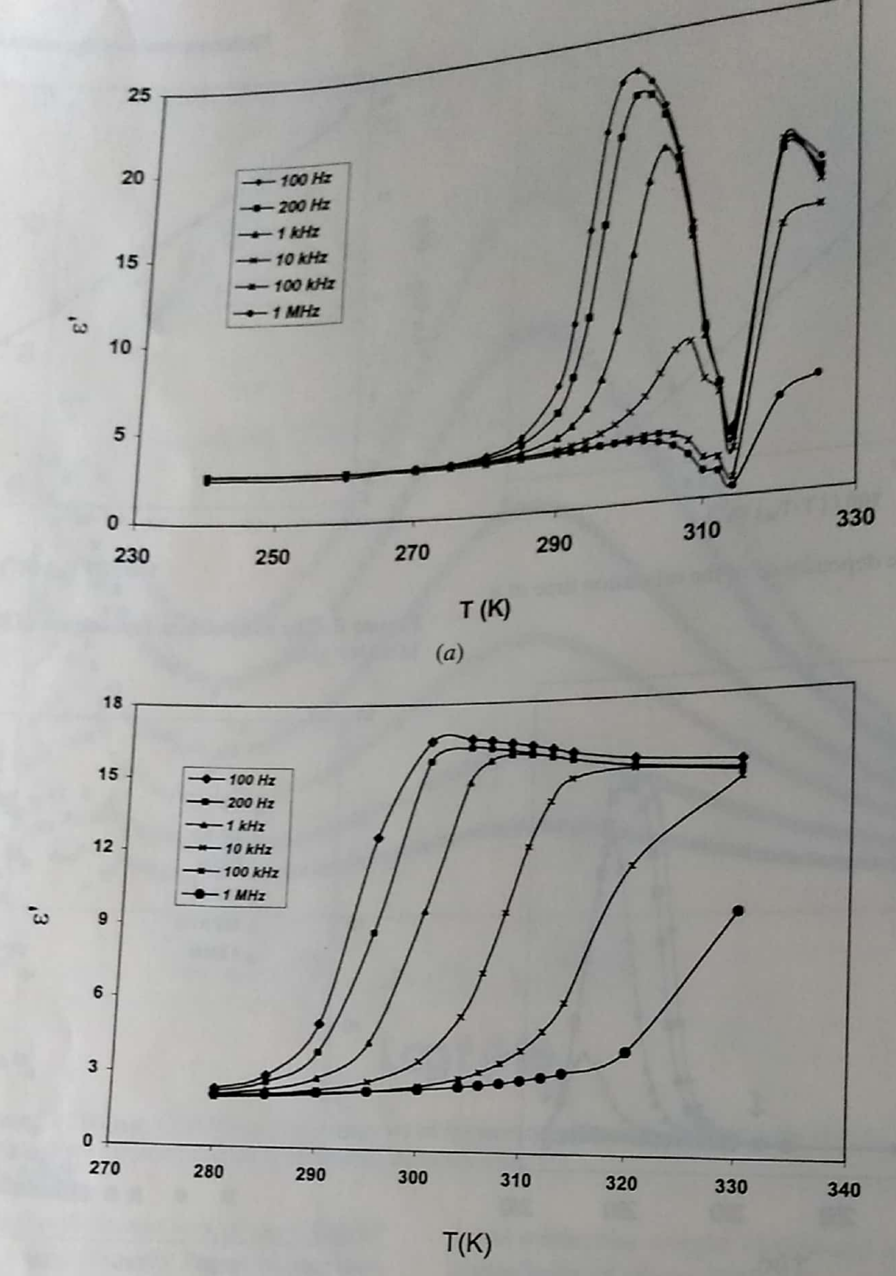


Figure 7. The dielectric permittivity of a 100 μm MBANP cell measured as a function of temperature at various frequencies.

For a MBANP glass, the frequency dependences of the dielectric permittivity and tangential dielectric loss are similar to those of the COANP glass. The dielectric loss peak appears at 290 K, and shifts to higher frequency as the temperature increases and reaches the high-frequency edge at 320 K. The height of the peak increases slightly with increasing temperature. The plot of the relaxation time of a 100 μm MBANP glass against temperature is given in figure 6. One can see that the relaxation time follows VF behaviour. The temperature dependence of the dielectric permittivity of the MBANP glass for various frequencies is given in figure 7. A series of lambda-like peaks divide the plot into three areas (see the two vertical arrows): crystal state, glass state and mixed transitional state. The critical



(*a*)

(*b*)

Figure 8. The temperature dependence of the dielectric permittivity of a 100 μm PNP cell measured after the sample was (*a*) cooled from the melt to a glass and heated to 325 K and (*b*) cooled down from 325 K to 240 K and heated again.

crystalline temperature of MBANP is given as 330 K by analogy with that of COANP glass.

For PNP glass, although the frequency dependence of tangential dielectric loss is similar to those of COANP and MBANP glass, the frequency dependence of the dielectric permittivity is different. Figure 8(*a*) gives temperature dependence of the dielectric permittivity of a 100 μm PNP glass for various frequencies. Below 310 K, the curves are similar to those in figure 5. The dielectric permittivity around 310 K is very low, it changes abruptly as the temperature increases above this temperature. We stopped at 325 K and let the sample cool down and stabilize at room temperature for 12 h and then cooled the sample down to 240 K, and repeated the dielectric measurement. The repeated temperature dependence of the dielectric permittivity of the sample is given in figure 8(*b*). The results in the figure 8(*b*) are reproducible if the sample is cooled and heated again. Figures 8(*a*) and 8(*b*) are quite different, but the corresponding curves of tangential dielectric loss are almost the same. The results in figure 8(*a*) and 8(*b*) are reproducible on different PNP sample although heterogeneity of a sample could not be excluded. It is reasonable to suggest that as in ethanol [6], there are two glass transition states in PNP: structure glass and glassy crystal. As the sample was heated to 310 K, the structure-glass state changed to the glassy-crystal state. Figure 9 gives the temperature dependence of the relaxation time of a 100 μm PNP glass. It can be seen that the relaxation time satisfies the VF equation well.

In a nuclear magnetic resonance (NMR) experiment [4], it was reported that sudden recrystallization occurs at 333 K for COANP, 328 K for MBANP and 325 K for PNP. In our dielectric experiment, 300 K and 330 K can be regarded as the critical crystalline temperatures of COANP and MBANP, respectively. COANP and MBANP above

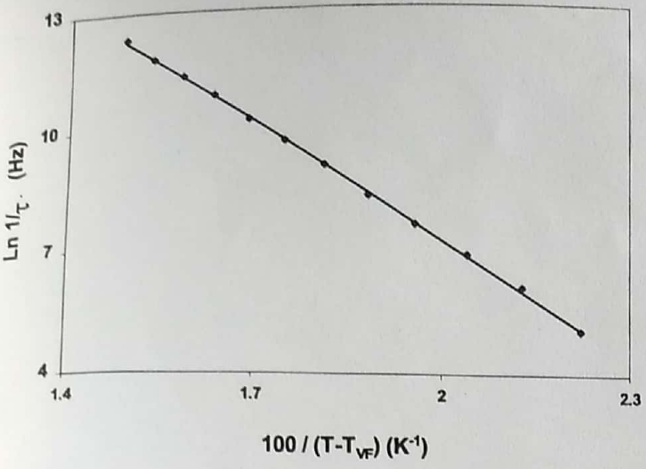


Figure 9. The temperature dependence of the relaxation time of a PNP glass.

their critical temperatures are in crystalline states, which cannot be converted into glass unless the compounds are remelted. However, PNP above 310 K is not a crystal. The dielectric permittivity of PNP glass around this temperature changes significantly, but there are no significant changes in the tangential dielectric loss.

The glassy states of COANP, MBANP and PNP were easily obtained with cooling rates as low as 0.1 K min^{-1}, but NPP glass could not be observed from melt even with a cooling rate as high as 20 K min^{-1}. The crystalline structure of PNP is nearly identical to the structure of its benzene-ring analogue NPP, and NPP shows the same molecular structure as PNP, but with a nitrogen replaced by a carbon atom [14]. However, their super-cooled states are quite different. They are good compounds to test the prediction of the theory on glass transition. We did not provide a dynamical relaxation time for NPP samples because there were no peaks in the plots of dielectric loss.

The frequency range in the experiment is limited, the data does not transform to complex conductivity which can give interesting information, such as scaling behaviour. To get more information about the organic glasses, broadband dielectric spectroscopy and dynamic light scattering experiments need to be conducted. Further investigations are in progress.

4. Conclusion

In summary, the dynamics of COANP, MBANP, PNP and NPP compounds have been studied by dielectric relaxation spectroscopy. The temperature dependence of the relaxation times of COANP, MBANP and PNP glasses were found to satisfy the empirical VF equation. The dynamical relaxation of NPP glass could not be measured due to the quick crystallization of the NPP glass and the narrow frequency range of the RLC meter. Table 2 gives the VF parameters extracted from dielectric measurements of COANP, MBANP and PNP. E_a and T_{VF} from NMR studies in [4] are listed for comparison. Except for the absolute values of the activation energy of COANP and MBANP, it is interesting to find that the dielectric results are consistent with the those of the NMR studies. The crystalline temperatures of COANP and MBANP glasses were given as 300 K and 330 K, respectively. An anomalous behaviour of PNP was observed.

Table 2. The VF parameters from dielectric measurements of COANP, MBANP and PNP. The parameters from the NMR studies of [4] are listed for comparison, in the two right-hand side columns.

Compound	E_a (meV)	T_{VF} (K)	τ_∞ (s)	E_a^{NMR} (meV)	T_{VF}^{NMR} (K)
COANP	54.5	239	3.8×10^{-10}	83.2	239
MBANP	86.2	249	4.9×10^{-13}	66	249
PNP	84.9	245	1.9×10^{-12}	85	245

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References

[1] Eich M, Looser H, Yoon Do Y, Twieg R, Bjorklund G and Baumert J C 1989 *J. Opt. Soc. Am.* B **6** 1590

[2] Leyderman A, Cui Y and Penn B G 1998 *J. Phys. D: Appl. Phys.* **31** 2711

[3] Leyderman A and Cui Y 1998 *Opt. Lett.* **23** 909

[4] Lahajnar G, Zupancic I, Blinc R, Zidansek A, Kind R and Ehrensperger N 1994 *Z. Phys.* B **95** 243

[5] Dobbertin J, Hannemann J, Schick C, Potter M and Dehne H 1998 *J. Chem. Phys.* **108** 9062

[6] Benkhof S, Kudlik A and Rossler E 1998 *J. Phys.: Condens. Matter* **10** 8155

[7] Tombari E, Ferrari C and Johari G P 1999 *J. Phys.: Condens. Matter* **11** A317

[8] Williams G, Smith I K, Holmes P A and Varma S 1999 *J. Phys.: Condens. Matter* **11** A57

[9] Ezquerra T A, Majszczyk J, Balta-Calleja F J, Lopez-Cabarcows E, Gardner K H and Haiso B S 1994 *Phys. Rev.* B **50** 6023

[10] Kind R, Liechti O, Korner N, Hulliger J, Dolinsek J and Blinc R 1992 *Phys. Rev.* B **45** 7697

[11] Dolinsek J, Koren M and Kind R 1998 *Phys. Rev.* B **57** 2812

[12] Gunter P, Bosshard Ch, Sutter K, Arend H, Chapuis G, Twieg R J and Dobrowolski D 1987 *Appl. Phys. Lett.* **50** 486

[13] Twieg R J, Jain K, Cheng Y Y, Crowley J I and Azema A 1982 *Polymer* **23** 147

[14] Twieg R J and Dirk C W 1986 *J. Chem. Phys.* **85** 3537

[15] Zyss J, Nicoud J F and Coquillay M 1984 *J. Chem. Phys.* **81** 4160

[16] Furukawa T, Imura M and Yuruzume H 1997 *Japan. J. Appl. Phys.* **36** 1119

[17] Havriliak S and Negami S 1967 *Polymer* **8** 161

[18] Richert R, Stickel F, Fee R S and Maroncelli M 1994 *Chem. Phys. Lett.* **229** 302

[19] Hansen C, Stickel F, Richert R and Fisher E W 1998 *J. Chem. Phys.* **108** 6408

[20] Wrobel S, Gowda B T and Haase W 1997 *J. Chem. Phys.* **106** 5904

[21] Ngai K L 1999 *J. Chem. Phys.* **111** 3639