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Phase-dependent dielectric properties and proton conduction of neopentyl glycol

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Phase-dependent dielectric properties and proton conduction of neopentyl glycol (NPG), which is an organic molecular plastic crystal, were studied *via* variable-temperature broadband dielectric spectroscopy (BDS). Permittivity and conductivity data show the phase transformations of NPG from the crystalline state to the plastic crystalline state at 315 K and then to the molten state at 402 K across the temperature range of 293–413 K. The Vogel temperatures (T_v) fitted from the Vogel–Fulcher–Tammann (VFT) equation agree well with the values extrapolated by the Stickel plot (linearized Vogel plot). Impedance and modulus data display a separation of the $-Z''$ (the imaginary part of the complex impedance) and M'' (the imaginary part of the complex electric modulus) peaks in the crystalline phase. However, they overlap in both the plastic crystalline phase and the molten phase, indicating long-range proton conduction. In both the molten phase and the plastic crystalline phase, the temperature dependence of direct current conductivity (σ_{dc}) obeys the VFT equation very well. While the vehicle mechanism (translational diffusion) is an intrinsic mechanism for ionic or protonic conduction in the molten phase, it is speculated that the Grotthuss mechanism also works due to the self-dissociation of NPG molecules, which are similar to water molecules. In the plastic crystalline phase, the proton hopping mechanism is most likely the underlying ion-conducting mechanism because of the rotational disorder and intrinsic defects (vacancies) of the NPG molecules. In the ordered crystalline phase, the proton conduction is presumed to follow the proton hopping mechanism as determined from the localized relaxation and the temperature dependence of σ_{dc} (Arrhenius behavior).

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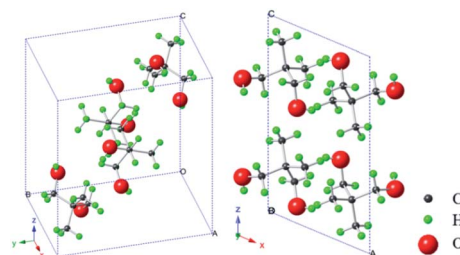
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Introduction

Molecular substances composed of globular or pseudo-globular molecules often lead to the formation of mesophases (meso-states) between the ordered crystalline state and isotropic liquid. This mesophase is usually referred to as the plastic crystalline state, and the molecular substances are known as plastic crystals.¹ Plastic crystals have the long-range center-of-mass crystalline order (positional order) and short-range dynamic disorder of molecular orientations, and thus are also known as the orientationally disordered crystals or rotator phases.^{2,3} Normally, they have a very low entropy of fusion and a relatively large entropy of solid–solid phase transition thus enabling high ionic conductivities, which makes them promising candidates for applications as protonic or ionic conductors in fuel cells, batteries, and supercapacitors.^{4–10}

Neopentylglycol (NPG) or 2,2-dimethyl-1,3-propanediol, an important representative of molecular plastic crystals, has been

widely studied in various aspects.^{11–37} Many studies focused on phase transitions and/or crystal structures.^{11–19} It can be concluded that within the investigated temperature range (*e.g.* from 150 K to 423 K), NPG undergoes one solid–solid phase transition and one solid–liquid phase transition successively. Specifically, NPG exhibits its solid–solid phase transition from the ordered crystalline state to the plastic crystalline state at around 314 K (the low temperature monoclinic α phase transforms into the high temperature cubic γ phase), and then the melting transition at around 403 K between the plastic crystalline state and the molten state.^{11–19} Scheme 1 shows the crystal structure (monoclinic α phase) of NPG at 295 K based on the results from Chandra *et al.*¹⁵



Scheme 1 Crystal structure (monoclinic phase) of NPG at 295 K.¹⁵ Notes: left, view along (1 1 1) crystal plane; right, view along (0 1 0) crystal plane.

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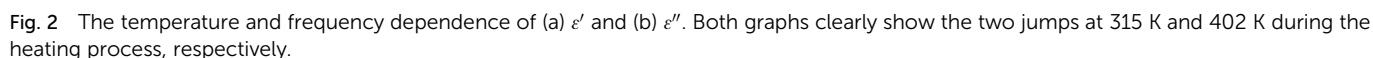
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Broadband dielectric spectroscopy (BDS) has the advantage of probing electrical properties, (dielectric) relaxation phenomena and thermal phase transitions over a wide range of temperatures and frequencies.^{38–40} In the present work, NPG was studied across a wide range of temperatures (from 293 K to 413 K) and frequencies *via* the BDS. Dielectric properties of NPG in three phases (the ordered crystalline, plastic crystalline and liquid phases) were studied. In addition, the possible proton conduction mechanisms were also explored.

Materials



To study the temperature dependence of σ_{dc} , a simple test (eqn (2)) to check whether σ_{dc} obeys a Vogel–Fulcher–Tammann (VFT) relation or an Arrhenius equation was introduced by Turnhout and Wübbenhorst:⁴²

Fig. 3 Three dimensional (3D) graph of the real part of complex conductivity (σ') as a function of frequency (10^{-1} to 10^6 Hz) and temperature (between 293 K and 413 K).

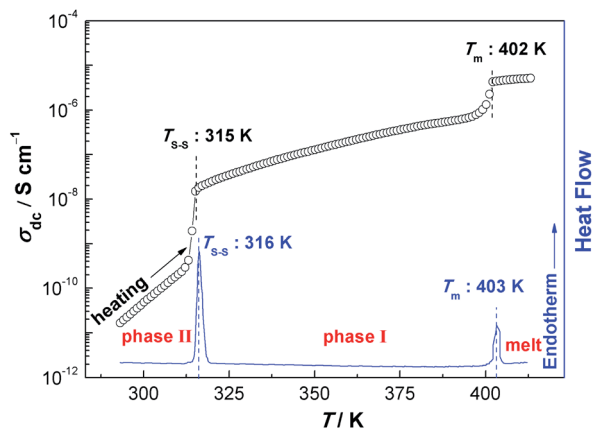


Fig. 4 σ_{dc} of NPG as a function of temperature (between 293 K and 413 K). Note: the DSC curve is cited from ref. 18.

$$\left(\frac{d \ln \sigma}{dT}\right)^{-1/2} = \left(\frac{R}{E_v}\right)^{1/2} (T - T_v) \quad (2)$$

where σ represents the conductivity, T the temperature, R the universal gas constant, T_v the Vogel temperature and E_v the activation energy at T_v . This equation combines both a VFT ($T_v \neq 0$ K) and an Arrhenius equation ($T_v = 0$ K) and thus allows an evaluation of E_v and T_v from the slope and the intersection of the extrapolated, linearized curves with the abscissa.⁴²

Fig. 5 shows linearized Vogel plots of NPG with the corresponding correlation coefficient (R^2) in the temperature range of 293–413 K. Overall, σ_{dc} of these three phases (phase II, phase I and the melt phase) can be fitted by three equations with high R^2 , respectively. Specifically, T_v values of phase II, phase I and the melt phase are 0 K, 153.1 K and 391.7 K, respectively. Because T_v is equal to 0 K in phase II, the temperature dependence of σ_{dc} most likely obeys the Arrhenius law. In addition, the temperature dependence of σ_{dc} most likely obeys the VFT equation for both phase I and the melt phase due to $T_v \neq 0$ K.

In order to quantitatively verify the above conclusion (Fig. 5), the σ_{dc} values in the three phases are fitted by the VFT equation (eqn (3)) and the Arrhenius equation (eqn (4)), respectively.^{43–45}

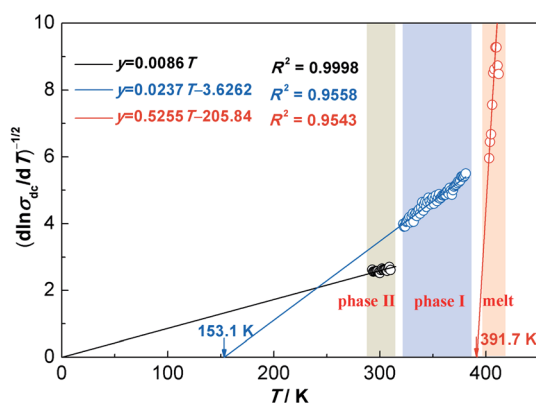


Fig. 5 Linearized Vogel plots of NPG with the fitted equations and the corresponding correlation coefficients (R^2) in the temperature range of 293–413 K.

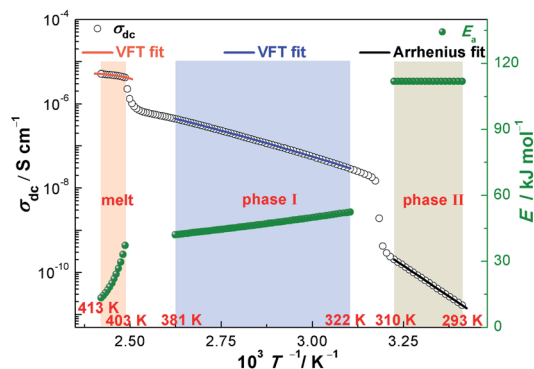


Fig. 6 The temperature dependence of σ_{dc} and the activation energy (E_a) for NPG in the temperature range of 293–413 K.

$$\sigma(T) = \frac{A}{\sqrt{T}} \exp\left(\frac{-B}{T - T_v}\right) \quad (3)$$

$$\sigma(T) = \sigma_0 \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

where A is proportional to the concentration of carrier ions, B the pseudo activation energy, T_v the Vogel temperature, σ_0 the pre-exponential factor, E_a the activation energy and R the universal gas constant. The fits are shown in Fig. 6 with the fitting results listed in Table 1. The T_v values (133.5 K and 385.4 K) obtained by the VFT fits agree well with the values extrapolated by the linearized Vogel plots (153.1 K and 391.7 K). Again, the temperature dependence of σ_{dc} values in the phase II, phase I and melt phase follow the Arrhenius law, the VFT equation and the VFT equation with high correlation coefficients, respectively. In addition, the value of E_a for ionic conduction in phase II is calculated to be 111.9 kJ mol^{−1} based on the Arrhenius law.

To study σ_{dc} in terms of energy landscape for the related temperature range, the activation energies in phase I and the melt phase are calculated based on eqn (6), which can be obtained by performing partial differentiation of eqn (3) in its logarithmic form with respect to T (eqn (5)).^{41,46,47}

$$E_a = RT^2(d \ln \sigma / dT) \quad (5)$$

$$E_a = RBT^2/(T - T_v)^2 - RT/2 \quad (6)$$

Obviously, activation energies are in function of temperatures because R , B and T_v are constants in eqn (6). The temperature dependence of E_a is also shown in Fig. 6. It is shown that E_a in the low temperature region (phase II) is a constant, which indicates the thermally activated conductivity. In phase I and the melt phase, as the temperature increases, E_a decreases rapidly (especially in the melt phase), which indicates the non-thermally activated conductivity, agreeing well with the analysis of relaxation time.²²

Impedance and modulus analysis

Fig. 7 illustrates the temperature dependence of M'' and $-Z''$ for NPG at selected temperatures. One or two temperatures are chosen as

Table 1 Fit results of NPG at different temperature ranges

T/K	$A/(S\ K^{1/2}\ cm^{-1})$	B/K	T_v/K	$\sigma_0/S\ cm^{-1}$	$E_a/kJ\ mol^{-1}$	R^{2a}
[293, 310]	—	—	—	1.4×10^9	111.9	0.9999
[322, 381]	6.8×10^{-2}	2.2×10^3	133.5	—	—	0.9999
[403, 413]	1.4×10^{-4}	8.1	385.4	—	—	0.9963

^a R^2 : the correlation coefficient for VFT or Arrhenius fit results.

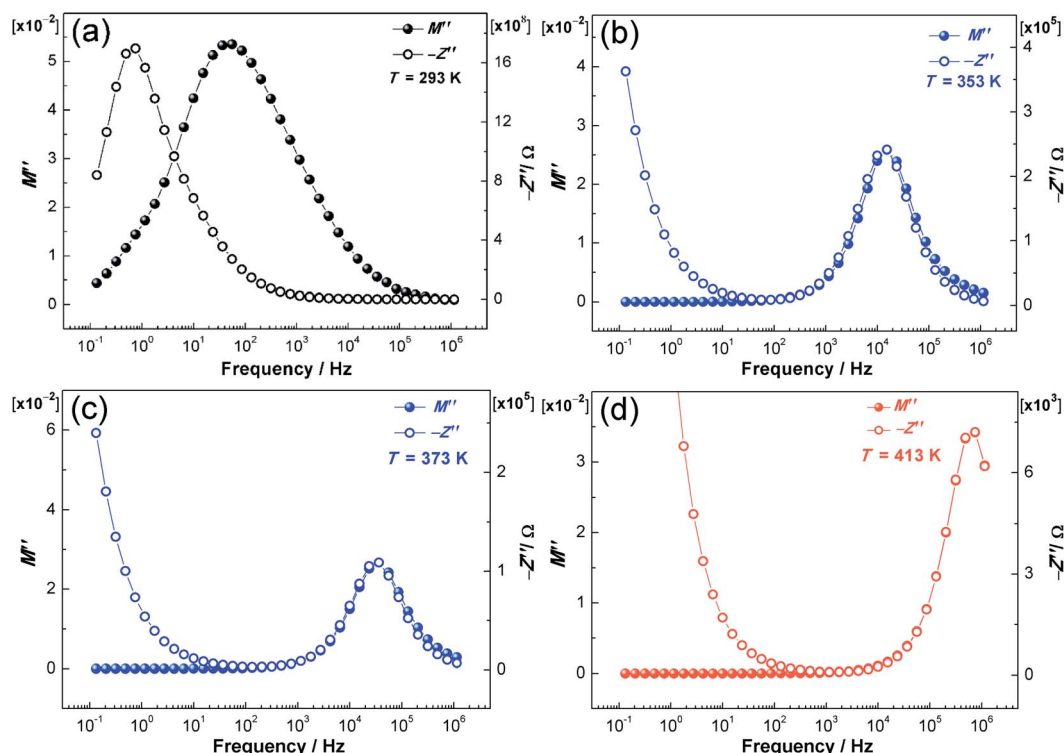
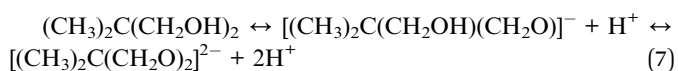


Fig. 7 The temperature dependence of M'' (the imaginary part of complex electric modulus) and $-Z''$ (the imaginary part of the complex impedance) at selected temperatures of 293 K (a), 353 K (b), 373 K (c) and 413 K (d).

representatives for each phase. Clearly, both the impedance and electric modulus data show a single relaxation response in the frequency range of 10^{-1} to 10^6 Hz. The separation of the $-Z''$ and M'' peaks (phase II: Fig. 7a) results from localized relaxation while the overlapping of the $-Z''$ and M'' peaks (phase I: Fig. 7b and c; melt: Fig. 7d) in the spectra reflects long-range migration of protons.^{48,49}

While the vehicle mechanism (translational diffusion) is an intrinsic mechanism for proton conduction in the melt phase, it is speculated that the Grotthuss mechanism should also function due to the self-dissociation of hydrogen-bonded NPG molecules (eqn (7)), which are similar to water molecules. Therefore, in the melt phase, the proton conduction results from both the vehicle and Grotthuss mechanisms.



In the plastic crystalline phase (phase I), the proton hopping mechanism is most likely the underlying ion-conducting mechanism because of the rotational disorder in the cubic

phase and intrinsic defects (vacancies) of the NPG molecules featured by the hydrogen bond network,²⁶ and the long-range migration of protons indicated by the overlapping of the $-Z''$ and M'' peaks.

In the ordered crystalline state (Fig. 7a), the proton conduction is presumed to follow the proton-hopping mechanism *via* the hydrogen bond network due to the localized relaxation and the temperature dependence of σ_{dc} (Arrhenius behavior).

Conclusions

Phase dependent dielectric properties and proton conduction of the molecular plastic crystal neopentyl glycol (NPG) were studied *via* the variable-temperature broadband dielectric spectroscopy. Permittivity and conductivity data show that NPG undergoes phase transitions from crystalline phase to plastic crystalline phase at 315 K and then to the molten state at 402 K successively from 293 K to 413 K. The Vogel temperatures obtained by the Vogel-Fulcher-Tammann (VFT) fits agree well



with the values extrapolated by the Stickel plots (linearized Vogel plots). Impedance and electric modulus data display the separation of the $-Z''$ and M'' peaks in the crystalline phase, and the overlaps of the $-Z''$ and M'' peaks in the plastic crystalline phase and the molten phase; the latter case indicates the long-range migration of protons. In both the molten phase and the plastic crystalline phase, the temperature dependence of direct current conductivity (σ_{dc}) obeys the VFT equation well. In the molten phase, the proton conduction results from both the vehicle and Grotthuss mechanisms. In the plastic crystalline phase, the proton hopping mechanism is most likely the main ion-conducting mechanism due to the rotational disorder and intrinsic defects (vacancies) of the hydrogen-bonded NPG molecules. In the ordered crystalline phase, the proton conduction is speculated to be intermolecular proton transport *via* proton hopping as determined from the localized relaxation and the temperature dependence of σ_{dc} (Arrhenius behavior).

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

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