

Stability of Quadruple Hydrogen Bonds in an Ionic Liquid Environment

Chenming Li, Rajesh Bhandary, Anja Marinow, Stephanie Bachmann, Ann-Christin Pöppler, and Wolfgang H. Binder*

Hydrogen bonds (H-bonds) are highly sensitive to the surrounding environments owing to their dipolar nature, with polar solvents known to significantly weaken H-bonds. Herein, the stability of the H-bonding motif ureidopyrimidinone (UPy) is investigated, embedded into a highly polar polymeric ionic liquid (PIL) consisting of pendant pyrrolidinium bis(trifluoromethylsulfonyl)imide (IL) moieties, to study the influence of such ionic environments on the UPy H-bonds. The content of the surrounding IL is changed by addition of an additional low molecular weight IL to further boost the IL content around the UPy moieties in molar ratios of UPy/IL ranging from 1/4 up to 1/113, thereby promoting the polar microenvironment around the UPy-H-bonds. Variable-temperature solid-state MAS NMR spectroscopy and FT-IR spectroscopy demonstrate that the UPy H-bonds are largely present as (UPy-) dimers, but sensitive to elevated temperatures (>70 °C). Subsequent rheology and DSC studies reveal that the ILs only solvate the polymeric chains but do not interfere with the UPy-dimer H-bonds, thus accounting for their high stability and applicability in many material systems.

structures in peptides (such as alpha-helices or beta-folds);^[2] mediate highly specific H-bonds in the duplex-formation of DNA mediate;^[3] and impart self-healing properties in many polymers,^[4] where the dynamics of the H-bonds allow crack healing and material reconstruction.^[5] H-bonds display two important features, hardly reachable by other supramolecular bonding systems: they are strongly directional and thus highly dependent on spatial arrangements;^[6] and they can be tuned over many orders of magnitude in their strength, which is expressed via their association constants ($K_{\text{assn.}}$) in solution.^[7] However, in many applications, as widespread in nature, there is one drawback: polar solvents and polar environments usually weaken H-bonds^[8] by presenting alternative acceptors/donors, and thus often limit their applicability.^[9] Cooperative effects in proteins can help overcome this drawback,^[10] and the formation of hydrophobic

1. Introduction

Hydrogen bonds (H-bonds) are known to induce dynamic properties in many macromolecular assemblies and materials.^[1] H-bonds, as in many supramolecular polymers and polypeptides, contribute to the formation of many assemblies or secondary

pockets or other noncovalent interactions^[11] surrounding the H-bonds can also shield them from detrimental polar environments. Several such “hydrophobic shields” have led to quite stable H-bonding systems in synthetic polymers, protecting them even in aqueous environments.^[12] However, most triple or multiple H-bonds fail in various strongly polar solvents,^[13] stimulating the development of as-strong-as-possible H-bonding moieties like the quadruple ureidopyrimidinone (UPy), being powerful functional groups used to create functional materials with distinct properties such as shape-memory,^[14] self-healing,^[15] and ultra-tough-polymer properties.^[16] In previous studies on H-bonds in solution,^[17,18] UPy moieties were reported to self-associate into dimers with a $K_{\text{assn.}} \cong 10^7 \text{ M}^{-1}$ in chloroform, or a $K_{\text{assn.}} \cong 10^8 \text{ M}^{-1}$ in toluene, indicative of a strong influence by the polarity of the molecules near the UPy moieties. When embedded in a polymer matrix, it becomes difficult to directly measure changes in the association strength of these H-bond moieties, and only a few studies of changes in bonding strength in bulk polymers have been reported,^[13,19-23] mainly focusing on the impact of organic solvents.^[24]

We here report a systematic study on the influence of ionic liquids (ILs) on the association of the quadruple H-bonding motif UPy, by systematically embedding them into a microenvironment of increasing IL content. As the behavior of such UPy-system is crucial in the design of self-healing electrolytes or

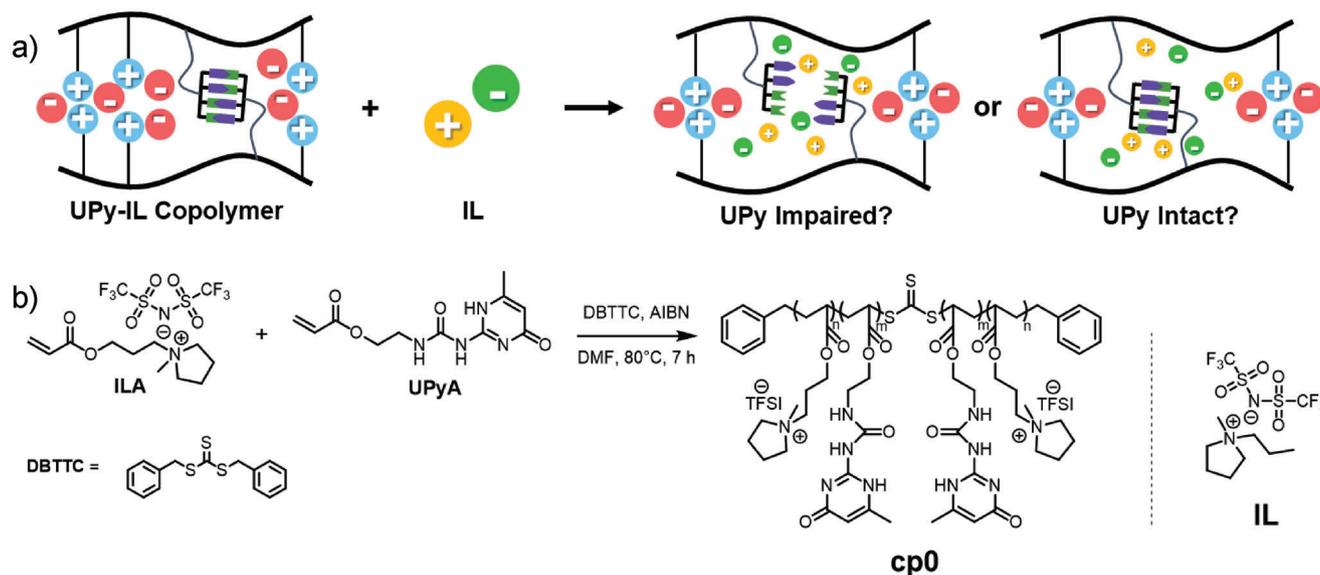
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Scheme 1. a) Schematic representation of UPy dimer formation in ionic liquid environments: UPy moieties are copolymerized in a polymeric ionic liquid with extra added ionic liquid molecules; b) structure of the copolymer **cp0** ($M_{n, NMR} = 11.5$ kDa, pyrrolidinium/UPy = 4.1:1) and the ionic liquid 1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl) imide **IL** used in this work.

3D-printing,^[25] knowledge of their stability in ILs is important. ILs are dipolar molecules that can offer strong polar molecular environments for UPy motifs, questioning their stability in such environments. However, since low molecular weight UPy molecules are poorly soluble in many ILs, such as pyrrolidinium-based ILs, we covalently embedded the UPy moieties into a polymeric ionic liquid (PIL) copolymer (see **Scheme 1**) composed of pyrrolidinium-ions along the chains via reversible addition-fragmentation chain-transfer (RAFT) polymerization. The adjacent pyrrolidinium moieties surrounding the UPy groups allow us to study the effects of this ionic microenvironment on the dissociation behavior of the quadruple UPy H-bonds. The chosen polymer also accomplishes the mixing of an additional pyrrolidinium-based IL to further increase the total amount of ILs around the UPy moieties systematically. Subsequent solid-state MAS NMR spectroscopy, FT-IR spectroscopy, differential scanning calorimetry (DSC), and rheology experiments then permit studying the binding state of the UPy moieties in these mixtures.

2. Results and Discussion

The pyrrolidinium-bis(trifluoromethylsulfonyl)imide-based copolymer **cp0** containing 20.7 pyrrolidinium moieties and 5.0 UPy moieties per polymer chain was synthesized via RAFT polymerization as reported^[26] to reach a controllable molecular weight of 11.5 kDa (as determined by NMR spectroscopy; for the detailed calculation and spectra, see Section S1, Supporting Information). The neat polymer **cp0**, now containing ≈ 4 IL units for every UPy moiety, can be further mixed with different ratios of 1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide (**IL**) to prepare the samples **cp25**, **cp50**, and **cp75**, with a molar ratio of UPy/IL-moiety of 1:39.3 (**cp25**), 1:73.5 (**cp50**), and 1:113.2 (**cp75**) respectively. The synthesis of **cp0** and the structure of the

Table 1. Composition of the parent sample **cp0** with the ratio backbone-IL/UPy = 4.1/1; and the samples **cp25**, **cp50**, and **cp75**, with a molar ratio of UPy/IL-moiety of 1:39.3 (**cp25**), 1:73.5 (**cp50**), and 1:113.2 (**cp75**) respectively.

Sample ID	cp0 ^{a)}	cp25	cp50	cp75
Polymer: IL (weight ratio) ^{a)}	Neat	1:0.25	1:0.50	1:0.75
Polymer: IL ^{a,b)}	–	1:6.9	1:13.6	1:21.4
Backbone-IL: UPy: Free IL ^{b)}	4.1:1:–	4.1:1:35.2	4.1:1:69.4	4.1:1:109.1

^{a)} For the detailed calculation of sample composition see Section S1 (Supporting Information); ^{b)} Molar ratio calculated by ¹H NMR; ^{c)} $M_{n, NMR} = 11.5$ kDa, backbone IL/UPy = 4.1:1.

added ionic liquid (**IL**) are shown in Scheme 1 and the sample information is listed in **Table 1**.

To study the behavior of the UPy H-bonds in such polar environments we firstly probed solid-state MAS NMR spectroscopy, as the bound/dissociated status of H-bonded protons can be directly detected by NMR spectroscopy both in solution^[13,17,19,28,29] and in the solid state.^[23,30–32] The ¹H MAS NMR spectrum of **cp0** shown in **Figure 1a** reveals the intramolecular H-bond H_a , and the intermolecular H-bonds H_b and H_c of the UPy-NH protons (denoted by the two gray dashed lines) in the neat copolymer **cp0**, matching well with the reported solid-state NMR spectra of UPy compounds known for non-ionic surroundings.^[23,33] Upon heating from 23 to 53 °C, these peaks do not shift to lower ppm values, forming evidence for still un-dissociated UPy moieties. As the actual temperature in the MAS rotor could be up to 30 °C higher than the set value due to the frictional heating upon rotation,^[27] we can state that there is no observable shift of the H-bond peaks at the temperature of $T_{actual} = 32–78$ °C. Similarly, the presence of still associated UPy moieties can be also evidenced by their immobility in their ¹³C NMR spectra (see ¹³C NMR spectra recorded under cross polarization (CP) and direct excitation (DE)

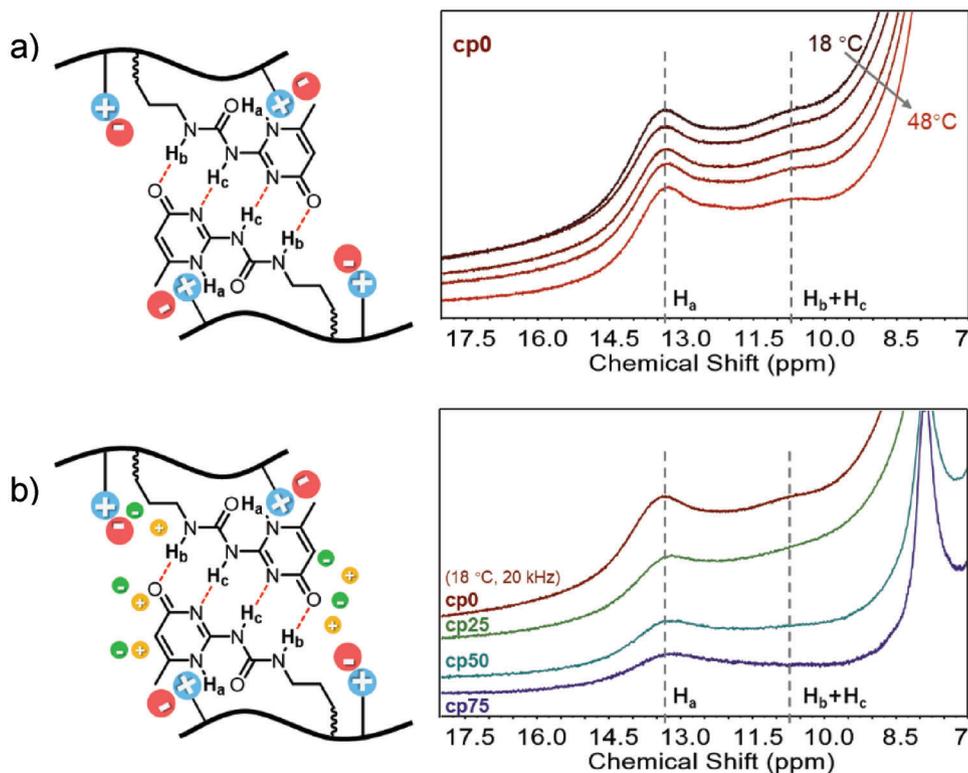


Figure 1. Schematic illustration of the UPy dimer in their DDAA (donor–donor–acceptor–acceptor) H-bonding array and extracts from ^1H MAS NMR spectra of a) **cp0** at variable temperatures, measured at 20 kHz and $T_{\text{set}} = 23, 33, 43, 48, 53\text{ }^\circ\text{C}$ (with T_{actual} with an additional $30\text{ }^\circ\text{C}$ due to the frictional heating upon rotation^[27]); b) ^1H MAS NMR spectra of samples **cp0**, **cp25**, **cp50**, and **cp75** with different IL content (recorded at $5\text{ }^\circ\text{C}$ actual sample temperature and a maximum stable MAS frequency of 15 kHz due to their gel nature under rotation). Though the DADA (donor–acceptor–donor–acceptor) H-bonding array of UPy dimers is possible due to the tautomeric exchange, all the UPy dimers in this work are assumed to be in their most stable DDAA array.^[17,23]

conditions in the Figure S2, Supporting Information). While polymeric backbone carbons, the pyrimidinone-carbonyls, and other UPy carbons appear in the CP-spectra, they are absent in the DE-spectra recorded with short interscan delays, where only the mobile moieties can be probed, indicating their immobility in the probed samples. To study whether a higher content of IL leads to changes in the dissociation state of the H-bonds, we have mixed the polymer samples with additional IL (see Table 1, samples **cp25**, **cp50**, **cp75**) to increase the ratio of IL/UPy. Upon mixing with the IL, the chemical shifts of the peaks remain unchanged as indicated by the gray dashed line in Figure 1b, demonstrating the invulnerability of the UPy dimers against the added IL up to a ratio UPy/IL $\approx 1/113$. The only observed change is the peak at $\approx 10.8\text{ ppm}$, which becomes broader, less intense, or overlaps with the adjacent peaks. This might be a result of the exchange of the UPy keto-enol tautomer promoted by reduced chain friction via IL mixing. To distinguish possible tautomers double quantum 2D NMR spectra of the samples were recorded and compared with the reported spectra (for the 2D spectra, see Figure S3, Supporting Information),^[23] which unfortunately did not provide further insight due to the poor spectral resolution and missing of the NH peaks. Analogous experiments at higher MAS frequency to obtain double quantum data with higher resolution were not successful due to the viscous nature of the gel samples,

as even upon cooling IL-containing samples pushed the cap out at MAS frequencies above 15 kHz.

We further probed FT-IR spectroscopy to reveal the open/close nature of the UPy H-bonds, since solid-state NMR spectroscopy was not applicable for all samples at elevated temperatures due to their reduced viscosities. Therefore, FT-IR analysis of the H-bonds at variable temperatures in a broader range ($25\text{--}150\text{ }^\circ\text{C}$) was performed for all samples. For the neat copolymer **cp0** two features were observed when the temperature was increased (Figure 2a,b): the NH peaks at $\approx 3200\text{ cm}^{-1}$ gradually became broader and increased in intensity when compared to the adjacent C–H peak ($\approx 2975\text{ cm}^{-1}$), whereas the peaks at $\approx 3400\text{ cm}^{-1}$ increased slightly, revealing indicative of an increase in free, dissociated N–H bonds in sample **cp0**. As the temperature was increased to $70\text{ }^\circ\text{C}$, a new peak at $\approx 1680\text{ cm}^{-1}$ was observed, separated from the main peak (at 1663 cm^{-1}) for the C = O of urea moieties of UPy (indicated by the gray dashed box), which is an indication of a weakening of the ureido H-bonds and a loss of the UPy stacking.^[34,35] Blueshifting of the C = O (pyrimidinone) stretching ($\approx 1702\text{ cm}^{-1}$, denoted by the gray arrow) upon heating also indicates weakening of the UPy H-bonds at elevated temperatures ($>70\text{ }^\circ\text{C}$), in line with the previously reported temperature-dependency of UPy H-bonds.^[36] However, mixing with IL does not interfere with the UPy H-bonds as indicated by the unshifted

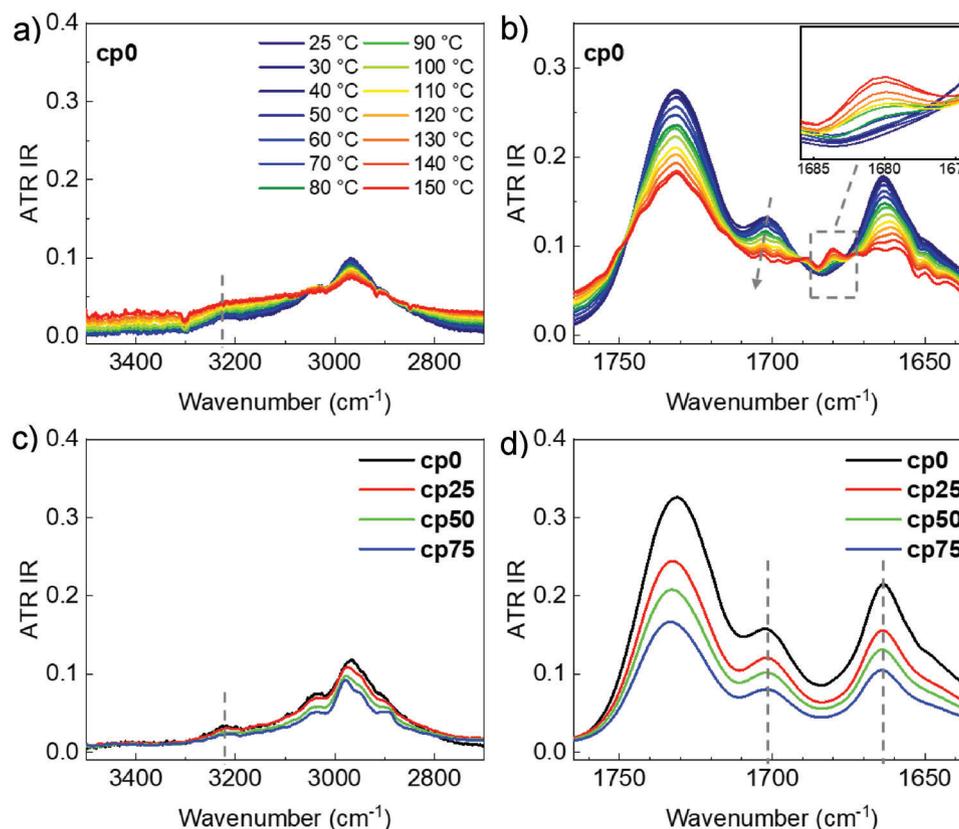


Figure 2. FT-IR analysis of a,b) **cp0** at variable temperatures and c,d) all samples at room temperature.

characteristic IR peaks of UPy in Figure 2c,d. Additionally, the samples with the added IL show similar FT-IR spectra compared to the sample **cp0** upon heating, which again proves the almost undisturbed H-bonds of UPy against the added IL (for detailed variable-temperature FT-IR spectra, see Figure S4, Supporting Information). Thus the UPy H-bonds are prone to dissociation at elevated temperatures (>70 °C), but not sensitive to the charged IL molecules in the charged PIL matrix at ambient conditions.

We also searched for changes in the UPy-bonded copolymer upon the addition of IL by differential scanning calorimetry

(DSC). The neat sample **cp0**, when compared to the reported homopolymers, showed an increase in the glass transition temperature T_g from -13 °C (homo PIL, $M_n = 11.0$ kDa)^[26] to 22.4 °C (**cp0**), suggesting closed UPy dimers in the charged PIL matrix that reduce the segmental motion and thus result in a higher T_g . When further IL is added, the T_g s of all samples were reduced from 22.4 °C (**cp0**), to -12.8 °C (**cp25**), to -35.2 °C (**cp50**), and to -56.1 °C (**cp75**) (see Figure 3a), demonstrating that the added IL induced faster chain dynamics. For comparison, this is in contrast to effects observed by the addition of metal salts

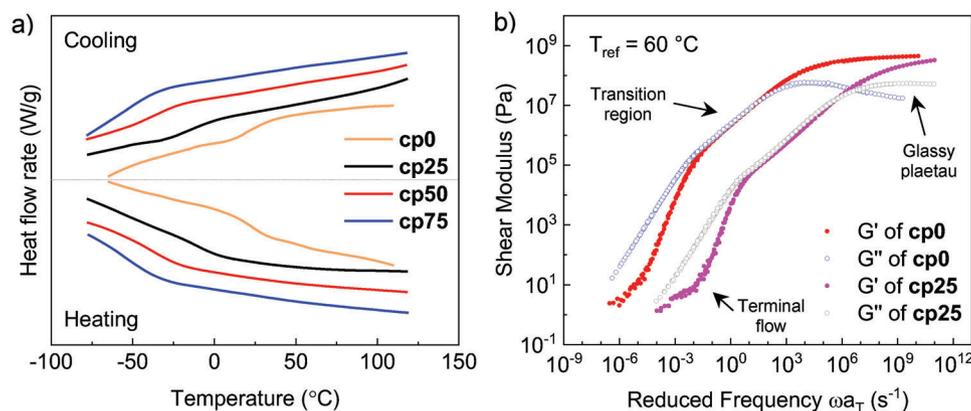


Figure 3. a) DSC analysis of all samples with a heating/cooling rate of 3 K min⁻¹ and thermal history was canceled by a pre-heating cycle; b) the master curves of **cp0** and **cp25** measured from -10 to 120 °C, with the reference temperature of 60 °C.

in UPy-containing polymers^[37,38] where an increase of T_g can be observed via chain stiffening effects attributed to crosslinking by metal-carbonyl coordination. In DSC analysis, the number of glass transitions can be used as indirect proof of microphase separation if the formation of the separated domains can be excluded.^[39-41] As shown in Figure 3a, there is only one glass transition occurred for every sample, suggesting that, though UPy forms dimers, there is no distinct microphase separation between the UPy dimers and the (poly-) ionic liquids moieties. To further test the influence of IL on the final H-bonded polymers, dynamic rheology measurements were performed. Owing to the technically too-low-to-detect viscosity of **cp50** and **cp75** at elevated temperatures, only the master curves of neat **cp0** and **cp25** were measured. As shown in Figure 3b, master curves of **cp0** and **cp25** demonstrate a typical Rouse behavior with a terminal flow, a transition region with a crossover of the storage modulus G' and the loss modulus G'' , and a glassy plateau, though the rubbery plateau is absent due to lack of chain entanglements or permanent crosslinking. The terminal flow in the low-frequency region proves the dynamic nature of these two H-bonded samples over a long timescale, whereas according to the Rouse model the crossover of the G' and the G'' reveal the loss of association among chains, where the material starts to flow, with the reciprocal of this crossover time representing the relaxation time (τ_b) of the polymer.^[22] The relaxation time τ_b of the sample added with IL in a 6.9 molar ratio (see Table 1 for sample compositions) is reduced from 1.20×10^{-1} s (**cp0**) to 1.94×10^{-6} s (**cp25**), indicative of the largely reduced total relaxation time by the added IL, resulting from synergic effects of the possible UPy H-bond relaxation and the solvation of the polymer chains by the added IL. Considering that **cp0** and **cp25** have the same parent polymer matrix (which is **cp0**), and their storage modulus at the glassy state, where all the segmental motion is frozen, are of similar value, we could thus further deduce that the associations that determine this modulus are also at a similar strength, which is most probably the association of UPy groups. Because **cp25** contains mobile IL molecules while **cp0** does not, and their modulus is of a similar value when segmental motion is frozen, we thus conclude that the UPy accounting for the mechanical strength is not influenced by the IL,^[22,42] whereas the IL only promotes the chain motion by reducing the chain friction via chain solvation rather than breaking/weakening the UPy H-bonds. Therefore, the H-bonds of UPy dimers are largely independent of the addition of IL and thus the increased polar environment.

3. Conclusion

In summary, as proven by MAS NMR spectroscopy, the H-bonds of UPy at ambient temperature stay largely undisturbed in their dimeric state, also upon mixing with additional IL up to a molar ratio of UPy/IL = 1/≈113. FT-IR analysis at elevated temperatures demonstrates a weakening of the UPy H-bonds at temperatures above 70 °C, although this is highly independent of the added IL at these temperatures (25–150 °C). We thus can prove that the UPy dimers remain stable in (poly-)ionic liquid environments, though the mobile IL molecules reduce chain friction and boost the chain dynamics of the polymeric ionic liquids matrix as evidenced by DSC and rheology. As the UPy-moieties

are used extensively in many materials systems, in recent times largely in poly(electrolytes) to impart self-healing properties, the findings here are important for the design of self-healing materials with strong polar surroundings, where UPy bonds are often used to generate transient crosslinks in highly charged media.

4. Experimental Section

Materials: 1-Methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide 99% was purchased from IoLiTech (Heilbronn, Germany) and dried under ultrahigh vacuum at 80 °C for 48 h then stored in a glovebox ($O_2 < 0.5$ ppm, $H_2O < 0.5$ ppm); dimethyl formamide (DMF) were purchased from Grüssing (Filsum, Germany) and purified/dried via a solvent purification system; 2,2'-azobis(2-methylpropionitrile) (AIBN) was purchased from Sigma-Aldrich (Merck KGaA, Darmstadt, Germany), and recrystallized in methanol before use; deuterated dimethyl sulfoxide ($DMSO-d_6$) were purchased from Chemotrade (Eckert and Ziegler Gruppe, Düsseldorf, Germany) and used as received.

Synthesis of Monomer ILA and UPyA, and RAFT Agent DBTTC: The synthesis was followed as described in reference.^[26]

The synthesis was followed as described in reference.^[26] The synthesis of ionic monomer **ILA**, UPy monomer **UPyA**, and the copolymer via RAFT polymerization was adapted from reference. The synthesis of ionic monomer **ILA**, UPy monomer **UPyA**, and the copolymer via RAFT polymerization was adapted from reference.^[26] Briefly, **ILA** (2993 mg, 6.26 mmol), and **UPyA** (417 mg, 1.55 mmol) were placed in DMF (8 mL) in a Schlenk tube. The tube was sealed with a rubber septum and the reaction mixture was purged with nitrogen for 30 min to deoxygenate under vigorous stirring. After deoxygenation, the tube was heated in an oil bath at 120 °C till a clear solution was obtained, then the temperature of the oil bath was cooled to 80 °C. In the meantime, in a flask **DBTTC** (114.3 mg, 0.39 mmol) and AIBN (7.0 mg, 4.26×10^{-2} mmol) were dissolved in deoxygenated DMF (0.5 mL), then this solution was transferred to the reaction Schlenk tube by a syringe to initiate the polymerization. After 7 h, the reaction was stopped by opening the septum and subsequently precipitated into DCM three times to eliminate the monomer residue. The polymer was collected by centrifugation and decantation and finally dried at 80 °C under a high vacuum for 24 h. The molecular weight was evaluated by 1H NMR using the characteristic methyl protons of the pendent pyrrolidinium ($\equiv N-CH_3$, 3nH, $\delta = 3.02$ ppm, with n being the degree of polymerization of **ILA**), the characteristic vinylic proton of the pendent UPy moiety ($-(CH_3-)C = CH-$, mH, $\delta = 5.80$ ppm, with m being the degree of polymerization of **UPyA**), and the characteristic aromatic protons of **DBTTC** (pH, 10H, $\delta = 7.36$ ppm). For the NMR spectrum of **cp0** in $DMSO-d_6$ and the detailed molecular weight calculation, see Figure S1 (Supporting Information). Briefly, **ILA** (2993 mg, 6.26 mmol), and **UPyA** (417 mg, 1.55 mmol) were placed in DMF (8 mL) in a Schlenk tube. The tube was sealed with a rubber septum and the reaction mixture was purged with nitrogen for 30 min to deoxygenate under vigorous stirring. After deoxygenation, the tube was heated in an oil bath at 120 °C till a clear solution was obtained, then the temperature of the oil bath was cooled to 80 °C. In the meantime, in a flask **DBTTC** (114.3 mg, 0.39 mmol) and AIBN (7.0 mg, 4.26×10^{-2} mmol) were dissolved in deoxygenated DMF (0.5 mL), then this solution was transferred to the reaction Schlenk tube by a syringe to initiate the polymerization. After 7 h, the reaction was stopped by opening the septum and subsequently precipitated into DCM three times to eliminate the monomer residue. The polymer was collected by centrifugation and decantation and finally dried at 80 °C under a high vacuum for 24 h. The molecular weight was evaluated by 1H NMR using the characteristic methyl protons of the pendent pyrrolidinium ($\equiv N-CH_3$, 3nH, $\delta = 3.02$ ppm, with n being the degree of polymerization of **ILA**), the characteristic vinylic proton of the pendent UPy moiety ($-(CH_3-)C = CH-$, mH, $\delta = 5.80$ ppm, with m being the degree of polymerization of **UPyA**), and the characteristic aromatic protons of **DBTTC** (pH, 10H,

$\delta = 7.36$ ppm). For the NMR spectrum of **cp0** in DMSO- d_6 and the detailed molecular weight calculation, see Figure S1 (Supporting Information).

Sample Preparation: In a glovebox, neat **cp0** and the desired amount of **IL** were weighed in a vial with a magnetic stir bar, and then a small amount of dry MeCN (≈ 1 mL) was added to support the mixing process. After homogeneity was reached, MeCN was firstly removed by heating the open vial in the glovebox at 120 °C overnight, then the vial was transferred to a closed heating kit with an ultrahigh vacuum applied and dried at 80 °C for 48 h before characterization.

Differential scanning calorimetry (DSC) measurements were performed on a calibrated heat-flux DSC (Mettler-Toledo, Greifensee, Switzerland) equipped with the FRSS sensor, connected to a TC100 Intracooler (Huber, Offenbach, Germany). About 0.5 mg of sample was placed in aluminum-sealed crucibles for measurements. The thermal history was canceled by heating the samples from 25 to 120 °C at 10 K min⁻¹, followed by isothermal annealing for 20 min, re-cooling to -80 °C at 3 K min⁻¹, and thermostating at -80 °C for another 10 min. The final DSC curves were then recorded from -80 to 120 °C at 3 K min⁻¹.

Rheology measurements were performed on an MCR 101 DSO rheometer (Anton Paar Germany GmbH, Ostfildern-Scharnhausen, Germany) using a parallel plate–plate geometry (plate diameter: 8 mm). All polymers were dried under an ultrahigh vacuum at 80 °C for 24 h before the rheology measurement. The samples were directly smeared on the lower plate of the sample holder at 80–100 °C, then thermostated for an hour before loading the upper kit. The sample temperature was regulated by thermoelectric cooling/heating in a Peltier chamber under a dry nitrogen atmosphere. At each temperature, the sample was equilibrated for 20 min before the measurement was initiated. All measurements were performed in the dynamic mode and repeated twice to ensure precise values. Data analysis was performed via Rheo Compass (version V1.30.1064).

Liquid-State Nuclear Magnetic Resonance Spectroscopy was performed on a Varian FT-NMR spectrometer (400 MHz for ¹H-NMR and 100 MHz for ¹³C-NMR, respectively) (Agilent Technologies Germany GmbH & Co. KG, Waldbronn, Germany). All samples were measured at 27 °C using deuterated dimethyl sulfoxide (DMSO- d_6). Chemical shifts (δ) were recorded in parts per million (ppm) relative to the remaining protonated solvent signals (DMSO- d_6 : 2.50 ppm (¹H) and 39.5 ppm (¹³C)). The data analysis was performed via MestReNova (version 9.0.1-13254).

Solid-State Magic Angle Spinning Nuclear Magnetic Resonance Spectroscopy (MAS NMR) was performed on a Bruker Avance III HD 600 MHz spectrometer using a 3.2 mm double-channel probe. The spinning rate was up to 20 kHz MAS and the temperature ranged from 263.0 to 326.4 K, although the sample temperature is up to 30 K higher due to frictional heating during magic angle spinning. The magic angle was optimized with KBr. α -glycine was used to calibrate the ¹H 90° pulse and the ¹³C cross-polarization conditions. For ¹³C cross-polarization experiments, a 90 to 100 ramp and SPINAL64 heteronuclear decoupling were used. To get more insights into the mobile parts, ¹³C NMR spectra with direct excitation and a short interscan delay of 1s were measured. Adamantane was used to reference the chemical shift. Rotor-synchronized ¹H(SQ)⁻¹H(DQ) BABA experiments were recorded.^[43,44] The data analysis was performed via MestReNova (version 9.0.1-13254) or with TopSpin (Version 4.0.8).

Variable-Temperature Attenuated Total Reflection (ATR) FT-IR Spectroscopy was performed using a Bruker Tensor vertex 70 (Bruker Optik GmbH, Bremen, Germany) equipped with a Golden Gate Heated Diamond ATR top plate (Specac Ltd, Orpington, UK). All wavenumbers are given in cm⁻¹. For FT-IR measurements at elevated temperatures, samples were heated with the heating rate of 10 K min⁻¹ and equilibrated at the desired temperature for 2 min before the measurement started. Data analysis was performed via the software OPUS (version 8.2) and Origin 2018 (version b9.5.0.193).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

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Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

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