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Glassy dynamics of model complex coacervate films with variable interaction strength quantified by the critical salt concentration

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Complex coacervates are widely studied in manufacturing, food processing, personal care, and therapeutics. While much research pertinent to coacervates has recently focused on their phase behavior, their glassy dynamics remains largely unexplored. We anticipated, based on a combination of the generalized entropy theory (GET) of the dynamics of glass-forming liquids and recent molecular dynamics simulation studies, that variations in these material's polymer charge density should significantly alter the glass transition temperature (T_g) and fragility (m) because of the known effect of charge on the cohesive energy density of polymer materials. To test this hypothesis, we performed dielectric spectroscopy measurements on model complex coacervate films formed by blending poly-diallyldimethyl ammonium chloride (PDDA) and adenosine triphosphate (ATP). The critical salt concentration (c_{salt}) was taken to be a quantitative measure of molecular interaction strength, ε. The films were vacuum annealed before dielectric measurements were conducted over a wide temperature range extending down to temperatures close to T_g. As anticipated, we find that increasing ε increases T_g, but progressively decreases m. We also find that our coacervate films exhibit high apparent dielectric permittivity ($>10^3$) at room temperature for a moderate frequency of 1 kHz, which naturally explains the observed high responsiveness of such materials to even relatively weak electric fields ($\approx 1\ \mathrm{V\ cm^{-1}}$). Finally, we show that moisture tends to plasticize the glassy dynamics of these materials, *i.e.*, reduce T_g. These trends are expected to hold rather generally for complex coacervate materials arising in diverse manufacturing and biophysical contexts.

Introduction

Complex coacervate is a historical term for blends of polyelectrolytes, often involving oppositely charged polymer blends in their metastable macro-phase separated state.[1] Such polyelectrolyte "blends" are sometimes termed polyelectrolyte complexes (PECs) when the material is in the 1-phase region, where the polymers are often found to be in an associated state.[2] Notably, the existence of oppositely charged polyelectrolytes is not necessary for complex coacervate formation. Specifically, Kim *et al.*[3] demonstrated complex coacervation in two positively charged polymers by virtue of an additional charge-π electron interaction between the polyelectrolyte chains. Within the food processing and cosmetic industry, these complex coacervates have found an immense number of applications[4,5] and have garnered significant biological interest in relation to this type of phase separation being involved in cell organelle formation, the occurrence of disease states, and as a vehicle for drug delivery.[6–8]

The fluidity of the coacervate material plays a major role in biological function and in other applications. As with polymer materials broadly, fluidity variation is influenced by a combination of polymer entanglement interactions, intermolecular association to form gel-like materials, and glass-formation. The highly charged nature of coacervates expectedly leads to significant changes in cohesive energy density – a thermodynamic quantity defined as the energy necessitated to separate a unit volume of a material into individual molecules – relative to uncharged polymers, and this leads to especially large changes in the glassy dynamics of these materials upon polymer charge

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density variation.[9,10] However, the quantitative estimation of changes in molecular interaction strength (ε) is complicated in complex coacervates, given the metastable nature of many coacervate systems and the presence of water and associated hydration effects. This forces us to consider an unconventional measure of ε in these materials.[6,11]

While previous computational studies have established that polymeric charge density corresponds to a higher cohesive energy density in polymer melts, as predicted by Eisenberg[12] and Tanaka,[13] and shown in experimental studies on charged glassy polymer materials, the quantitative application of these arguments to blends of polycations and polyanion in an associated and phase separated coacervate state is unclear. Another complicating factor in estimating the cohesive energy density of these materials is that these PECs are normally heavily hydrated and as a result, the hydrated counter-ions around the charged polymer alters the magnitude of the effect charge and thus alters the strength of the polymer–polymer interactions within the polymer complex. Finally, complex coacervates are inherently non-equilibrium phase separated materials whose structure and properties are expected to evolve in time. It is then unclear how to accurately estimate the cohesive energy density of such a complex material. Nonetheless, it is possible to measure properties that reflect the relative ''strength'' of charge interaction. In particular, the amount of salt required at a fixed temperature (T) to form a miscible polyelectrolyte blend solution, termed as the ''critical salt concentration'' (c_{salt}), is a measure of the effective interaction strength because the presence of salt progressively weakens the interaction strength between the polymers.[14–16] Thus, a higher c_{salt} is required for complex coacervate solutions in which the polymers have a higher charge density.[16] Since a higher salt concentration is required to compensate for a higher polymer charge, we propose that c_{salt} can be taken as a measure of the relative intermolecular interaction strength (ε), and we adopt this quantity as a proxy for the estimation of cohesive energy density. Cohesive energy density is also normally reflected in the shear modulus, and this property should also be reflected in the adhesive strength of the material. These properties might also serve as proxies for cohesive energy density in complex coacervate materials, but c_{salt} has the advantages that it is readily estimated experimentally and extensively tabulated in previous studies.

The generalized entropy theory (GET) of glass-formation provides a general framework for how ε influences both T_g and fragility (m) of glass-formation.[9,17] Fragility is a measure of the ''sharpness'' of the glass transition in the sense of how rapidly relaxation time changes near T_g.[18] It has important implications for the long-term stability of encapsulated biomolecules, including RNA and DNA, which are prone to degradation under conditions of high molecular mobility. In low-fragility glasses (steep rise in relaxation time approaching T_g), the reduced molecular motion below T_g creates a kinetically stabilized environment that can preserve the structure and function of labile biomolecules over long periods. This phenomenon can be highly useful in the enhanced preservation of protein and RNA drugs, such as those used for covid vaccines.[19–22] Previously, low fragility sugar matrices have shown their value as preservatory matrices for proteins and other biomolecules by suppressing the amplitude of molecular motion and the permeability of gases that could cause chemical degradation.[22,23]

Our work indicates that the enhanced cohesive interaction strength of complex coacervate materials leads to an increased T_g and to a reduction of the fragility m of glass-formation, thereby creating an environment that could markedly reduce the rate of RNA degradation within such a preservation matrix. We also speculate that enhanced RNA stability in such a medium may have been critical for the emergence of life if the coacervate protocell hypothesis[24] and the RNA World[25,26] hypotheses are proven to be correct. In particular, the protective ''anti-plasticization'' effect of the coacervate protocell could be expected to help ensure that RNA molecules retain their structural integrity and chemical functionally over a much larger timescale than free RNA in solution. Such enhanced RNA stability was probably necessary for these molecules to evolve in their molecular complexity to the degree necessary for the complex metabolic behavior required of living systems. Moreover, the low fragility of complex coacervates is expected to be important in the context of food preservation,[21] as well as for enhancing the shelf-life of biomolecular drugs.[19,20,22]

Recent complementary experimental studies have indicated unusual fragility trends in some polymer materials under investigation in connection with energy storage and generation and in the development of more sustainable polymer materials in comparison to traditional petroleum-based polymers which are typically uncharged in nature and processed at elevated temperatures in organic solvents. Complex coacervate polymer materials are representative of this new type of material which can retain many of the properties of petroleum-based polymer, but whose charged groups make it suitable water for processing in salt water at low temperatures and seems to allow for the avoidance of microplastic pollution upon the breakdown of the polymer material in seawater.[27,28] Careful dielectric measurements on another representative charged polymer material, mussel-inspired elastomers,[29] have indicated that T_g and fragility vary in opposite directions when the physical crosslinking density, involving charged or polar groups, was increased.[29] The results of these measurements came as a surprise because T_g and fragility usually change in a near proportionate way when molecular parameters are varied.[30,31] Even earlier, Fragiadakis *et al.*[32] were one of the first experimentalists to show the inverted T_g – fragility trend in polyethylene-derived copolymer ionomers with variable Li^+ ionic content. Even earlier, Ueno *et al.*[33] observed this type of puzzling, inverted variation between T_g and fragility in a family of protonic ion liquids of similar molecular structure, but increasing charge density. Little physical insight was offered at the time for the physical origin of this trend, however more recently, Zheng *et al.* observed an inverted trend between T_g and m in simulated polymer networks when the magnitude of the cohesive energy density was increased significantly, while keeping other molecular parameters fixed.[34] From a theoretical standpoint, an inverted trend between T_g and m was predicted some time ago by the generalized entropy theory GET under conditions where the intermolecular interaction strength is significantly increased, while other molecular parameters are held fixed.[17]

Since the inverted trend between the variation of T_g and fragility has repeatedly been found in recent studies of novel polymer materials,[32,35] we briefly discuss the physical origin of this predicted trend within the GET. A more in-depth discussion of the inverted between these basic properties of glass-forming polymer materials having variable structure and interaction is discussed by Xu *et al.*[10] First, we again emphasize that it is quite uncommon for typical uncharged polymers having van der Waals interactions to show the inverted trend between T_g and fragility. This trend is attributed by the GET to the relatively limited variation of the cohesive interaction density for this class of materials when molecular parameters are varied such as chain stiffness, monomer geometrical structure and chemistry, and the overall polymer molecular mass. The rubbery polymer material polyisobutylene (PIB) provides a rare exception to this general trend and this special polymer, and the variation of fragility in polymer materials generally, is discussed by Xu *et al.*[10] One of the interesting consequences of this relatively slow variation of the cohesive energy density within "typical" petroleum-based polymers is that T_g and fragility vary in a nearly proportionate way[36] when the polymers are long enough to be considered polymeric. Notably, this near proportionality between T_g and fragility accounts for the near universality of the temperature dependence of the relaxation time of uncharged polymer materials discovered by Williams, Landel and Ferry (WLF),[37] which involves a mathematical expression for the structural relaxation time of common polymer materials that has no explicit dependence on fragility.[18] This situation arises because magnitude of T_g also approximately determines the magnitude of the fragility. One could get the impression from the observation of the empirical WLF scaling relation in common polymers that fragility is irrelevant to understanding the dynamics of polymer materials, but this correlation is certainly not general even as originally inferred by WLF for even petroleum-based polymers.[18] Observed large deviations from this type of approximate universal scaling are becoming increasingly common in polymer materials used in energy applications where charged groups and salts are often involved to alter the material conductivity, and in the development of new materials having strong associating side-groups that are of interest in the design of more sustainable polymer materials where the associating groups can aid in the recycling of polymer materials.

Within the same GET theoretical framework, the inverted trend between T_g and fragility is predicted to arise in polymer materials in which the cohesive energy density is relatively large and variable, such polyzwitterion and charged polymer materials, polymer materials with charged groups acting as physical cross-links, *etc.* The large intermolecular interaction strength between the monomers of opposite charge in the polyelectrolyte blends would strongly suggest that complex coacervates should likewise exhibit this type of inverted trend. We next briefly discuss the mathematical mechanism of the inverted trend within the GET.

It is well known from numerous previous studies of glass-formation that increasing the cohesive energy density tends to increase T_g,[38–41] along with the melting temperature T_m and other characteristic temperatures of polymer materials,[42] so this part of the inverted trend is self-evident. Increasing cohesive interaction strength generally tends to increase T_g. The unexpected part of the inverted trend is then the reduction of fragility with increasing cohesive interaction strength. The GET predicts that increasing the cohesive energy density has the effect of enhancing the relative packing efficiency of the polymer material, as quantified by the changes in the relative density of the material, the reduced isothermal expansion coefficient and reduced isothermal expansion coefficient (for detailed discussion and explicit GET computation and validation using molecular dynamics simulations, we would recommend that the reader take a look at the recent work done by Xu *et al.*[10]). Importantly, this reduction of the relative packing frustration caused by increasing the cohesive energy density is also predicted by the GET to lead to significant increase in the relative configurational energy density of the polymer material and it is this property change that explains why an increase of the cohesive energy density should cause a drop in fragility. This is the crucial link between dynamics and thermodynamics in the GET. An inverted trend is also predicted by the GET, and confirmed by simulation, upon increasing the applied external pressure on polymer materials not exhibiting strong hydrogen bonding or other directional intermolecular interactions since an increase of pressure[43,44] since an increase of pressure also tends to lead to a densification of polymer materials, and a reduction of the thermal expansion coefficient and isothermal expansion coefficient. It is the reduction of the fragility with an increase of the magnitude of either the cohesive energy density (internal pressure) or external pressure that explains the origin of the inverted relation between T_g and fragility.

Given previous theoretical findings of the inverted trend between T_g and fragility in materials having a relatively high and variable cohesive energy density, and the evident strong intermolecular interaction strength between charged polymers in coacervates, we were led to specifically test whether increasing ε should increase the T_g, while lowering m in dielectric measurements on a model coacervate material that our group has extensively studied previously in connection with other property measurements.[45–49] Below, we confirm the expected inverted trend between T_g, and m in these materials through dielectric spectroscopy measurements. Notably, we are not aware of any previous studies of the fragility of complex coacervate materials, a property of potential significant interest in relation to enhancing the preservation of biological materials against degradation, a phenomenon that could have been of crucial significance in the origin of life if protocells were composed of complex coacervate materials, as many scientists currently believe.[24]

Results and discussion

We synthesized three coacervate systems from poly diallyldimethyl-ammonium chloride [PDDA; M_W = 8.5 kDa] and adenosine triphosphate (ATP) with different PDDA : ATP molar ratios to have three distinct intermolecular strengths ε quantified by c_{salt} (see Experimental methods in SI). Among the various polyelectrolyte systems available, PDDA–ATP complex coacervates offer chemical simplicity, ease of synthesis and an electrostatically rich model system. The robust electrostatic interactions are credited to the presence of multivalent ATP anions and cationic PDDA chains, enabling tunable interaction strength simply by varying composition. Additionally, ATP's biological relevance is a major contributor influencing our continual interest in studying the physics of this system. These characteristics make PDDA–ATP coacervates an attractive platform for systematically studying how charge-mediated cohesion influences glassy dynamics in complex coacervates. As reported previously, the presence of salt ions in the complex coacervate solution screens the intrinsic ion's (Pol^+ Pol^-) interactions.[2,14,16] This weakening of intermolecular interaction strength between the charged polymers ultimately leads to the formation of a stable one-phase polymer solution,[2,50] as can be directly inferred from optical microscopy (Fig. S1) and UV-Vis (Fig. S2A–C) measurements. The interaction strength, defined by ε ($\equiv c_{\text{salt}}$), is the highest for stoichiometric ratio and decreases upon deviating from it (*i.e.*, $\varepsilon_{1:1} > \varepsilon_{2:1} > \varepsilon_{4:1}$).

We performed dielectric spectroscopy (DS) on the different PDDA : ATP molar ratios cast films, after annealing them at 373 K (100 °C) under vacuum for an hour. For each system, the tan (δ) *versus* frequency curve was fitted using the commonly-utilized Havriliak–Negami (HN) equation (Fig. S5) at each T at which the DS measurements were performed.[29,51] HN parameters resulting from our fits are indicated in Tables S1–S3 (Scheme 1).

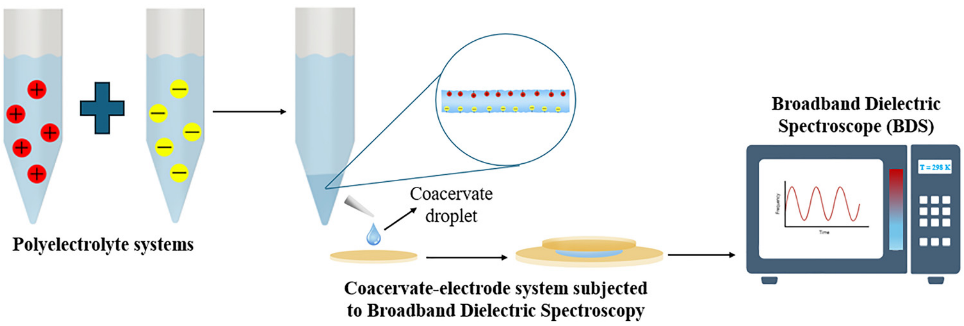
Fig. 1A indicates that the systems having a higher ε relax on a longer timescale at a given T in our model coacervate materials. This trend is expected to be quite general in complex coacervates having a similar structure because increasing the ε normally corresponds to an increase in cohesive energy density and T_g. From Fig. 1B, we also observe a decline in the coacervate material's conductivity with increasing ε, indicating a reduced counter-ion mobility accompanies the slowing down of the relaxation as the charge interaction is increased. The behavior of relaxation time ($\tau_{\max}$) as a function of T indicates a non-Arrhenius behavior (Fig. 1A) over the entire temperature range so it is not possible to meaningfully model $\tau_{\max}$ using the Arrhenius equation ($\log \tau_{\max} = \log \tau_0 + \frac{B}{T}$, where B denotes the activation energy). This temperature variation is typical of polymeric glass-forming liquids and the Vogel–Fulcher–Tammann (VFT) equation is normally found to describe relaxation data,.[34]

$$\log \tau_{\max} = \log \tau_0 + \frac{DT_0}{T - T_0} \tag{1}$$

where T is the temperature, T_0 is the VFT temperature and $K = \frac{1}{D}$ is the "Vogel fragility parameter" describing the strength of the temperature dependence of the relaxation time and the degree to which the relaxation process deviates from Arrhenius relaxation. At very high temperatures, Arrhenius relaxation is often observed in glass-forming liquids above an onset temperature T_A that is often about twice T_g,[9] but many polymer start to degrade before such a temperature can be reached so that Arrhenius relaxation is of limited interest from a practical stanpoint. This VFT equation, which can be viewed as corresponding to a T dependent activation energy,[35] is closely related to the Williams–Landel–Ferry (WLF) expression for the relaxation time of glassy materials, and both of these expressions can be expected to hold to a good approximation in a T range above T_g, but well below T_A, where glassy dynamics is prevalent.[18]

In Fig. 2A–C, we find that the VFT equation describes the T dependence of $\tau_{\max}$ rather well, allowing us to determine T_g in the three coacervate systems based on the conventional criterion, $\tau_{\max}$ = 100 s at $T = T_g$.[18,52,53] Notably, our measurements happen to be made above T_g at which physical aging effects under normal measurement conditions become highly prevalent. Note that this method of T_g estimation involves an extrapolation to the T at which the relaxation time equals 100 s and allows for a precise cooling rate independent estimation of T_g. While some uncertainty exists in this method of estimating T_g due to the requirement of temperature extrapolation, alternative methods of estimating T_g based on "kinks" in the T dependence of the density variation, or peaks in the non-equilibrium specific heat measurements over a range of decreasing cooling rates, also have their uncertainties.

It is observed in Fig. 3A that T_g increases with the relative value of c_{salt}, *i.e.*, the stoichiometric system has the highest T_g.



Scheme 1 Illustrates the model system of the coacervates being subjected to broadband dielectric spectroscopy.

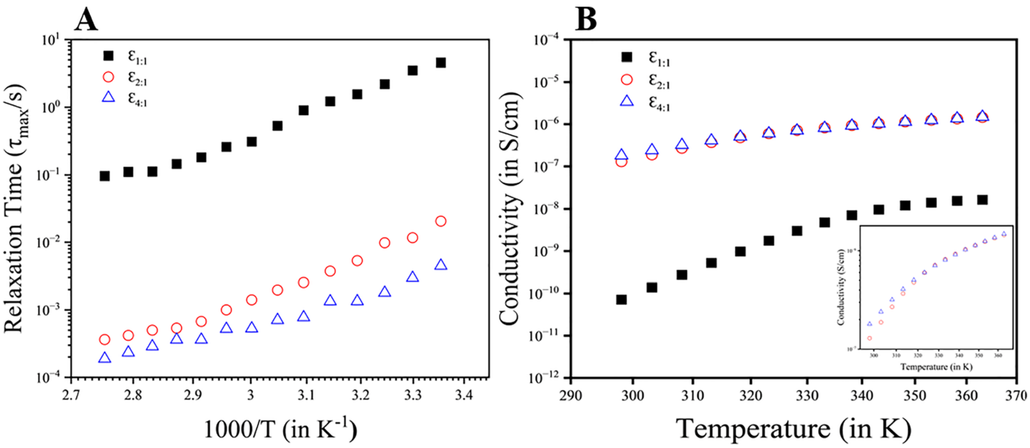


Fig. 1 (A) Relaxation time (τ_{max}) increases with reducing temperature for each of the three systems. Among the three systems under investigation, the one with the strongest interaction strength (ε) takes the longest to relax; (B) the conductivity is lowest for the system with the highest ε, which explains the low mobility and therefore, the longer relaxation time at any given temperature. These results were obtained as a result of performing DS after vacuum annealing the drop-casted coacervate films for an hour at 373 K.

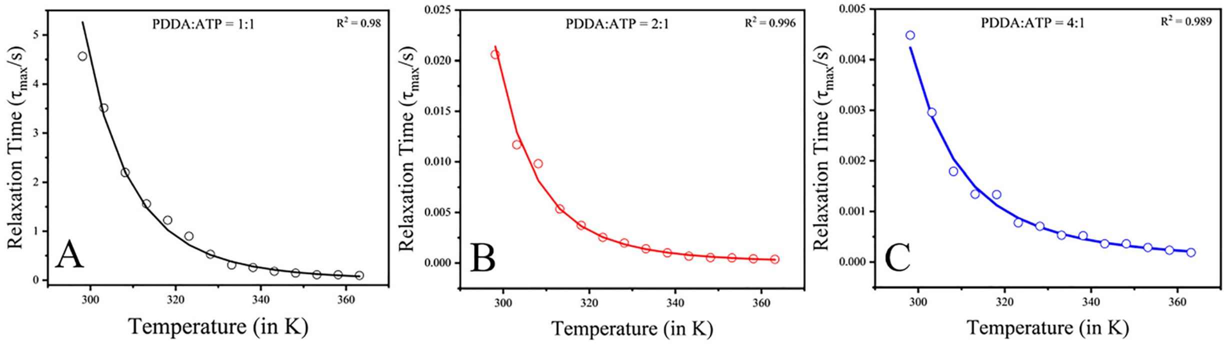


Fig. 2 Vogel–Fulcher–Tammann (VFT) fits on the relaxation time *versus* temperature data for PDDA : ATP = 1 : 1 (A), 2 : 1 (B) and 4 : 1 (C). The difference in stoichiometric ratios of the three samples is representative of the different cohesive energy densities that these samples possess.

This is coherent with many other studies wherein a similar trend in T_g was observed upon strengthening internal interactions.[9,10,29,54] Schlenoff and co-workers[55] reported that stoichiometric coacervates (*i.e.*, molar ratio of Pol$^+$ to Pol$^-$ = 1) attain their T_g at a more elevated T than non-stoichiometric coacervates due to matched attractive interactions, and our result accords with this observation.

As described by Spyridakou *et al.*,[29] a glass forming polymer is termed "fragile" if it shows a strongly non-Arrhenius dependence with T, which is the case with PDDA–ATP coacervates. To examine the relationship between fragility and ε, we follow three well-established measures of fragility. Firstly, the "Vogel fragility parameter" $\left(K = \frac{1}{D}\right)$, which describes the strength of the temperature dependence of the structural relaxation time, is a primary measurement parameter for quantifying fragility. A larger value of K implies a larger fragility, explaining why K is defined as reciprocal of D in the VFT equation. From Fig. 3C, we observe that K reduces with increasing ε and this implicates toward a decrease in fragility with stronger interaction strength. Secondly, in an attempt to relate the WLF parameters with VFT parameters, it was mathematically established by Angell[56] that the ratio T_0/T_g too is a measure of a material's fragility (m). Through our dielectric spectroscopy experiments, it is observed (Fig. 3B) that increasing ε points towards a decreasing trend in fragility. Lastly, the steepness index $m_s = \left(\dfrac{\partial(\log \tau_{max})}{\partial\left(\dfrac{T_g}{T}\right)}\right)\Big| T = T_g$, which defines the steepness of the Arrhenius plot for the relxation time near T_g is also a common measure of the fragility of glass-formation where a larger m_s corresponds to fragility higher fragility.[9,18,29,34,57] In Fig. 3D, we observe that as a consequence of m_s decreasing with ε, the fragility decreases. Notably, the estimation of two of the three above-mentioned fragility determining parameters, namely m_s and T_0/T_g, require a precise estimation of T_g, which can lead to significant uncertainty in fragility (m) estimates associated with the inherent uncertainty in estimating T_g. This type of uncertainty in estimating "m" is especially large in computational studies. All these fragility measures are closely inter-related, but we do not discuss these well-known relationships here. In the present work, we emphasize on K since this

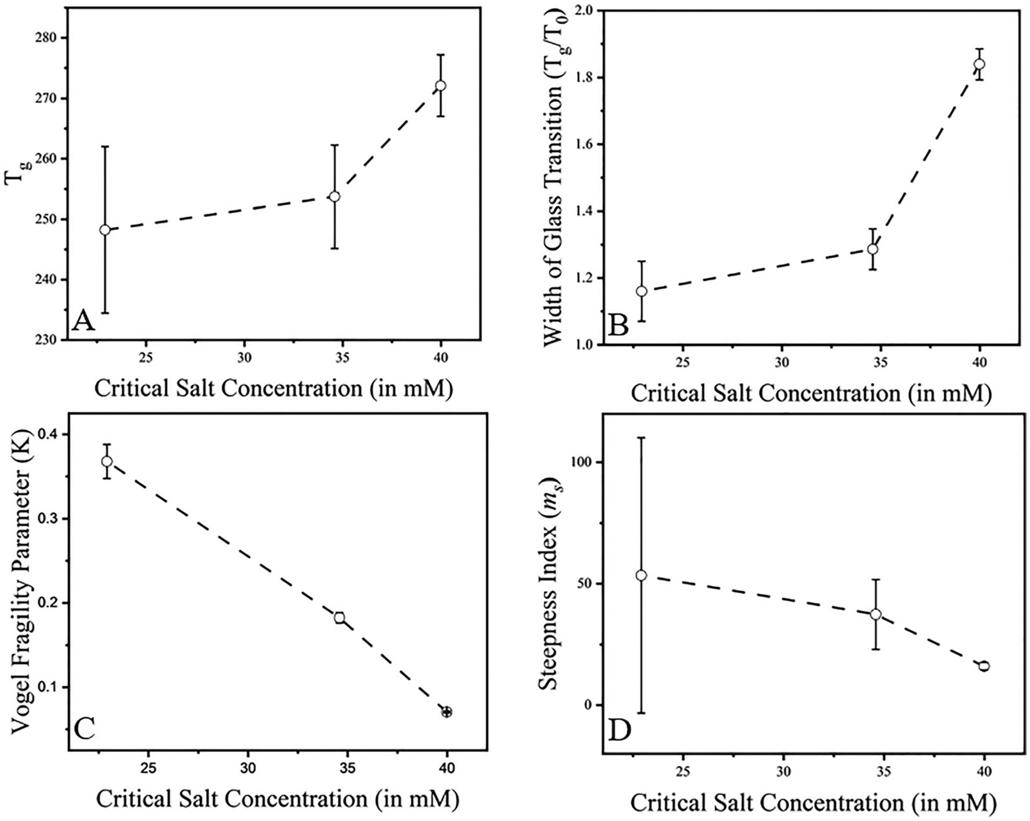


Fig. 3 (A) The glass transition temperature T_g increases with the critical salt concentration (c_{salt}) for different PDDA : ATP stochiometric ratio such that c_{salt} = 39.98 mM (1 : 1), 34.59 mM (2 : 1), 22.91 mM (4 : 1); (B) lower ratio of T_0 and T_g[56] implies lower fragility, which is observed as c_{salt} increases; (C) with increasing c_{salt}, the "Vogel fragility parameter" K decreases and this implies that fragility decreases; (D) the steepness index (m_s), which is inversely related to a system's fragility, decreases with increasing c_{salt}. Each of the three criterias to determine the fragility (m) of the coacervates is consistent with it decreasing with increasing interaction strength ε, defined as, $\varepsilon \equiv c_{salt}$.

measure of fragility, which quantifies the strength of the temperature dependence over a large temperature range, does not rely on the precise estimation of T_g.

As observed from Fig. 3B–D that the coacervate materials with a higher ε have a lower fragility. More interestingly, we observe for coacervate systems, akin to polyzwitterionic and other charged systems studied in the literature,[54] that the T_g and fragility follow inverse trends, which is unusual for polymeric glass formers. As summarized above, there have been a number of studies reporting a similar trend for a range of materials in which the cohesive interaction strength is likely varied appreciably, while the polymer molecular structure is not greatly altered. This general physical situation applies to our model system and in Fig. S7 we directly compare T_g and various measures of fragility where we observe these quantities vary linearly with each other an with a negative slope. This approximate linear relationship, with negative slope, between fragility and T_g was first discovered theoretically in GET calculations by Stukalin *et al.*[58] for a polymer model in which the molecular structure was fixed and the potential interaction strength was varied over a large range, though neither GET calculations nor molecular dynamics simulations of glass-formation have not yet been performed yet on coacervate materials due to the complexity of the interactions in these materials. Our observations on glass-formation in our model coacervate materials are quite consistent with these theoretical and simulation observations.

The seminal theoretical work relating to the inverted trend by Stukalin *et al.* did not provide any explanation of the inverted trend and an physical understanding of this counterintuitive phenomenon; that has only recently been reported by Xu *et al.*[18] Recapping our discussion above, the analysis of Xu *et al.*,[10] based on the GET framework indicated that increasing intermolecular interaction strength gives rise to more efficient molecular packing, *i.e.*, reduced packing frustration, similar to the effect of increasing pressure in most materials, which, in turn, increases the relative configurational entropy of the fluid and correspondingly causes a reduction in the fragility of glass-formation. This same general mechanism can be seen to be at play in previous studies in which the inverted trend between T_g and fragility have been observed and we discuss these previous observations in some greater detail from the GET perspective.

In cross-linked systems, fragility is often observed to increase with chemical cross-linking density, which has the effect of decreasing the configurational entropy of the material.[59] In the language of GET, cross-linking increases packing frustration, which can be quantified by the configurational entropy S_c of the material at elevated temperatures. The

GET has also revealed that increasing the molecular mass of polymers likewise decreases the configurational entropy of polymer melts and the variability of fragility in polymers predicted by the GET is mainly due to this thermodynamic effect. Zheng *et al.*[34] found in their molecular dynamics simulations that by increasing the potential molecular interaction strength in a network having fixed cross-linking density and monomer structure an inverted trend between T_g and fragility is observed, similar to our observations on our model coacervate material. Interestingly, Spyridakou *et al.*[29] observed the inverted trend between T_g and fragility in a cross-linked network material inspired by mussels, in which the chemical cross-links were replaced by charged (iron-catechol) physical cross-links that likely increase the cohesive interaction strength of these materials. Evidently, the charged physical cross-links can overcome the normal tendency of cross-linking to increase fragility. These observations are contrasted with recent observations on the progressive replacement of chemical cross-links in epoxy-amine thermoset materials with uncharged aromatic disulfide groups, which led to a concerted decrease of both T_g and fragility.[60] The observation of the inverted trend between T_g and fragility by Angell[61] and coworkers upon progressively increasing the protonation of decahydroisoquinole and also by increasing the ion content in PEO derivative polyester copolymer ionomer materials having increasing Li^+ ion content[32] can be understood to arise from a similar physics as in our coacervate materials-a progressive increase of the charge interaction strength through the increased ion content of the material leads to a robust tendency for T_g to increase while the fragility of glass-formation becomes reduced.

We note again that the inverted trend between T_g and fragility is uncommon for uncharged polymers since their cohesive interaction tends to be less sensitive to the variation of molecular parameters such as chain stiffness, monomer structure and molecular mass.[10] This is because the cohesive energy density in neutral polymeric systems can be widely varied. Even though these interactions are weaker than those in their charged counterparts, their cohesive energy density is much easily modulated through simple variations in side-group polarity, chain architecture, *etc.* This broad tunability greatly influences local packing efficiency and configurational entropy near T_g, thereby enhancing both T_g and fragility, as predicted by GET.[62]

We also consider the variation of the dielectric permittivity and relaxation time when T and moisture content in the coacervate were altered. The PDDA–ATP coacervates was drop-casted on one of the electrodes before being examined for dielectric permittivity and relaxation dynamics within the T range of 273.15 K to 363.15 K (see SI). The permittivity of the coacervates is $\approx 10^3$ to 10^4 at a frequency of 1 kHz – which is in conformity with those reported by Michaels *et al.*,[63] albeit for a different PEC system (Fig. S3). However, given minimal control on the coacervate film's thickness because of drop-casting, the exact value of permittivity cannot be underpinned with certainty. Michaels[63] reported that when salt concentration in their PEC system increased to 0.46 equivalents (per equivalent of PEC), the permittivity meteorically increased to $>10^3$ (at $f = 1$ kHz) compared to those with no salt. Notably, the coacervate system examined in Fig. S3 also has salt ions in the form of residual counterions and upon drawing parallels with Michaels' observation, we believe that these salt ions residing within the coacervate matrix are responsible for the high apparent permittivity observed. It is also noteworthy that the permittivity is much lower after drying and the high permittivity of the wet system is associated with hydration and the presence of added salt, an effect which is also reported by Michaels[63] and Durstock[64] for their respective PEC systems. Moreover, the permittivity, regardless of T, is very much higher at lower frequencies (≈ 0.1 Hz). This low frequency enhancement of the apparent permittivity in measurements such as ours is a commonly observed phenomenon and is normally attributed to the Maxwell–Wagner–Sillars (MWS) polarization, wherein the ions of the coacervate accumulate at its interface with the electrode of the instrument making the dielectric measurements.[65] At moderate frequencies, the surface polarization effect due to this effect drops precipitously and the apparent permittivity of the material plummets. This behavior has been reported previously for similar materials as ours by Michaels[63] and Durstock.[64] While the MWS effect creates some uncertainty in the estimation of the true permittivity of polyelectrolyte materials, measurements at moderate frequencies can still be taken as being reliable approximate estimates of the material permittivity in this frequency range. We also observe that a decrease in T reduces the dielectric permittivity (Fig. 4A, C and E) and decelerates the relaxation dynamics (Fig. 4B, D and F), a common trend found in charged polymer solutions. The formation of complexes of polyanions and polycations results in the loss of counterions to the supernatant, but a small population of these ions still reside within the matrix, and their mobility influences the patterns observed in Fig. 4. With decreasing T, the counterions within the coacervate matrix lose thermal energy, thereby reducing their mobility. When subjected to high frequency alternating field at low T, given the low mobility, the ions fail to promptly respond. This ultimately leads to the maximization of permittivity and loss at lower frequencies, because of which the relaxation dynamics are sluggish, and permittivity is low at low T.[64]

Water at moderate concentrations is well-known to act like a plasticizer of polymer materials and the variability of moisture in coacervate materials is of evident interest in various applications of these materials. To qualitatively assess this moisture's dependence on the dynamics on the coacervate materials that we study, we conducted frequency sweeps with no prior annealing at room temperature and vacuum conditions. We observe, from Fig. 5A, that the permittivity at 0.1 and 10^7 Hz were 2.87 and 4.03 times higher than that obtained under dry conditions, and presence of moisture accelerated the relaxation dynamics (Fig. 5B). This trend presumably arises because water "plasticizes" the dynamics of the coacervate material by reducing T_g, which is a common phenomenon in water soluble polymers.[55,66] We also observe this by conducting dielectric spectroscopy of wet coacervate samples. Also, for non-stoichiometric samples, *i.e.* the ones possessing higher water content,[67] the relaxation was faster than in stoichiometric

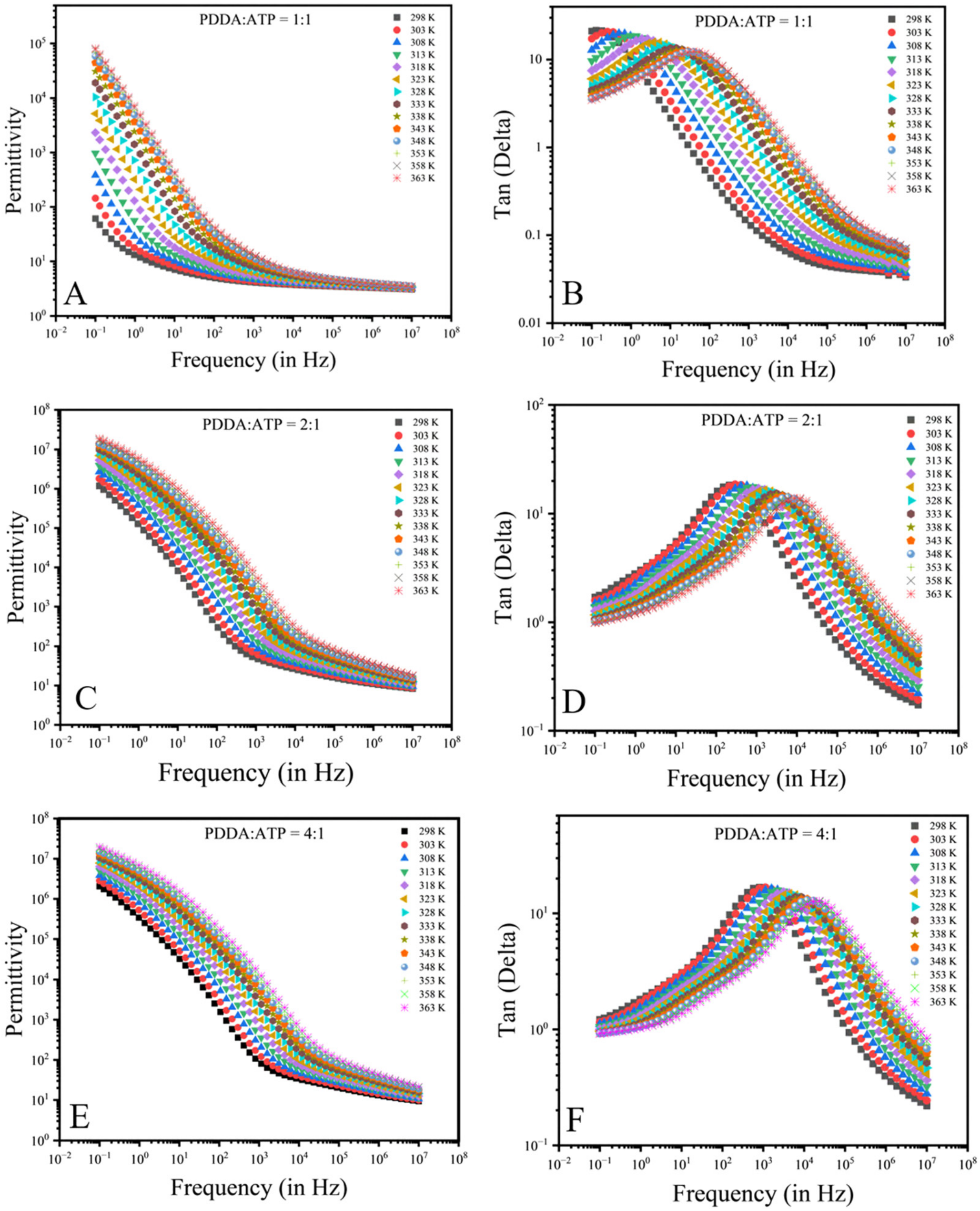


Fig. 4 (A), (C) and (E) The permittivity increases with temperature at a given frequency and it plummets as the frequency is increased; (B), (D) and (F) the relaxation becomes faster as the temperature increases. The frequency sweeps were performed after the films were annealed in vacuum for an hour to remove moisture.

ones (Fig. S6) and this is presumably attributed to a reduction in T_g – which is due to higher plasticizer (water) content. Additionally, we compared the coacervate's conductivities at dry and wet conditions at room temperature, and found that more moisture in a coacervate film led to an increase in the conductivity of the material (see Fig. S4). Thus, the enhanced segmental mobility of the polyelecrolyte chains in the complex coacervate is also reflected in the conductivity of the counterions around these complexes that dominate the coacervate conductivity.

Moisture can evidently have an appreciable influence on the conductivity of coacervate materials, as well known in many biological materials which often share a similar mixture of charged groups. This result is certainly not surprising and has been observed previously for other charged polymer materials, as described by Durstock,[64] De[67] and Schönhoff.[68] We mention this general property of complex coacervates as moisture can greatly influence their relaxational and mechanical properties.

Conclusion

Different polyelectrolyte complexes have been previously observed to exhibit glass transition as found in other polymer materials.[6,45–49] An inverted trend between the variation of T_g and fragility (m) to ε is observed, in contrast with the

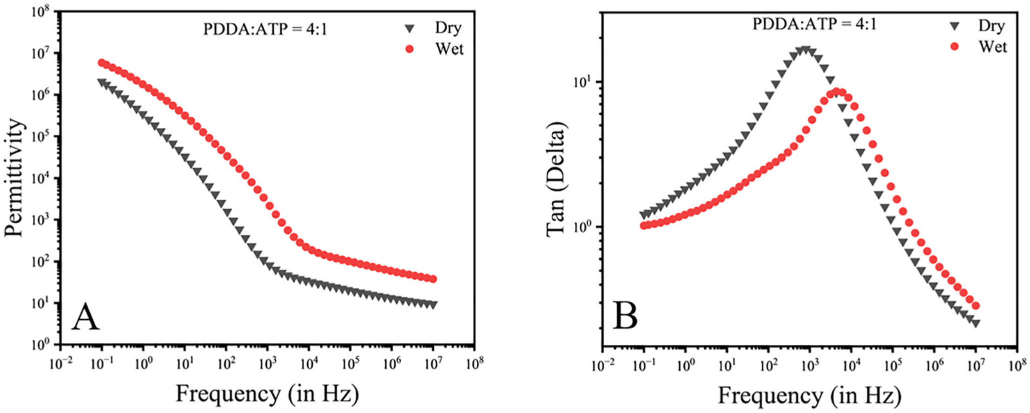


Fig. 5 At room temperature, (A) the permittivity is higher when the coacervates are hydrated; (B) relaxation times are shorter when coacervates are hydrated.

observations of most uncharged polymers.[29,34,54] In particular, we observe that an increase in the interaction strength ε within the coacervate material, as quantified by c_{salt}, leads to an increase in T_g and a decrease in m. This trend is exactly that anticipated from simulation studies in the glass-transition of charged and dipolar polymer melts,[9,10,34] and the predicted trend for neutral polymer melts from GET[9] when the cohesive energy density is increased while holding other molecular parameters fixed. As our secondary aim, we also explored the dielectric permittivity and relaxation dynamics of coacervates. In a previous work, our group showed that complex coacervate droplets can be highly sensitive to weak electric fields where a high permittivity of coacervates naturally accounts for this E-field sensitivity.[69] The measurements of the present conform this previous conclusion about coacervate materials. Lastly, we briefly explored the influence of varying relative humidity and found that the permittivity of the coacervate material decreases and relaxation time increases with increasing moisture content, a general trend evidenced for other charged polymer materials.[64]

Disclaimer

Certain commercial materials and equipment are identified to specify adequately the experimental procedure. In no case does such identification imply recommendation by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

Conflicts of interest

The authors declare no conflict of interest.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: **https://doi.org/10.1039/d5sm00969c**.

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