Synthesis of poly-*p*-phenylene terephthalamide (PPTA) in ionic liquids

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Several ionic liquids (ILs) were tested for their suitability to synthesize the aramid polymer PPTA in an attempt to diminish the dependence on the toxic *N*-methylpyrrolidone (NMP) that is currently used in industry. The room-temperature IL 3-methyl-1-octylimidazolium chloride ($[C_8MIM][Cl]$) showed the highest promise as with this medium the polycondensation reaction proceeds with a similar mechanism as it happens in the solvent mixture of NMP with $CaCl_2$. With this IL, PPTA polymer with an inherent viscosity of 1.95 dL/g was obtained in a low-temperature polycondensation reaction. This is the highest reported molecular mass of PPTA to date that was obtained by polymerization in an ionic liquid. An EXAFS and solid state NMR spectroscopic study showed that $[C_8MIM][Cl]$ and the current industrial solvent of NMP and $CaCl_2$ show similar characteristics when it comes to the synthesis of PPTA.

Keywords: Kevlar, PPTA, aramids, polycondensation reaction, ionic liquids, coordinating anions, reaction gelation

Introduction

Poly-*p*-phenylene terephthalamide (PPTA), commonly known under the brand names Kevlar® and Twaron®, is one of the best- known and widely used aramids (aromatic polyamides) worldwide.[1] The structure of PPTA, a concatenation of aromatic rings connected by secondary amide groups in para orientation, is very rigid. This rigidity, in combination with the ability to form an extended hydrogen bond network between polymer chains, promotes crystallization of the material.[2] In fact, not a single neutral solvent exists that is able to keep PPTA polymers in a dissolved state. The synthesis of PPTA is quite unique since prevention of precipitation via gelation of the reaction mixture rather than dissolution is needed to achieve PPTA with reasonable molecular masses. At present, industry relies on a solvent mixture of *N*-methylpyrrolidone (NMP) and $CaCl_2$ as polymerization medium for the synthesis of PPTA. The addition of a salt is essential for preventing early precipitation of the polymer during the polycondensation reaction.[3] The chloride anion of the salt acts as a hydrogen-bond acceptor with the secondary amide functional groups and blocks aggregation of growing polymer chains during synthesis.[4] Furthermore, the interactions that take place between solvent, salt and the growing PPTA chains result in gelation of the reaction mixture.[5] The polycondensation reaction can continue in the "solid" or gelled state until a molecular mass is obtained that is suitable for fibre spinning and commercialization, i.e. PPTA polymer with an inherent viscosity (η_{inh}) of 4 to 5 dL/g. The inherent viscosity is used to express the molecular mass of PPTA because of its limited solubility. Due to toxicity issues with NMP[6] and the need to use a salt to prevent precipitation of PPTA during synthesis, ionic liquids (ILs) are proposed as an alternative polymerization medium.

ILs are solvents with low melting points that consist entirely of ions.[7] Because of their low flammability and low volatility, ILs are considered to be safer and more environmentally friendly than conventional molecular solvents.[8,9] Our previous work has shown that ILs with coordinating anions exhibit much higher dissolution strength towards PPTA oligomers compared to the industrial reaction medium composed of NMP and CaCl$_2$.[10] However, ILs are also unable to dissolve high molecular mass PPTA. It was learnt that using ILs diluted in a cosolvent as medium, gelation of the reaction mixture during synthesis is also a requirement for a successful polymerization of PPTA.[11] The hydrogen bonding and accepting characteristics of imidazolium and 2-methylpyridinium chloride ILs were found to aid most efficiently in postponing precipitation of the polymer during synthesis which eventually leads to gelation and crumbling of the reaction mixture. However, it was concluded that apart from amide solvents, adding a co-solvent does not help in preventing premature precipitation of the PPTA polymer during synthesis. Promising results were obtained by adding only small amounts of non-amide solvents to reduce the reaction mixtures viscosity.

Little is known about the synthesis PPTA in pure ILs. So far, only low molecular mass PPTA could be achieved using ILs as polymerization medium.[12,13] In this paper, the possibilities of other ILs as a medium for the synthesis of PPTA are investigated. PPTA is formed by a condensation reaction between *p*-phenylenediamine (PPD) and terephthaloyl chloride (TPC).

Experimental

Chemicals

All the ionic liquids used in this study were purchased from IoLiTec (Heilbronn, Germany), Cytec (New Jersey, USA) or Sigma-Aldrich (Diegem, Belgium). *N*-methylpyrrolidone extra dry (99.5%), terephthaloyl chloride (99+%), *p*-phenylenediamine (99+%) and sulfuric acid (96 wt%)

were purchased from Acros Organic (Geel, Belgium). Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) was purchased from Merck (Overijse, Belgium). p-Phenylenediamine (99+%) was purified by sublimation at reduced pressure on a vacuum line at 95 °C [12]. White crystals were obtained which were stored in a desiccator in a dark place. α-Picoline was dried using molecular sieves (4Å) so that the water content was below the detection limit of the Karl-Fischer coulometer [14].

Equipment

A Karl Fischer DL39 coulometer from Mettler-Toledo was used to measure the water content of all the solvents before polymerization. Determination of inherent viscosities was performed with a certified calibrated Ubbelohde 10-100 mm^2/s (0.1 K) capillary viscometer from SI analytics in a Lauda thermostatted water bath at 25 °C. Solvent viscosities were measured using a LOVIS 2000 ME Microviscometer from Anton Paar using a temperature scan for 40 °C up to 80 °C with a temperature interval of 5 °C. A Bosch Ergomix 750 W mixer was used to break up the gels formed after a polymerization reaction.

Polycondensation reaction of PPTA at 80 °C

Each time an aliquot of the ionic liquid (40 g) was added to a three-neck flask. The ionic liquid was dried on a vacuum line (5 mm Hg) at 100 °C until the water content of the ionic liquid was below 100 ppm. Reagents were added in such a manner that the same molar ratio was kept between solvent and monomers in polymerization reactions with various ionic liquids. *p*-Phenylenediamine (1.00 eq, 3.35 mol%) was added to the reaction mixture under a nitrogen flow. Dissolution of the monomer took place at 80 °C. An overhead stirrer (4 cm collapsible 2-blade impeller fitted in a Cowie universal stirrer guide) was placed on top of the flask. α-Picoline (2.00 eq, 6.70 mol%) was added. Terephthaloyl chloride (1.00 eq, 3.35 mol%) was added to the reaction mixture as solid flakes while the mixture was stirred with a mechanical stirrer at a

stirring rate of 2000 rpm. A rapid polycondensation reaction occurred and stirring was continued for 10 minutes. After the reaction, the obtained polymer/gelated reaction mixture was precipitated/coagulated with water. The polymer was filtered off, and washed with 100 ml of water, 50 ml of dimethyl sulfoxide. Further washing was done by Soxhlet extraction in water overnight. Afterwards, the polymer was dried on a vacuum line (5 mm Hg) at 130 °C and a bright yellow powder was obtained. The yield was quantitative. Afterwards, the PPTA polymer was dissolved in sulfuric acid (96 wt%) at a concentration of 0.50 dL/g and its inherent viscosity was determined.

For the benchmark reaction using NMP/5.5 wt% $CaCl_2$, Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) (2.91 g, 19.8 mmol) and N-methylpyrrolidone extra dry (< 5 ppm) (40 g) were added to a three-neck flask. The excess water was distilled off by fractionated distillation on a vacuum line at a temperature of 75 °C. Additional dry NMP was added to compensate for solvent losses during distillation. Solvent was dried until the water content was less than 100 ppm.

Polycondensation reaction of PPTA at 0 °C

Ionic liquid (40 g) was added to a three-neck flask. The ionic liquid was dried on a vacuum line (5 mm Hg) at 100 °C until the water content of the ionic liquid was below 100 ppm. Reagents were added in such a manner that the same mole ratio was kept between solvent and monomers in polymerization reactions with various ionic liquids. p-Phenylenediamine (1.00 eq, 3.35 mol%) was added to the reaction mixture while under a nitrogen flow. Dissolution of the monomer took place at 50 °C. An overhead stirrer (4 cm collapsible 2-blade impeller fitted in a Cowie universal stirrer guide) was placed on top of the flask. Afterwards, the three-neck flask was placed in an ice bath and still a continuous nitrogen flow was applied. α-Picoline (2.0 eq,

6.70 mole%) was added. Terephthaloyl chloride (1.00 eq, 3.35 mol%) was added to the reaction mixture as a melt via a syringe while the mixture was stirred with a mechanical stirrer at a stirring rate of 2000 rpm. A rapid polycondensation reaction occurred and stirring was continued for 10 minutes. After the reaction, the obtained polymer/gelated reaction mixture was precipitated/coagulated with water and if necessary, further grounded with a blender. The polymer was filtered off, and washed with 100 ml water and 50 ml dimethyl sulfoxide. Further washing was done by Soxhlet extraction in water overnight. Afterwards, the polymer was dried on a vacuum line (5 mm Hg) at 130 °C and a bright yellow powder was obtained. The yield was quantitative. Afterwards, the PPTA polymer was dissolved in sulfuric acid (96 wt%) at a concentration of 0.50 g/dL and its inherent viscosity was determined.

Determination of inherent viscosity

A stirring bar and 0.1 g of dried PPTA were added to a 20 mL glass vial with screw cap. A volumetric pipette was used to add 20 mL of concentrated sulfuric acid (96%) to the vial. PPTA was dissolved overnight under heavy stirring to obtain a PPTA/sulfuric acid solution with a concentration (c) of 0.5 g/dL. With an Ubbelohde viscometer in a water bath at 25 °C, the flow time was measured of pure sulfuric acid and the PPTA/sulfuric acid solution. By calculating the ratio of the flow times between solvent ($t_{solvent}$) and solution ($t_{solution}$), the relative viscosity (η_{rel}) and consequently the inherent viscosity (η_{inh}) could be determined. The equations used for calculating the inherent viscosity are noted in the ESI.

EXAFS spectroscopy

Extended X-ray Absorption Fine Structure (EXAFS) spectra of the Cl K-edge (2822 eV) were collected at the Elettra synchrotron in Trieste (Italy) at the XAFS beamline.[15] The energy of the

X-ray beam was tuned by a double-crystal monochromator operating in fixed-exit mode using a Si(111) crystal pair. The measurements were done in transmission mode using Ar/He gas-filled ionization chambers at ambient pressure. A brass sample holder with Kapton® windows and a flexible polymeric spacer (VITON®) with a thickness of 1 mm was used as a sample holder. The sample compartment was flushed several times with helium and the sample holder was set under a small He overpressure to minimize absorption of X-rays by air.

Standard procedures were used for pre-edge subtraction and data normalization to isolate the EXAFS function (χ). The isolated EXAFS oscillations, accomplished by a smoothing spline as realized in the software program Viper,[16] were k^3-weighted and Fourier transformed over the k range from 3.10 to 7.9 Å^{-1}. The data were fitted using the ab initio code FEFF 7.0,[17] which was used to calculate the theoretical phase and amplitude functions that subsequently were used in the non-linear least-squares refinement of the experimental data. Fitting of the model was performed in R space between 0 and 3.7 Å. Estimated standard deviations are shown between parentheses and calculated by VIPER. S0 was fixed at 0.95 and calibrated by measuring a solution of 12 M HCl.

Solid state NMR spectroscopy

A sample of a polymer gel was filled in a 4 mm zirconia MAS rotor and placed in a spectrometer with ^{1}H resonance frequency at 300.12 MHz on a Bruker Avance 600 MHz spectrometer. ^{1}H spectra were recorded at a Magical Angle Spinning frequency (MAS) of 2 kHz. Using this frequency, spectra with a good resolution could be obtained, while residual dipolar coupling remained strong enough to perform RFDR experiments. ^{1}H-^{1}H Radio Frequency Driven Recoupling (RFDR) NMR was recorded at 20 mixing loops with 8 mixing cycles and a mixing

time of 1.344 ms and 8.064 ms was applied for each sample. Spectra were recorded and processed using Topspin 3.2.

Results and discussion

Every polycondensation reaction performed in this study was done by reacting terephthaloyl chloride (TPC) and *p*-phenylenediamine (PPD) preferably in the presence of a base for neutralizing HCl which is released during polymerization (Scheme 1).
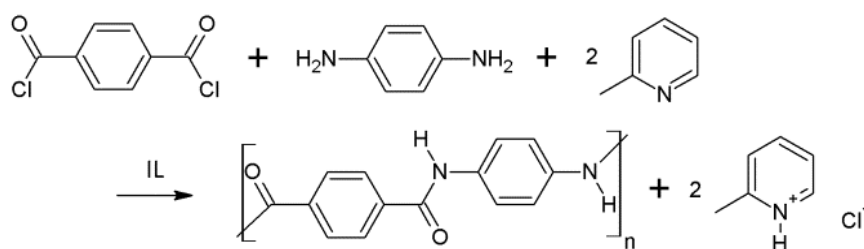
Scheme 1. Reaction scheme for the formation of PPTA by a polycondensation reaction in ionic liquids. α-Picoline is used as a base to capture HCl.

The focus is on ionic liquids with strongly coordinating anions (chloride and diethylphosphate) they have the capability to block the intermolecular hydrogen-bond interactions between the PPTA chains. The use of acetate was not considered as this anion is too nucleophilic and forms a condensation product with terephthaloyl chloride as was observed in preliminary experiments. Especially ILs liquid below room-temperature have to be considered as the low-temperature polycondensation reaction of PPTA is best performed at temperatures of 0 °C or lower.[18,19] These conditions limit the number of ionic liquids that are suitable for the polymerization reaction. Figure 1 shows the ILs investigated in this study. Not all of these compounds are room-temperature ionic liquids.
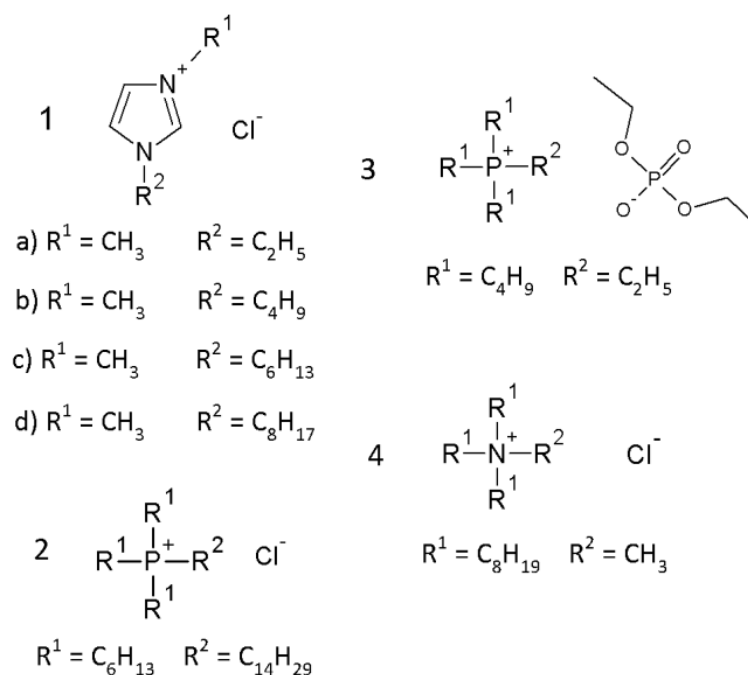
Figure 1. Overview of ionic liquids used in this study. 1a) [C$_2$MIM][Cl], 1b) [C$_4$MIM][Cl], 1c) [C$_6$MIM][Cl], 1d) [C$_8$MIM][Cl], 2) [P$_{66614}$][Cl], 3) [P$_{4442}$][Et$_2$PO$_4$], 4) [N$_{8881}$][Cl].

Although these ILs can exhibit high dissolution power towards aramid oligomers,[10] one must consider their viscosity if these solvents are applied as polymerization media. Dry ILs, especially those with coordinating anions, have much higher viscosities than conventional organic solvents.[20,21] It was opted to first perform the polymerization reactions at a temperature of 80 °C. This is a deviation from the ideal reaction conditions but it enables to compare all ionic liquids under the same experimental conditions regardless of their melting point. Furthermore, this reaction temperature coincides with the melting point of terephthaloyl chloride which facilitates a homogeneous monomer distribution. The results of the polymerization reactions with pure ILs performed at 80 °C are shown in Table 1. The monomer concentration in each reaction was adjusted according to the solvents molecular mass in order to maintain the same molar ratio

between the monomers and the solvent as in the currently used industrial procedure i.e. 3.35 mole% per monomer.[3] As a benchmark, the polymerization reaction was also performed in NMP/5.5wt% $CaCl_2$.

Table 1. The molecular mass represented by the inherent viscosity of PPTA polymer obtained by a polycondensation reaction at 80 °C in NMP/$CaCl_2$ and in various ionic liquids.

Solvent	Viscosity at 80 °C (cP)	Inherent viscosity (dL/g)
NMP/5.5 wt% $CaCl_2$	0.83	2.01
[C_8MIM][Cl]	293	2.08
[C_4MIM][Cl]	142[15]	1.84
[C_6MIM][Cl]	194	1.23
[C_2MIM][Cl]	65[15]	0.95
[P_{4442}][Et_2PO_4]	32	0.65
[P_{66614}][Cl]	104	0.28
[N_{8881}][Cl]	n.d[a]	0.25

[a] n.d.: not determined

Higher temperatures have a negative influence on the molecular mass of PPTA, as the resulting inherent viscosity is lower compared to a polycondensation reaction at 0 °C. This can be seen from the reaction using NMP/5.5 wt% $CaCl_2$ as solvent. Nevertheless, PPTA with a variety of molecular masses were obtained and this can be attributed to the differences in solvent performance of the ionic liquid. Interestingly, the molecular mass of PPTA obtained using 3-methyl-1-octylimidazolium chloride, [C_8MIM][Cl], was on par with the current industrial solvent NMP/$CaCl_2$. This is a first indication for [C_8MIM][Cl] to possess the potential to be an

alternative solvent for the synthesis of PPTA. However, as already mentioned, gelation of the reaction mixture is considered a key condition to obtain higher molecular mass PPTA. Preliminary precipitation of PPTA occurred in all reaction media, except in NMP/5.5 wt% CaCl$_2$.

Performing polymerizations at lower temperatures with cooling is beneficial for the reactions thermodynamics and yield better results. Therefore, reaction temperatures between 0 °C and 80 °C were not tested as it was considered that the gain in dissolution and reaction kinetics because of lowering the solvent viscosity would not overcome the negative influence that higher reaction temperature can have on the resulting PPTA molecular weight. The ILs that were liquid below room temperature were applied as medium for a PPTA polymerization reaction at 0 °C. In this case, the viscosity of the solvent was much higher and terephthaloyl chloride was added as a melt to ensure rapid monomer distribution. Again, the monomer concentration was adjusted according to the molecular mass of the ionic liquid. The results of the low-temperature polycondensation reactions in ILs are summarized in Table 2.

Table 2. The molecular mass indicated as the inherent viscosity of PPTA polymer obtained from a polycondensation reaction at 0 °C in various ionic liquids and the currently industrial solvent of NMP and CaCl$_2$.

Solvent	Viscosity at 0 °C (cP)[a]	Inherent viscosity (dL/g)
NMP/5.5 wt% CaCl$_2$	11.5	5.45
[C$_8$MIM][Cl]	$2.48 \cdot 10^5$	1.95
[C$_8$MIM][Cl]/[C$_4$MIM][Cl][b]	$1.88 \cdot 10^5$	1.05
[C$_6$MIM][Cl]	$1.56 \cdot 10^5$	0.98

[P$_{66614}$][Cl]	$1.32 \cdot 10^4$	0.31
[P$_{4442}$][Et$_2$PO$_4$]	$3.03 \cdot 10^3$	n.p.[c]

[a]Value extrapolated from viscosity data at higher temperatures (see ESI). [b]in a (1:1 mole ratio). [c]n.p. no polymerization observed.

The same trend in performance of the ILs was observed as with the polymerization reactions at 80 °C. More importantly, this time gelation of the reaction mixture was observed when [C$_8$MIM][Cl] was used as the medium (Figure 2). This was the first observation of an ionic liquid forming a gel during the PPTA polymerization reaction. This gives the proof-of-principle that pure [C$_8$MIM][Cl] is able to serve as an alternative solvent for the polymerization of PPTA. In previous work, an inherent viscosity of 1.86 dL/g could be obtained with a 9:1 mixture of [C$_8$MIM][Cl] and tri-*n*-butylphosphate.[11] This time, by improving our reaction set-up and preparation, we were able to force a reasonable polymerization reaction in a pure ionic liquid. Therefore, the knowledge is given that adding a co-solvent is not an ultimate requirement. The inherent viscosity values are still much smaller than the industrial benchmark i.e inherent viscosity values of 4 to 5 dL/g. An improved reactor set-up and more powerful stirring[18] might enable a more efficient terephthaloyl chloride addition, leading to the formation of PPTA with a higher molecular mass. The much higher viscosity of ionic liquids at low temperatures inhibits rapid monomer dissolution and mobility of the reactants. As the reaction proceeds, the reaction mixture turns even more viscous, making it increasingly more difficult for the polycondensation reaction to proceed. A collapsible blade impeller with electric stirring motor was not able to apply enough shear stress to the increasingly visco-elastic solution. To be a sustainable process, reusability of the reaction solvent is of prime importance. Since ionic liquids are non-volatile and with a high thermal stability,[7] vacuum distillation could be used to remove the solvents used for

washing and also potential unreacted monomers. If a base was used to neutralize the acid released during the reaction, it can be precipitated by dissolution into an organic solvent or released again by adding an inorganic base. Imidazolium chlorides dissolve well in organic solvents, protonated and inorganic salts on the other hand do not.

Figure 2. Gel formation as a result of the polymerization reaction of PPTA in [C$_8$MIM][Cl] at 0 °C.

To find further confirmation that [C$_8$MIM][Cl], just as an NMP/CaCl$_2$ solvent mixture, can successfully polymerize PPTA, an EXAFS and a solid-state NMR study were performed. Extended X-ray Absorption Fine Structure (EXAFS) is a spectroscopic technique that probes the local coordination of a specific element within a structure.[22] It is not possible to directly derive the structure of the sample from an EXAFS spectrum, so that modeling of the structure is required to find the highest agreement between the experimental and the calculated spectrum. If more than one local structure is present, the EXAFS technique yields an average structure. In our

case, EXAFS experiments were performed on the K-edge of chlorine. It was investigated if a high correspondence exists between the local structures of the chloride anion of NMP/5.5wt% $CaCl_2$ and that of $[C_8MIM][Cl]$, with and without added benzanilide, a simple model compound for PPTA. Unfortunately, it was very challenging to obtain a high resolution EXAFS spectrum when measuring on an element as light as chlorine[23,24] and reliable data could be obtained only for the NMP/5.5 wt% $CaCl_2$ solvent mixture (Figure 3 and 4) and subsequently only for this spectrum data fitting could be done (Table 3). Fitting of the model was performed in R space between 0 and 3.7 Å.

Table 3. EXAFS results for NMP/5.5 wt% $CaCl_2$ obtained (Cl K-edge) from data fitting, depicting the coordination of chloride with elements in close proximity.

Interaction	Coordination number (N)	Distance (Å)	σ^2	R^2
Ca-Cl	0.7	2.77(1)	0.014	
N/O-Cl	0.8	2.98(5)	0.025	2.2

14
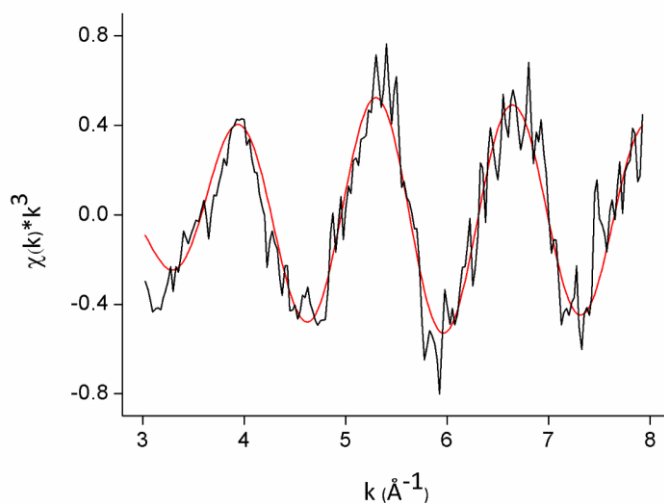
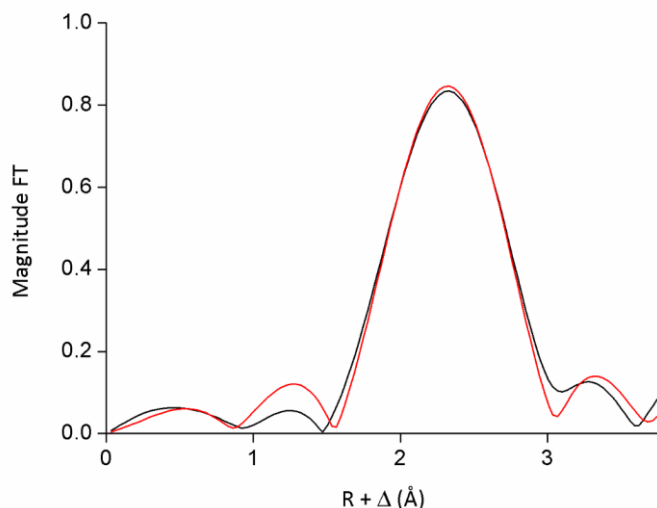**Figure 3.** EXAFS function (black) and model (red) of the Cl K-edge of NMP/5.5 wt% CaCl$_2$.

Figure 4. Fourier transform (black) and model (red) of Cl (k-edge) X-ray absorption spectrum of the NMP/CaCl$_2$ solvent mixture.

Data fitting suggested that on average 1.5 chloride ions are in the neighborhood of the Ca^{2+} cation in NMP/5.5 wt% CaCl$_2$ which means that one chloride is always loosely bound to the cation. This is complementary to the insights of the work of Westerhof where it was also concluded from conductivity measurements on NMP/CaCl$_2$ that on average two cationic complex forms are present, namely CaCl$^+$ and Ca$_2$Cl^{3+}.[25] The bond length of Ca-Cl can be determined very accurately with EXAFS. The bond length is also specific for the coordination of the central Ca atom. A bond length of 2.77 Å corresponds to a calcium ion which is probably 4-coordinated. The other three possible ligands surrounding the calcium ion are too far away from the chloride ligand to be visible with EXAFS, also suggesting a tetrahedral configuration around the Ca^{2+} ion. The data fitting improved when an oxygen or nitrogen atom was put at a distance of

2.98 Å near a chloride anion. It is difficult to distinguish between nitrogen and oxygen atoms in EXAFS as they are very similar in size and number of electrons.

However, it is assumed that the Ca^{2+} ion interacts with the oxygen atom of the carbonyl functionality of NMP.[26] This means that the partially positively charged nitrogen atom is available to interact with a chloride anion. With the coordination of a cationic cluster to NMP combined with a loosely bound chloride anion, a structure is possible that resembles an imidazolium chloride IL i.e. a large cationic structure with an anion that is loosely bound to the cation but is still available for hydrogen bond interactions (Figure 5). Representing it in this way, $[NMP_3 - CaCl][Cl]$ or $[NMP_4 - Ca_2Cl_3][Cl]$ can be thought of as a salt which is diluted in an excess of *N*-methylpyrrolidone. From this point of view, structural similarities exist between a $NMP/CaCl_2$ solvent mixture and $[C_8MIM][Cl]$ with the IL having the advantage of being already liquid at low temperatures without the need of adding an additional organic solvent. It is considered that the alkyl chain on the imidazolium cation does not significantly interact with the PPTA polymer. However, a long alkyl chain, such as in $[C_8MIM][Cl]$ could contribute in more efficient blocking of interactions between different PPTA chains and prevent premature precipitation of the polymer during reaction. Imidazolium chlorides with even longer alkyl chains result in an increase of melting point and an enormous increase in solvent viscosity and are therefore not suitable for a low temperature polymerization reaction.

Also solid-state ^{1}H-NMR was performed on gelated reaction mixtures obtained from the polymer reaction using different solvents, for investigating the structural makeup of these gels.
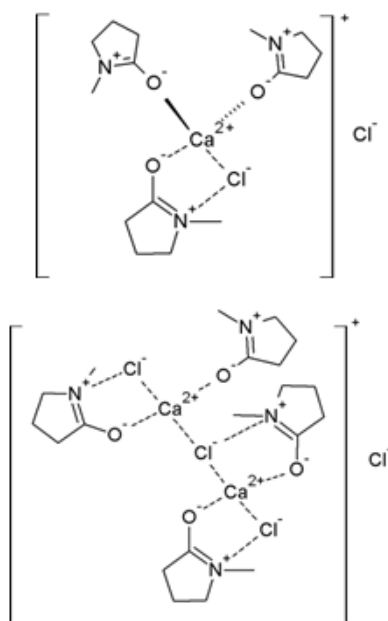
Figure 5. Two proposed complexation interactions between NMP and CaCl$_2$ based on data fitting of Cl K-edge EXAFS data.

Assuming that the chloride anion will always be in close contact with the PPTA polymer, it has to be checked if it is the NMP or the imidazolium cation that mainly fills the solvent shell around the chloride – PPTA complex. Three different gelated reaction mixtures after polymerization were analyzed: NMP/5.5 wt% CaCl$_2$, 75 wt% *N*-methylpyrrolidone/25 wt% [C$_8$MIM][Cl] which was synthesized in previous work[11] and pure [C$_8$MIM][Cl]. Of course, the polymers present in the sample do not have the same molecular mass distribution. However, it is assumed that solvent – polymer interactions are independent of the PPTA chain length. $_1$H spectra were recorded of all the gels and the different resonance peaks were assigned. Via ^{1}H-^{1}H Radio Frequency Driven Recoupling (RFDR) NMR, a two-dimensional ^{1}H/^{1}H chemical shift correlation spectrum was obtained with mixing times of 8.064 ms and 1.344 ms.[27] With short dipolar recoupling times, only spins in close spatial proximity lead to cross peaks. Comparing the

spectra with different mixing times helped to indicate which species lays in closest proximity to each other (Figure 6 to 11).
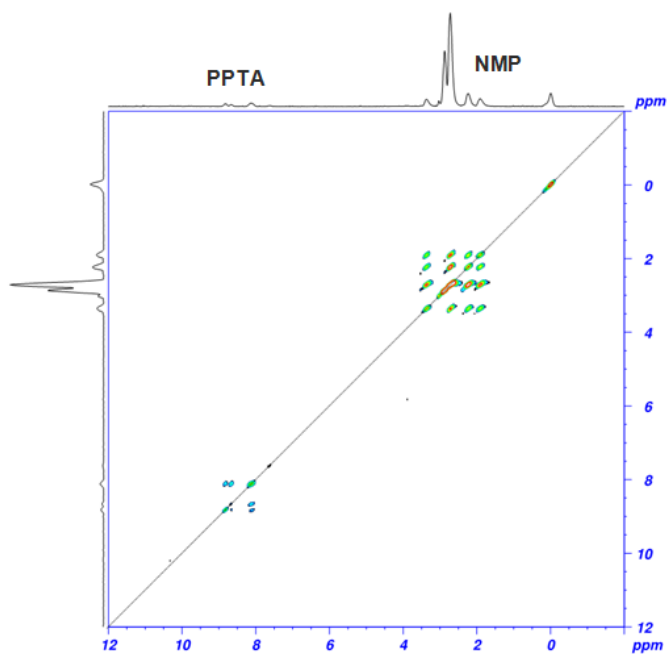

Figure 6. ^{1}H-^{1}H Radio Frequency Driven Recoupling (RFDR) NMR with a mixing time of 1.344 ms of a gel containing PPTA and NMP/5.5 wt% $CaCl_2$ as solvent.
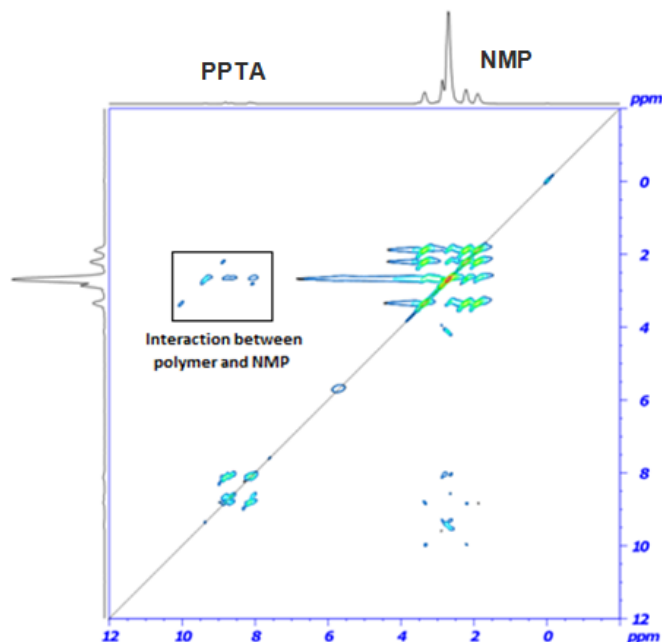
Figure 7. ^{1}H-^{1}H Radio Frequency Driven Recoupling (RFDR) NMR with a mixing time of 8.064 ms of a gel containing PPTA and NMP/5.5 wt% CaCl$_2$ as solvent.

The 2D-spectrum depicted in Figure 6 shows cross peaks between the protons of different NMP molecules and between PPTA polymer chains. Raising the mixing time from 1.344 to 8.064 ms revealed extra cross peaks between NMP and PPTA (Figure 7) indicating that protons of NMP exhibit interactions with PPTA but are located at a further distance. This means that aside from the chloride anion, the calcium from the calcium – NMP cationic complex is probably in closest proximity with the PPTA polymer. The NMP molecule is also spatially close to the PPTA polymer because of interactions with both the chloride anion and the calcium cation. This shows that interactions with all components within the reaction mixture are needed for gelation during synthesis of PPTA.
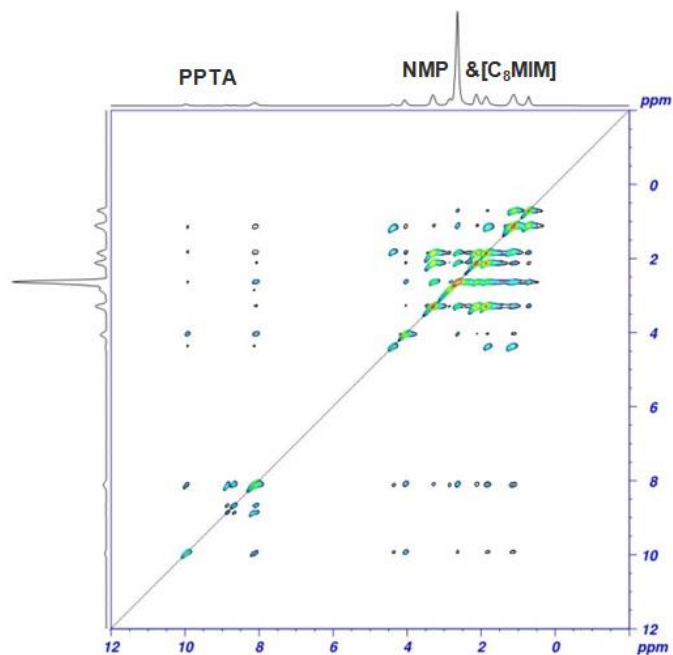
Figure 8. ^{1}H-^{1}H Radio Frequency Driven Recoupling (RFDR) NMR with a mixing time of 1.344 ms of a gel containing PPTA, 25 wt% [C$_8$MIM][Cl] and 75 wt% NMP.

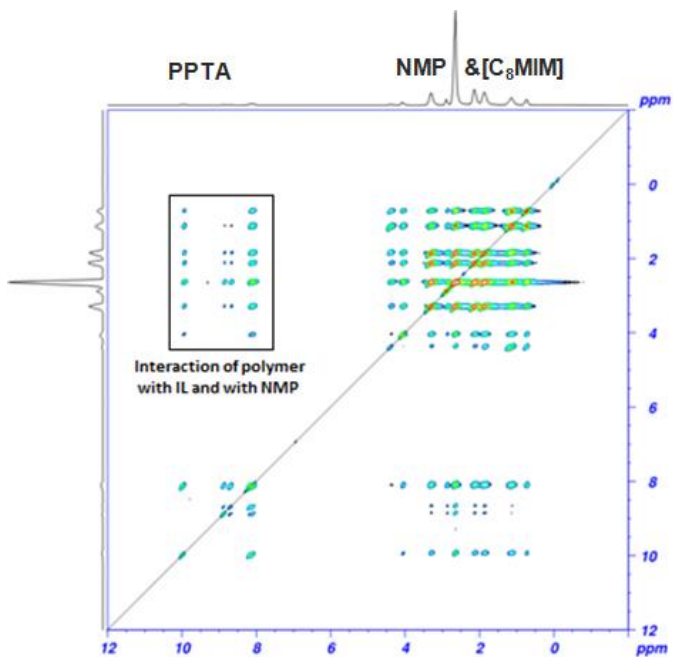**Figure 9.** ^{1}H-^{1}H Radio Frequency Driven Recoupling (RFDR) NMR with a mixing time of 8.064 ms of a gel containing PPTA, 25 wt% [C$_8$MIM][Cl] and 75 wt% NMP.

The 2D-spectrum depicted in Figure 8 and 9 above shows cross peaks between the protons of various entities: NMP – NMP, IL – IL, IL – NMP, NMP – PPTA, IL – PPTA. Even the protons of the long alkyl chain on the imidazolium cation show correlation with PPTA. Only small correlation between PPTA – PPTA is observed, indicating that these chains are separated well. This is again a confirmation that gelation took place by interactions between all components.

Importantly, raising the mixing time from 1.344 to 8.064 ms revealed extra cross peaks for both IL – PPTA, NMP – PPTA and IL – NMP. The cation of the ionic liquid is not particularly closer to the PPTA molecule than NMP is. They seem to have more or less equal contribution in interactions with the polymer.
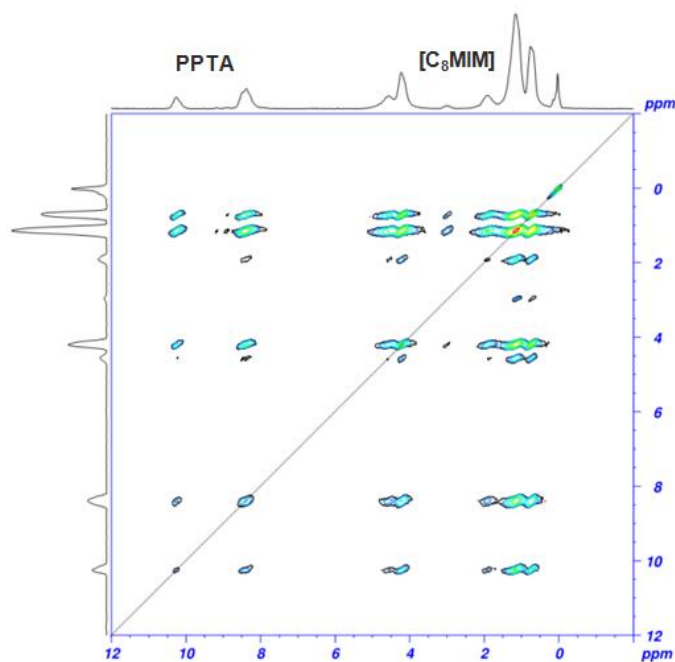

Figure 10. ^{1}H-^{1}H Radio Frequency Driven Recoupling (RFDR) NMR with a mixing time of 1.344 ms of a gel containing PPTA and [C$_8$MIM][Cl].

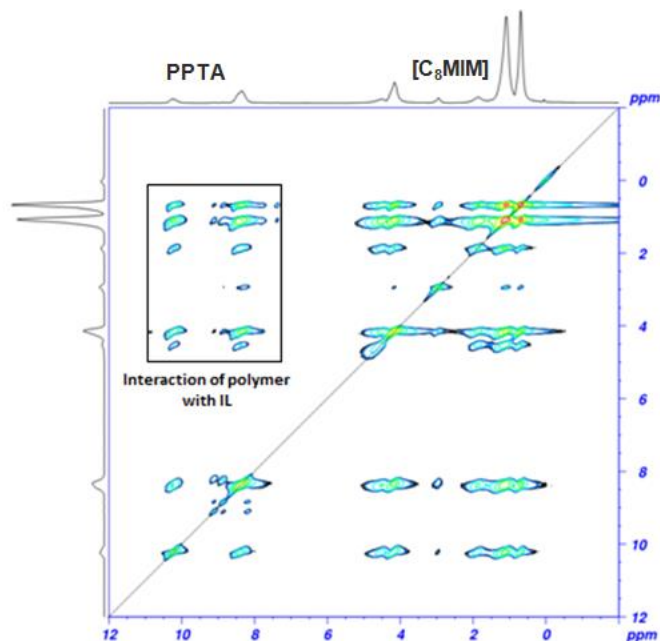**Figure 11.** ^{1}H-^{1}H Radio Frequency Driven Recoupling (RFDR) NMR with a mixing time of 8.064 ms of a gel containing PPTA and pure [C$_8$MIM][Cl].

The 2D-spectrum depicted in Figure 10 and 11 above shows cross peaks between IL – IL and IL – PPTA. No extra cross peaks appeared when raising the mixing time from 1.344 to 8.064 ms. The imidazolium is in close presence to the PPTA chain as no other entities (Ca – NMP complex or NMP) compete for interaction with the PPTA chain.

A complete structure determination could not be elucidated of these gels as all the components are thoroughly mixed. However, by increasing the mixing time, allowing more extensive dipolar interaction for the protons, some structural insights were gained. It is assumed that the chloride anion is always in close contact to the amide bonds of the polymer. In a gel with NMP/5.5 wt% CaCl$_2$, the calcium cation could be in closest contact with the polymer, closely followed by the complexed NMP as is presented in the upper part of the graphical abstract. This was demonstrated by the increased number of protons of NMP revealing interactions with PPTA as

mixing time is increased. Also for 25 wt% [C$_8$MIM][Cl] in NMP as solvent both the cation and NMP were in close contact with PPTA, showing that the NMP molecule does not dominate in complexation interactions with the polymer. Only when [C$_8$MIM][Cl] is used as pure solvent, as it is the only solvent species exhibiting interactions with PPTA. The bulky 3-methyl-1-octylimidazolium cation seems to take over the role of the Ca^{2+} – NMP complex in interactions with PPTA and the chloride anion for establishing gelation within the reaction mixture as presented in the lower part of the graphical abstract.

It has to be mentioned that in all these cases protonated α-picoline was present in the polymer gels as it neutralized the HCl generated during reaction. For each repeating unit of the polymer, there are two equivalents of this salt present. However, it was difficult to assign their resonance peaks as they have values in the same range as PPTA, NMP and the ionic liquid. This salt could also show significant interaction to the other species present in the gels.

Conclusions

This study investigated the potential of pure ionic liquids as polymerization medium for PPTA. First, polymerization reactions were performed at 80 °C to diminish their viscosities and ensure rapid monomer mixing. Only ILs with a chloride anion were deemed suitable as polymerization medium as other, more coordinating anions can react with the highly reactive terephthaloyl chloride monomer. [C$_8$MIM][Cl] performed as best ionic liquid as it was able to produce PPTA with an inherent viscosity of 2.08 dL/g. However, precipitation of PPTA occurred during synthesis and a further improvement is not expected. Next, low-temperature polycondensation reactions were performed in ionic liquids that are still liquid at 0 °C. The acid chloride was added as a melt. Also here, [C$_8$MIM][Cl] as solvent resulted in PPTA with the highest inherent

viscosity i.e. 1.95 dL/g. More importantly, gel formation was established within the reaction mixture, confirming the potential of [C$_8$MIM][Cl] as alternative solvent for the synthesis of PPTA. Finally, EXAFS and solid state NMR experiments were performed to investigate if [C$_8$MIM][Cl] has the right characteristics to be an alternative polymerization medium for the synthesis of PPTA. EXAFS spectroscopy showed that NMP/5.5 wt% CaCl$_2$ has many similarities to an IL with a large cationic structure diluted in NMP. Solid state NMR-spectroscopy revealed that there is no preferential interacton of NMP or the imidazolium cation with PPTA when both components are mixed together but that the imidazolium cation can take over the role of the Ca^{2+} – NMP complex in gel formation of the reaction mixture when polymerization is performed in a pure ionic liquid.

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Supporting information

The Supporting Information is available free of charge on the ACS Publications website. Equations for determination inherent viscosity and solvent viscosity data of ionic liquids at different temperatures.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Dedicated to Prof. István T. Horváth on the occasion of his 65th birthday

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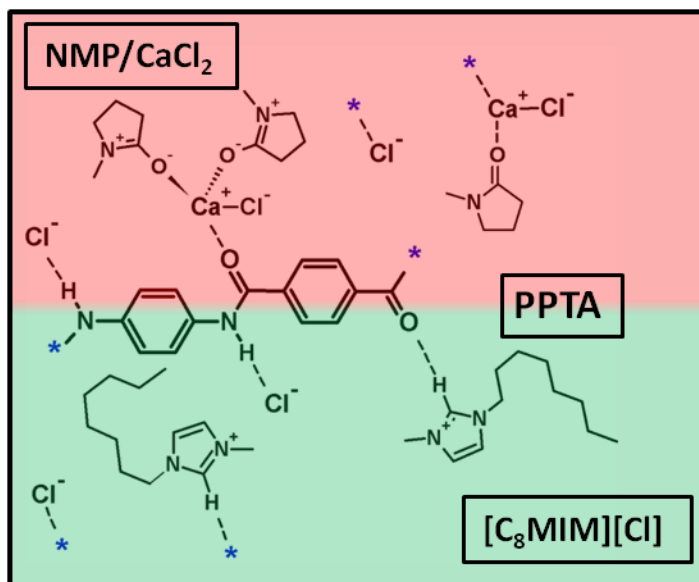
[C$_8$MIM][Cl] is an ionic liquid with the right properties to mimic the polymerization process of PPTA as it occurs in NMP/CaCl$_2$.