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Relaxation and Diffusion of an Ionic Plasticizer in Amorphous Poly(vinylpyrrolidone)

– Supporting Material –

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Here, we present loss modulus spectra for $PVP_{0.84}PT_{0.16}$, shear storage spectra for $PVP_{1-x}PT_x$ with x = 0.16. 0.33, and 0.66, as well as ε' and ε''_{der} spectra for $PVP_{1-x}PT_x$ with x = 0.16. 0.33, and 0.66. Additionally, we provide details regarding the measurements carried out using differential scanning calorimetry and how they were analyzed. Furthermore, viscosity and conductivity data are presented in a Walden-type plot.

S1. Additional spectra from shear rheology

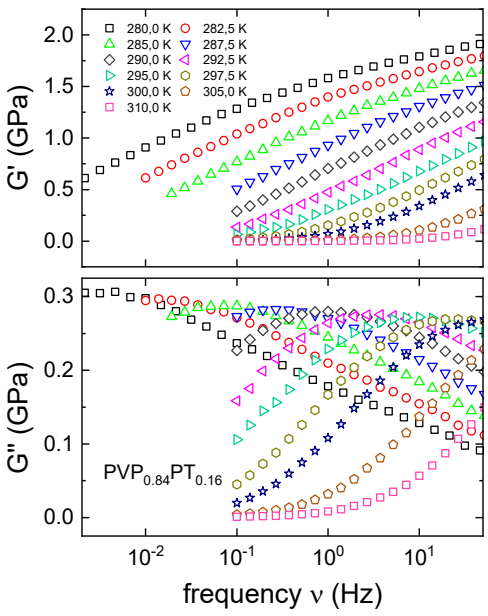

Fig. S1. Shear storage and (b) shear loss modulus spectra measured for $PVP_{1-x}PT_x$ with x = 0.16.

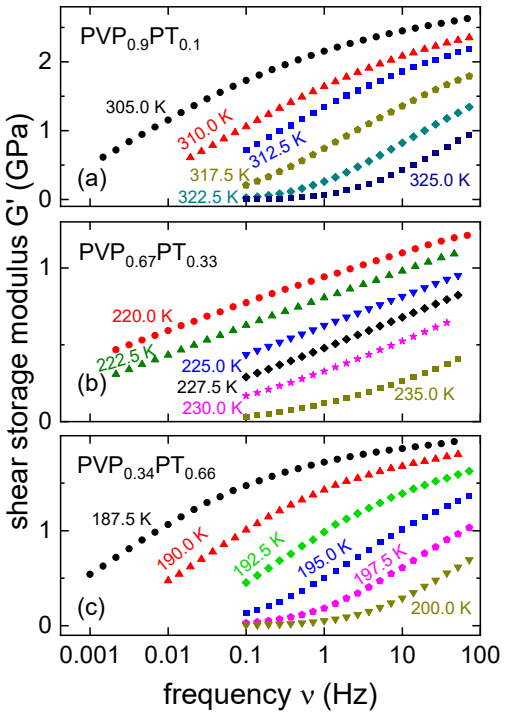

Fig. S2. Shear storage spectra for $PVP_{1-x}PT_x$ with x given by (a) 0.10, (b) 0.33, and (c) 0.66.

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S2. Additional spectra from dielectric spectroscopy

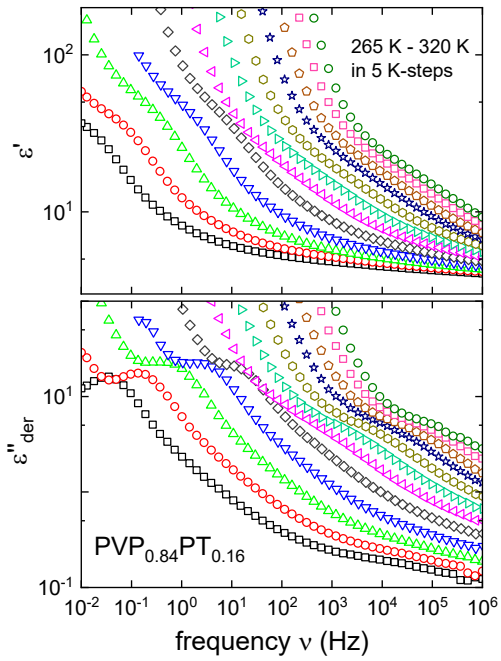

Fig. S3. Dielectric data of $PVP_{0.84}PT_{0.16}$ presented in terms of (a) the permittivity ε' and (b) the dielectric loss ε''_{der} derived thereof.

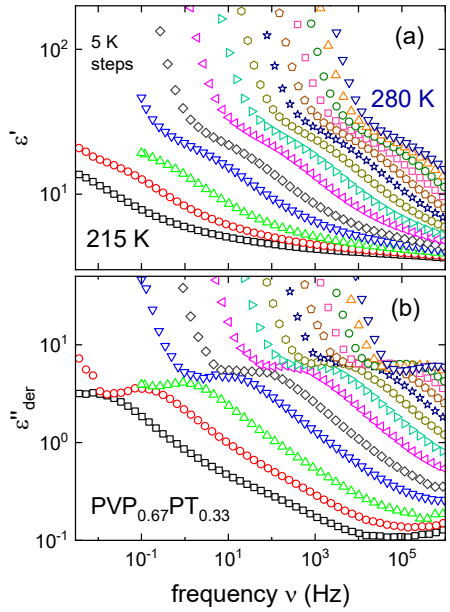

Fig. S4. Dielectric data of $PVP_{0.66}PT_{0.33}$ presented in terms of (a) ε' and (b) ε''_{der}.

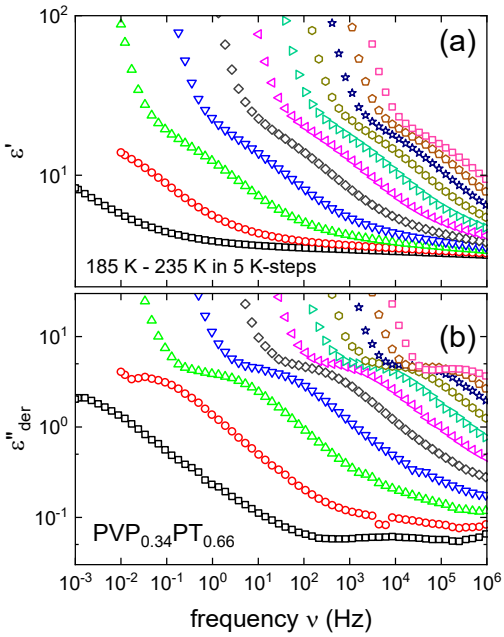

Fig. S5. Dielectric data of $PVP_{0.34}PT_{0.66}$ presented in terms of (a) ε' and (b) ε''_{der}.

S3. Differential scanning calorimetry

A Q2000 differential scanning calorimeter from TA Instruments located in the Department of Biochemical and Chemical Engineering at TU Dortmund University was used for the DSC measurements. Details of the employed procedures have been described previously.[S1]

The thermograms shown in Fig. S6 were recorded by employing a heating rate q of 10 K/min. From the intersection of the red lines Fig. S6 the onset glass transition temperature T_g was determined. Typically, the glass transition occurs where the structural relaxation time is on the order of 100 s. For a better estimate of τ_{DSC} the approach described in Ref. S2, is useful. Here, as additional parameter, the effective energy barrier ΔE against structural rearrangements enters, so that

$$\tau_{DSC} = \frac{k_B T_g^2}{q\ \Delta E} \qquad \text{(S1)}$$

The difference between the effective energy barriers from dielectric spectroscopy to those from rheology that one can infer from Fig. 8(a) near T_g, was used to assess the error bar for τ_{DSC} which is shown in that figure.

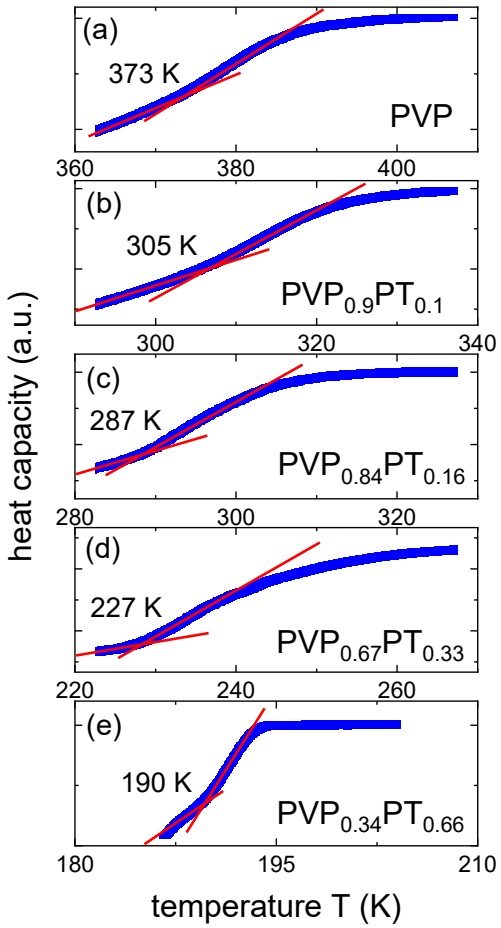

Fig. S6. The blue symbols represent the raw DSC traces measured for $PVP_{1-x}PT_x$. The intersection of the straight red lines was used to assess the onset transition temperatures T_g. For x = 0.33, the large "creeping" deviation of the high-temperature line to the DSC data is taken to signal the appearance of a bimodal calorimetric signature.

S4. Walden-type plot

To test the relation of the shear viscosities η_0 and the DC conductivities σ_0, in Fig. S7 we collect the corresponding data from Fig. 7. One observes that power laws, $\eta_0 \propto \sigma_0^{-\xi}$, with exponents ξ emerge in the representation of Fig. S7. For neat PT, an exponent $\xi = 1$ signals a coupling of the two transport coefficients, as expected for an ionic liquid. For the mixed liquids, a fractional exponent is found and for several compositions a high- and a low-temperature regime is discernible on the basis of a change of slope.

Note that according to the Nernst-Einstein relation, Eq. (9), the (charge) diffusion coefficient should be proportional to σ_0. Therefore, an exponent $\xi < 1$ can be taken to signal the existence of a fractional Stokes-Einstein relation.

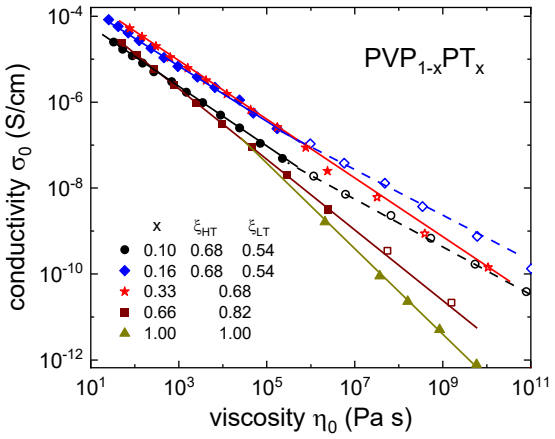

Fig. S7. Walden-type plot of DC conductivity σ_0 versus zero-shear viscosity η_0. The full symbols refer to data points where η_0 was determined directly from the data, the open symbols were determined on the basis of frequency temperature superposition. The lines reflect power laws, $\eta_0 \propto \sigma_0^{-\xi}$, that apply at high temperature (HT) or at low temperature (LT). If a break in slope ξ exists, then dashed lines are used for the LT regime. The inset summarizes the exponents.

[S1] Mansuri, A.; Münzner, P.; Feuerbach, T.; Vermeer, A. W. P.; Hoheisel, W.; Böhmer, R.; Thommes, M.; Gainaru, C. The Relaxation Behavior of Supercooled and Glassy Imidacloprid. *J. Chem. Phys.* **2021**, *155*, 174502.

[S2] Hodge, I. M. Enthalpy relaxation and recovery in amorphous materials, *J. Non-Cryst. Solids* **1994**, *169*, 211–266.