S. Dewilde, J. Winters, W. Dehaen, K. Binnemans
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Polymerization of PPTA in ionic liquid/cosolvent mixtures

*Sven Dewilde, Jonas Winters, Wim Dehaen and Koen Binnemans**

KU Leuven, Department of Chemistry, Celestijnenlaan 200F, bus 2404, B-3001 Leuven, Belgium

Ionic liquids, imidazolium chloride, PPTA, aramids, *N*-methylpyrrolidone, hydrogen bonds

1-Octyl-3-methylimidazolium chloride ([C_8MIM][Cl]) shows the greatest potential to replace *N*-methylpyrrolidone/$CaCl_2$ as solvent for the synthesis of poly-*p*-phenylene terephthalamide (PPTA), a high-strength material when spun into a fibre. Coordinating anions are crucial to prevent precipitation of the polymer during synthesis. Additionally, the imidazolium cations play an essential role in gelation of the reaction mixture and enable the polycondensation reaction to continue in a gel-state. Analysis of Kamlet-Taft parameters and Gutmann donor and acceptor numbers of ionic liquids and various solvents showed that balanced interactions between the secondary amide bonds of the polymer, anion, cation and solvent are required to form a network of hydrogen bond interactions throughout the reaction mixture. This hypothesis was supported by the fact that tri-*n*-butyl phosphate (TBP), containing similar Kamlet-Taft and Gutmann solvent parameters as *N*-methylpyrrolidone, was able to produce PPTA with an inherent viscosity as high as 1.86 dL/g in combination with [C_8MIM][Cl]. Such a high value without the use of *N*-methylpyrrolidone or hexamethylphosphoramide has not yet been reported.

1. Introduction

Poly-*p*-phenyleneterephthalamide (PPTA), mostly known under the brand names Kevlar® or Twaron® is one of the best known and most used aramids (aromatic polyamides) worldwide.[1] Aramids belong to the class of high-performance polymers which excel in mechanical strength, chemical and/or temperature stability.[2;3] Therefore, PPTA fibers are used to strengthen materials because of their superior strength-to-weight ratio. In fact, these fibers are five times stronger than steel on an equal weight basis.

The PPTA polymer is a concatenation of aromatic rings and secondary amide bonds which are all oriented in *para*-position. The amide bond is one of the strongest and most chemically inert functional groups known in organic chemistry. Delocalization of the lone electron pair of the nitrogen atom to the carbonyl group gives a partly double bond character to the C−N bond in the amide functional group, resulting in a hindered bond rotation.[4] The hindered rotation of the amide group along with the fact that all amide bonds are connected by phenyl rings in *para*-position, give PPTA a very rigid structure, which promotes crystallization of the material.[5] However, the extended hydrogen bond (H-bond) network built up by secondary amide functional groups plays the major role in the crystallization of aramids, since they can act both as a hydrogen- bond donor and acceptor. The bonds occur between the carbonyl and amino groups in the amide repeating unit. They effectively link adjacent chains which laterally reinforces the crystal.[6] The attractive interactions between the aromatic rings via π–π stacking could give an additional reinforcement.[7]

While these strong interactions between the polymer chains are beneficial for their applications, it makes PPTA on the other hand very difficult to process. In fact, not a single neutral solvent exists that is capable of keeping high-molecular weight PPTA in a dissolved state.[8] The polycondensation of PPTA occurs via an unconventional gel-state during synthesis.[9] Initially, when the industrial production of PPTA started in the 1970s, a mixture of the highly polar hexamethylphosphoramide (HMPA) and *N*-methylpyrrolidone (NMP) was the polymerization medium,[10] but the use of HMPA in industry was stopped in 1982 due to its high carcinogenity.[11] In the current industrial process for preparation of PPTA, a mixture of NMP and $CaCl_2$ is used as solvent.[12;13] Research has shown that NMP and $CaCl_2$ interact in such a manner that the chloride anion is available to form H-bonds with the secondary amide bonds so that precipitation of the polymer during synthesis is prevented.[14-17] However, there are also some toxicity issues related to NMP. This solvent is known to be teratogenic and it has been placed on a list of substances of very high concern (SVHC-list) by the European Commission (EC).[18] Being on the SVHC list means that the use of a substance within the EU will be subject to authorization under the REACH regulation. This implies that companies will have legal obligations concerning that compound and its use may be restricted.

We suggest the use of ionic liquids (ILs) as another alternative, less harmful solvent for the synthesis of PPTA. ILs are solvents with low melting points that consist entirely of ions.[19;20] A typical IL is built up by large and/or asymmetric organic cations with an organic or inorganic anion. Since ILs have a negligible vapor pressure, conventional molecular solvents can be replaced by ILs to reduce the release of volatile organic compounds to the atmosphere.[21] This makes ILs interesting candidates for replacing NMP/$CaCl_2$ as solvent for the polymerization of PPTA. Furthermore, ILs have a low flammability, a high thermal stability and a wide liquidus range.[22;23] ILs could contain much higher concentrations of active anions than NMP/$CaCl_2$. In a recent paper, we used PPTA oligomers as model compounds for dissolution of PPTA polymers in ILs. A wide screening test indicated that some ILs have a much greater capability to dissolve PPTA oligomers compounds compared to NMP/$CaCl_2$.[24] Spectroscopic studies showed that a coordinating anion is of prime importance for the disruption of the H-bond network between the PPTA oligomers, just as is the case for NMP/$CaCl_2$. Ionic liquids with acetate, phosphate and chloride anions and with phosphonium or ammonium cations were the best solvents for PPTA oligomers. Cations with acidic C–H bonds, e.g. imidazolium and pyridinium cations, are poor solvents as they prevent the formation of H-bonds of the anions with the secondary amide functional groups of the PPTA oligomers. However, none of the ILs used in the screening tests were able to dissolve high molecular weight PPTA at concentrations that occur during a polycondensation reaction.[25] Little research has been done on the synthesis of PPTA in ILs. A few research groups have investigated the direct synthesis of new aramids in ionic liquids.[26-28] Only one experiment mentions PPTA but only low molecular weight material was obtained.[29] Furthermore, the direct synthesis method uses pyridine and triphenylphospite and is not considered a green method. To the best of our knowledge, only Vygodskii *et al*. used ionic liquids to synthesize PPTA *via* a low-temperature polycondensation reaction.[30] They used the ionic liquids 1-butyl-3-butylimidazolium bromide and tetrafluoroborate as solvents, but they obtained only low molecular weight oligomers. We reckon that the wrong type of IL was used for this synthesis.

In this paper, we describe the polymerization of PPTA by a low-temperature polycondensation reaction using ionic liquids as solvent. However, several boundary conditions must be taken into account to achieve PPTA polymers with a high molecular weight. First of all, side reactions of the highly reactive terephthaloyl chloride with the ionic liquid must be avoided,[31] since this has a negative influence on the molecular weight of PPTA.[32] Secondly, the polymerization solvent must be as dry as possible, preferably with a water content <100 ppm, to avoid decreasing the solvent strength and to avoid that water reacts with the acid chloride functionalities.[33] Thirdly, the highest molecular weights of PPTA are obtained with intensive cooling, with the reaction usually starting at 0 °C or lower.[34] Finally, the solvent must be capable of dissolving the acid chloride at a fast rate and keeping it distributed homogeneously in the reaction mixture to ensure equimolarity.[35;36] Dry ILs are solid or have a much higher viscosity than NMP at low temperatures. In order to assess the performance of ionic liquids for the synthesis of PPTA with reasonably high molecular weights in a low-temperature polycondensation reaction, it was chosen to dilute the ILs in a cosolvent. In this way, a lower melting point, a lower viscosity and lower hygroscopicity of the solvent could be obtained. First, lab-scale benchmark experiments were performed with a NMP/$CaCl_2$ solvent mixture. Next, a broad set of ionic liquid/*N*-methylpyrrolidone solvent mixtures were prepared and applied in PPTA polymerization reactions. Then, other, potentially greener, cosolvents were tested. Finally, solvent polarity parameters of both ionic liquid and organic solvent were analyzed in order to gain a better understanding of the polymerization process of PPTA.

2. Experimental

General

All the commercially available ionic liquids were purchased from IoLiTec (Heilbronn, Germany), Cytec (New Jersey, USA) or Sigma-Aldrich (Diegem, Belgium). 1-Butylimidazole (99%), 1-chlorobutane (99.5%), *N,N*-diethylamine (>99.5%), pyrrolidine (99%), hexanoyl chloride (97%), acetyl chloride (99%), *N*-methylpyrrolidone extra dry (99.5%), *N,N*-

tetramethylurea (99%), *N,N*-dimethylimidazolidinone extra dry (>99.5%), dichloromethane anhydrous (>99.8%), tri-*n*-butyl phosphate (>99%) and α-picoline Lonza quality (>99%) were all purchased from Sigma-Aldrich (Diegem, Belgium). Acetone extra dry (>99.8%), acetonitrile extra dry (99.9%), toluene extra dry (99.8%), terephthaloyl chloride (>99%) and *p*-phenylenediamine (99+%), sulfuric acid (96 wt%) from Acros Organic (Geel, Belgium). Calcium chloride dihydrate was purchased from Merck (Overijse, Belgium). *p*-Phenylenediamine (99+%) was purified by sublimation at reduced pressure on a vacuum line at 95 °C. 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.[37] The ^1H (300 MHz) and ^{13}C NMR spectra (75 MHz) have been recorded on a Bruker Avance 300 MHz NMR spectrometer. D_2O and $CDCl_3$ were used as deuterated solvents. Analysis of the NMR spectra was done with the Bruker Topspin 2.1 software package. CHN analysis was performed on a Flash 2000 Elemental analyzer from Thermo Scientific Interscience. Viscosities were measured using a LOVIS 2000 ME Microviscometer Anton Paar. A Karl Fischer DL39 coulometer from Mettler-Toledo was used to measure water content of all the solvent mixtures before polymerization. A Bosch Ergomix 750 W was used to break up the gels formed after a polymerization reaction. 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 thermostated water bath at 25 °C.

2.2 Synthesis and characterization

1,3-Dibutylimidazolium chloride

1-Butylimidazole (1.0 eq, 201 mmol, 25 g) was dissolved in acetonitrile (200 mL). To this solution 1-chlorobutane (1.1 eq, 221 mmol, 26.71 g) was added. The reaction mixture was refluxed for 24. The solvent as well as the excess of 1-chlorobutane was removed by evaporation on a rotary evaporator. Further drying and purification was done on a vacuum line. An orange viscous liquid was obtained. Yield: 49.1 g (95%). ^{1}H NMR (300 MHz, D_2O, δ): 9.15 (1H, s), 7.85 (1H, J = 1.1 Hz, d), 7.78 (1H, J = 1.2 Hz, d) 4.25 (2H, 7.4 Hz, t), 4.13 (2H, J = 7.3 Hz, t), 2.19 (2H, m), 1.67 (2H, m), 1.48 (2H, m), 1.24 (2H, m), 1.01 (3H, J = 7.0 Hz, t), 0.87 (3H, J = 7.1 Hz, t). ^{13}C NMR (75 MHz, D_2O, δ): 137.2, 122.8, 122.6, 48.4, 46.3, 32.3, 32.0, 19.3, 19.2, 13.3, 12.8. Elemental analysis for $C_{11}H_{21}N_2Cl$ (M = 216.8 g/mol) expected (%): C: 60.95, H: 9.77, N: 12.92; found (%): C: 60.89, H: 9.86, N: 12.80.

N,N-Diethylhexanamide

N,N-Diethylamine (2.1 eq, 468 mmol, 34.2 g) was dissolved in dry tetrahydrofuran (500 mL) in a dried three-neck flask flushed with argon. The flask was placed in an ice bath. With a syringe, hexanoyl chloride (1.0 eq, 224 mmol, 30 g) was added dropwise. The reaction was further stirred at room temperature for 3 h. Afterwards, the formed ammonium salt was filtrated off and the solvent evaporated. A yellow liquid was obtained. Yield: 33.4 g (87%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 3.34 (4H, m), 2.29 (2H, t), 1.65 (2H, m), 1.33 (4H, m), 1.14 (6H, m), 0.90 (3H, t, J = 0.90). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 171.92, 42.00, 40.07, 33.10, 25.03, 22.20, 14.20, 13.90, 13.38. Elemental analysis for $C_{10}H_{21}NO$ (M = 171.3 g/mol) expected (%): C: 70.12, H: 12.36, N: 8.18; found (%): C: 70.01, H: 12.23, N: 8.36.

***N,N*-Diethylbenzamide**

N,N-Diethylamine (2.1 eq, 427 mmol, 31.2 g) was dissolved in dry tetrahydrofuran (500 mL) in a dried three-neck flask flushed with argon. The flask was placed in an ice bath. With a syringe, benzoyl chloride (1.0 eq, 213 mmol, 30 g) was added dropwise. The reaction was further stirred at room temperature for 3 h. Afterwards, the formed ammonium salt was filtrated off and the solvent evaporated. A dark brown liquid was obtained. Yield: 30.6 g (81%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.79 (2H, m), 7.54 (1H, m), 7.45 (2H, m), 3.62 (4H, m), 1.20 (6H, m) ^{13}C NMR (75 MHz, $CDCl_3$, δ): 170.86, 137.13, 128.20, 126.09, 42.92, 38.89, 13.84, 12.58. Elemental analysis for $C_{11}H_{1}NO$ (M = 177.24 g/mol) expected (%): C: 74.54, H: 8.53, N: 7.90; found (%): C: 74.46, H: 8.64, N: 7.99.

***N*-Acetylpyrrolidine**

Pyrrolidine (2.1 eq, 802 mmol, 57.0 g) was dissolved in dry tetrahydrofuran (500 mL) in a dried three-neck flask flushed with argon. The flask was placed in an ice bath. With a syringe, acetyl chloride (1.0 eq, 382 mmol, 30 g) was added dropwise. The reaction was further stirred at room temperature for 3 h. Afterwards, the formed ammonium salt was filtrated off and the solvent evaporated. A yellow liquid was obtained. Yield: 38.1 g (88%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 3.46 (2H, m), 2.00 (3H, s), 1.89 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 170.3, 47.4, 46.1, 26.1, 24.8, 22.5. Elemental analysis for $C_6H_{11}NO$ (M = 113.2 g/mol) expected (%): C: 63.68, H: 9.80, N: 12.38; found (%): C: 63.46, H: 9.88, N: 12.19.

2.3 Benchmark polymerization reaction

Calcium chloride dihydrate ($CaCl_2 \cdot 2\ H_2O$) (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. *p*-Phenylenediamine (1.0 eq, 13.5 mmol, 1.46 g) was added to the reaction mixture while under a nitrogen flow. Dissolution of the monomer took place under vacuum at 50 °C. Afterwards, the three-neck flask was transported to an ice bath and a nitrogen flow was applied. The magnetic stirring bar was removed and an overhead stirrer (4 cm collapsible 2-blade impeller fitted in a Cowie universal stirrer guide) was placed on the flask. α-Picoline (2.0 eq, 27.0 mmol, 2.51 g) was added. Terephthaloyl chloride (1.01 eq, 13.6 mmol, 2.76 g) was added to the reaction mixture, while the reaction flask was placed in an ice bath, a continuous nitrogen gas flow was applied and the mixture was stirred with a mechanical stirrer at a stirring rate of 200 rpm. After dissolution of the acid chloride, swelling and a sharp increase in the viscosity was observed after only a few seconds and the stirring rate was increased to 3000 rpm. Stirring was continued for 5 min., during which a very thick paste or crumble was formed. After the reaction, the obtained polymer was coagulated with water and further grounded with a blender. The polymer was filtered off, and washed with water, dimethyl sulfoxide and acetone. Further washing was done by refluxing in boiling water overnight. Afterwards, the polymer was dried on a vacuum line at 130 °C and a bright yellow powder was obtained. The yield was quantitative. PPTA with an inherent viscosity of 5.45 dL/g was obtained.

Further improvements to the reaction conditions for this benchmark reaction were made. As the polymerization reaction proceeds, the reaction mixture turns more viscoelastic, which makes the liquid rise upwards on the stirring rod instead of being thrown outwards (*Weissenberg* effect).[38] When this effect occurs, there is no longer efficient mixing. Therefore, it was tried to perform the reaction in a cylindrical shaped reaction vessel with an anchor stirrer. By applying the same procedure as in the main reaction, PPTA with an inherent viscosity of 6.48 dL/g was obtained.

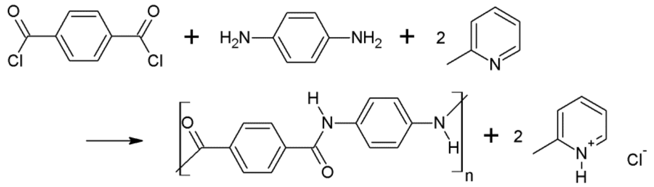
The same reaction procedure was performed in a cylindrical reaction vessel, but α-picoline was omitted from the reaction mixture. Reaction kinetics were lower compared to when a base is used. Swelling and a sharp increase in the viscosity only occurred after a couple of minutes. PPTA was obtained with an inherent viscosity of 5.47 dL/g.

2.4 Determination of inherent viscosity

To a 20 mL glass vial with screw cap was added 0.1 g of dried PPTA powder and a stirring bar. To the vial was added 20 mL of concentrated sulfuric acid (96%) with a volumetric pipette. PPTA was dissolved overnight under heavy stirring to become 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 as a measure for the molecular weight of the polymer.

3. Results and discussion

All polymerization experiments were performed in close relation to the industrial process procedure.[12] This is a low-temperature polycondensation reaction between the highly reactive terephthaloyl chloride and p-phenylenediamine. However, to ensure a fluent reaction for every experiment, a base was used to capture the HCl gas that is released during the condensation between the monomers (Scheme 1). Preliminary experiments had shown that α-picoline as a base resulted in PPTA with the highest molecular weights compared to experiments using *N,N*-dimethylaniline, triethylamine and imidazole.



Scheme 1. Reaction scheme of the low-temperature polycondensation reaction for PPTA synthesis, used in almost all of the polymerization experiments. α-Picoline is used as a base to capture HCl.

3.1 Benchmark

Industrially prepared PPTA has an inherent viscosity of 4 to 5 dL/g as industry has to find a trade-off between high molecular weight and processability during the spinning process. In the literature, it has been shown that PPTA can be prepared on lab-scale with inherent viscosities up to 14 dL/g.[39;40] To compare different polymerization experiments, PPTA was synthesized on lab scale using the NMP/$CaCl_2$ solvent mixture. The applied reaction conditions were as close as possible to those described in the original patent on the NMP/$CaCl_2$ solvent.[12] However, for most experiments, it was opted to lower the concentration of $CaCl_2$ to 5.5 wt% as 10.5 wt% $CaCl_2$ in NMP resulted in a supersaturated solution when cooling is applied and often precipitation of $CaCl_2$ occurred before the polymerization reaction could start. Experiments were scaled down so that 40 g of NMP was used for a single experiment. Table 1 shows the results of the benchmark reactions that were performed at different reaction conditions.

Table 1. Results of several polymerization reactions with varying reaction conditions using the NMP/$CaCl_2$ solvent mixture.

Concentration $CaCl_2$ (wt%)	**Vessel**	**Base**	**Inherent viscosity (dL/g)**
10.5	three-neck flask	α-Picoline	4.31
5.5	three-neck flask	α-Picoline	5.38[a]
5.5	cylindrical	α-Picoline	6.48
5.5	cylindrical	none	5.47
0	three-neck flask	α-Picoline	0.55

[a] Repeating the experiment three times resulted in a standard deviation of 0.0650 dL/g.

As can be seen in Table 1, it is possible to obtain PPTA polymers with a relatively high molecular weight on a lab scale, with the currently used industrial solvent system. Only when no $CaCl_2$ was added to the solvent, precipitation of low molecular weight PPTA occurred. Each polymerization reaction with NMP/$CaCl_2$ as solvent resulted in swelling after dissolution of the acid chloride, followed by gelation of the reaction mixture. Continuation of the reaction with intense stirring, resulted in the formation of a solid crumble (Figure 1), an indication that PPTA with relatively high molecular weight is obtained. By performing polymerization experiments with different ionic liquid/cosolvent mixtures using the same synthetic procedure, relevant evaluations can be made by comparing them to the benchmark experiments.

Figure 1. Reaction mixture after polymerization reaction in the presence of a base performed in a cylindrical reaction vessel. The polymer and reaction mixture have formed a solid, yellow crumble.

3.2 Polymerization in ionic liquid/NMP solvent mixtures

In order to maintain the same reaction conditions, ionic liquids were diluted with *N*-methylpyrrolidone to ensure that the solvent did not solidify at a temperature of 0 °C or to avoid large deviations in solvent viscosity, which has a huge influence on the reaction kinetics. It was chosen to set 25 wt% IL and 75 wt% NMP as the default mass ratio. The concentration of the monomers in the polymerization reaction was kept constant, which means it is attempted to synthesize PPTA polymers in a lesser amount of amide solvent. Consequently, the ILs can be considered part of the solvent and not merely as a salt additive.

Of course, with the changes in molecular mass between the different ILs, different salt concentrations were present in the reaction mixture. Since variations in salt concentrations in NMP give different results for the inherent viscosity of the resulting PPTA polymer,[41] it might be that the optimal salt concentration has not been used for a given IL. However, it is considered that the chemical properties of the ionic liquid will be decisive for a successful or unsuccessful polymerization reaction. Chart 1 gives a summary of the ILs that were tested, while the results of the polymerization reaction using a 25 wt% ionic liquid in NMP solvent mixture are given in Table 2. All reactions were performed according to the reaction procedures used for the benchmark reactions. In these experiments, 10 g of IL and 30 g of NMP were added to a three-neck flask as this vessel is more facile in use on a lab scale.

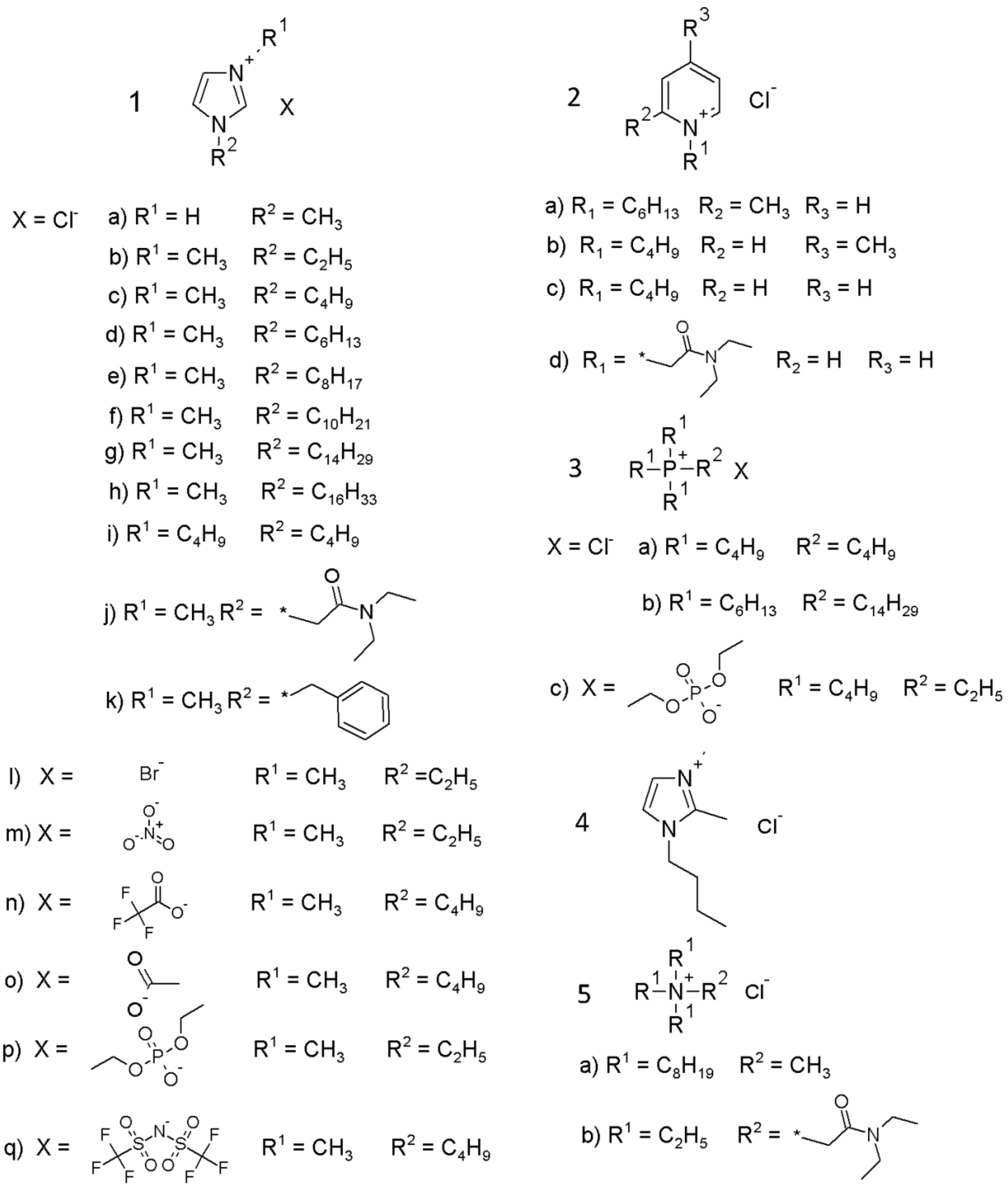


Chart 1. Overview of all ionic liquids used in the 25 wt% ionic liquid/75 wt% NMP polymerization tests. 1a) [HMIM][Cl], 1b) [C_2MIM][Cl], 1c) [C_4MIM][Cl], 1d) [C_6MIM][Cl], 1e) [C_8MIM][Cl], 1f) [C_{10}MIM][Cl], 1g) [C_{14}MIM][Cl], 1h) [C_{16}MIM][Cl], 1i) [C_4C_4IM][Cl], 1j) [C_1IMCH_2CON$(Et)_2$][Cl], 1k) [BzMIM][Cl], 1l) [C_2MIM][Br], 1m) [C_2MIM][NO_3], 1n)

$[C_4MIM][CF_3COO]$, 1o) $[C_4MIM][OAc]$, 1p) $[C_2MIM][Et_2PO_4]$, 1q) $[C_4MIM][NTf_2]$, 2a) [2-Me-C_6Pyr][Cl], 2b) [3-Me-C_4Pyr][Cl], 2c) [C_4Pyr][Cl], 2d) $[CH_2CON(Et)_2Pyr][Cl]$, 3a) $[P_{4444}][Cl]$, 3b) $[P_{66614}][Cl]$, 3c) $[P_{4442}][Et_2PO_4]$, 4) $[C_4C_1MIM][Cl]$, 5a) $[N_{8881}][Cl]$, 5b) $[N_{222}CH_2CON(Et)_2][Cl]$.

Table 2. Molecular weight indicated as the inherent viscosity of PPTA polymer obtained from a low-temperature polycondensation reaction in a 25 wt% ionic liquid/75 wt% NMP solvent mixture.

Entry	Ionic liquid	Inherent viscosity (dL/g)
1	$[C_8MIM][Cl]$	4.73[a]
2	[2-Me-C_6Pyr][Cl]	4.50
3	$[C_4C_4IM][Cl]$	3.89
4	$[C_4MIM][Cl]$	3.78
5	$[C_6MIM][Cl]$	3.61[b]
6	$[C_2MIM][Cl]$	3.59
7	$[C_{14}MIM][Cl]$	3.55
8	$[C_{10}MIM][Cl]$	3.50
9	[BzMIM][Cl]	2.98
10	$[C_4C_1MIM][Cl]$	2.81
11	[3-Me-C_4Pyr][Cl]	2.75
12	$[P_{4444}][Cl]$	2.51
13	$[P_{66614}][Cl]$	1.90
14	$[N_{8881}][Cl]$	1.73
15	$[C_1IMCH_2CON(Et)_2][Cl]$	1.54

16	$[C_2MIM][Br]$	1.44
17	$[P_{4442}][Et_2PO_4]$	1.02
18	[HMIM][Cl]	0.85
19	$[C_4MIM][CF_3COO]$	0.61
20	$[C_2MIM][NO_3]$	0.55
21	$[C_4MIM][NTf_2]$	0.50
22	$[C_2MIM][Et_2PO_4]$	n.p[c]
23	$[C_4MIM][OAc]$	n.p[d]
24	$[N_{222}CH_2CON(Et)_2][Cl]$	n.s[e]
25	$[C_4mPyrr][Cl]$	n.s
26	$[C_4Pyr][Cl]$	n.s
27	$[CH_2CON(Et)_2Pyr][Cl]$	n.s
28	$[C_{16}MIM][Cl]$	n.s

[a] Repeating the experiment three times resulted in a standard deviation of 0.0556 dL/g. [b] Repeating the experiment three times resulted in a standard deviation of 0.155 dL/g. [c] No polymerization occurred, as terephthaloyl chloride was not soluble in the solvent mixture. [d] No polymerization reaction did occur, due to a side reaction. [e] No complete solubility of IL in NMP at 0 °C at selected concentration.

By performing experiments using ionic liquids with different types of cations and anions, PPTA polymers were obtained with a variety of inherent viscosities. Almost all ILs could be dissolved in *N*-methylpyrrolidone in a 33 wt% concentration at 0 °C, except the ammonium ILs with short alkyl chain lengths (entry **24** and **25**), some pyridinium ILs (entry **26** and **27**) and imidazolium ILs with a very long alkyl chain (entry **28**). It was not possible to perform a polymerization reaction with 1-ethyl-3-methylimidazolium diethyl phosphate (entry **22**) because terephthaloyl chloride could not be dissolved in the reaction mixture. The polarity of the solvent was probably too high, as the solubility of the acid chloride decreases with increasing polarity.

Aside from that, other several interesting observations were made, which can be divided according to the type of cation and anion used in the IL/NMP solvent mixture.

As observed in the dissolution studies of PPTA oligomers, ILs with coordinating anions must be used for the polymerization reactions. These anions are essential in the occupation of H-bonds of the secondary amide bonds of the polymer chain and prevent premature precipitation of the PPTA polymer during the polycondensation reaction. This necessity was observed when experiments with ILs containing weakly H-bond accepting anions, such as 1-ethyl-3-methylimidazolium nitrate and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (entry **19** and **20**, respectively) were performed. Rapid precipitation occurred at the start of the reaction (Figure 2). The inherent viscosity of the obtained polymer has approximately the same value as the PPTA polymer obtained via a polymerization reaction in NMP without the addition of any salt i.e. 0.55 dL/g. It can thus be concluded that the lack of a strongly coordinating anion makes the IL inactive in occupying the H-bonds of the growing polymer chain, incapable of forcing the reaction further towards gel formation, so that no PPTA with a reasonably high molecular weight could be obtained.

The necessity of strongly coordinating anions was also observed when an IL with a bromide anion was used (entry **15**). This anion has a higher tendency to form H-bonds than the bis(trifluoromethylsulfonyl)imide or nitrate anion and is thus able to prolong the duration of the reaction until a molecular weight of 1.44 dL/g was reached. However, the bromide anion lacks the strength to keep the growing polymer chain in dissolution after this inherent viscosity has been obtained and precipitation of PPTA still occurred (Figure 2).

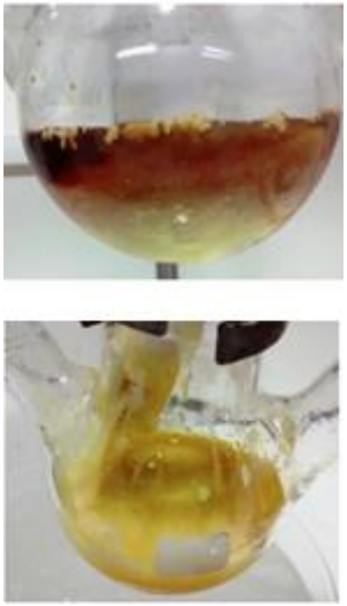
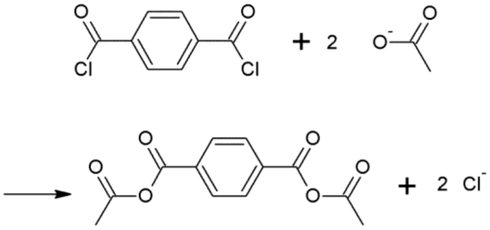


Figure 2. Top: Reaction mixture after a polymerization reaction in a [C_2MIM][NO_3]/NMP solvent mixture. Rapid precipitation of PPTA was observed. Bottom: Reaction mixture after a polymerization reaction in a [C_4MIM][Br]/NMP solvent mixture. The bromide anion has a higher H-bond accepting character and precipitation only occurs at a later stage of the reaction.

The best results were obtained with ILs that contained the chloride ion, an anion that has an even higher tendency to form H-bonds (entry **1** to **14**). In all these cases, gel formation occurred regardless of the type of IL cation and inherent viscosities were obtained well above 0.50 dL/g (Figure 3). Furthermore, by using 3-methyl-1-octylmethylimidazolium chloride ([C_8MIM][Cl]) (entry **1**) and 1-hexyl-2-methylpyridinium chloride ([2-Me-C_6Pyr][Cl]) (entry **2**) in the solvent mixtures, PPTA could be synthesized on a same level as in the industrial process, and this with a reduced amount of NMP.

Figure 3. Reaction mixture after a polymerization reaction in a [2-Me-C_6Pyr][Cl]/NMP solvent mixture. The chloride anion successfully prevented precipitation of the growing polymer chain in the early stage of the reaction and a gel in the form of a solid crumble was formed.

Furthermore, the chloride anion seems to be the only suitable anion for coordination with the amide bonds of the polymer, as stronger H-bond accepting anions such as diethyl phosphate and acetate (pK_a of their conjugate acid being 1.39 and 4.75 respectively) also have a higher nucleophilic character. Nucleophiles compete with *p*-phenylenediamine in reacting with the highly reactive acid chloride to form a condensation product. Even a small fraction of side reactions diminishes the molecular weight significantly. The nucleophilicity of the anion in 1-butyl-3-methylimidazolium acetate (entry **23**) was so high that only condensation between terephthaloyl chloride and the acetate anion occurred, as confirmed by ^{1}H NMR spectroscopy (Scheme 2).



Scheme 2. Side reaction that occurs when a low-temperature polycondensation reaction is performed using acetate ionic liquids. The acetate is sufficiently nucleophilic to react with the acid chloride.

In an attempt to perform the reaction in the presence of an anion with a lower nucleophilicity than acetate, an IL with the trifluoroacetate anion was used. Unfortunately, precipitation of the PPTA polymer occurred and only low-molecular weight PPTA was obtained (entry **18**). Lowering the nucleophilicity of a carboxylate anion also reduced the ability of the anion to interact with the H-bond network of PPTA and precipitation could not be avoided.

Condensation reactions with the anion probably also occurred to a lesser extent when tributylethylphosphonium diethyl phosphate was used as IL (entry **16**). Gel formation and thus no precipitation of the polymer was observed during the reaction, which indicates that this anion is successful in avoiding the aggregation of different chains. However, the molecular weight of the polymer did not increase any further, as probably a small fraction of the condensation product with the phosphate anion effectively acted as a chain stopper.

Overall, a balance must be found between a high tendency to form H-bonds (to avoid precipitation) and an as low as possible nucleophilicity (to avoid side reactions). So far, the chloride anion has proven to provide this trade-off as only with these types of ILs, relatively high molecular weight polymers could be obtained.

When looking at the results from reactions in solvent mixtures containing chloride ILs (entry **1-14** and **17**), it is evident that also the type of cation has an influence on the outcome of the polycondensation reaction. Surprisingly, the imidazolium and 2-methylpyridinium ILs gave polymers with the highest inherent viscosities, while they were found to be less efficient solvents for the dissolution of PPTA oligomers in previous research.[24] This discrepancy in IL performance for PPTA dissolution and polymerization can be explained by the fact that the mechanisms of these processes are different. A successful polymerization of PPTA relies on gel formation and not on dissolution, as will be discussed in further detail later on.

Interestingly, even after performing multiple polymerization experiments, 3-methyl-1-octylimidazolium chloride ([C_8MIM][Cl]) (entry **1**) stood out as the best IL for preparing PPTA polymers compared to all the other imidazolium chloride ILs (Figure 4). The explanation for an optimum in inherent viscosity of the resulting PPTA polymer by varying the alkyl chain length can also be found in the mechanism of gel formation during the polymerization reaction. Furthermore, the quality of the gel changed during polymerization when the alkyl chain length on the imidazolium cation was increased. Longer alkyl chain lengths on the imidazolium ring of the IL resulted in reaction mixtures which eventually formed softer gels. The long hydrocarbon chains probably do not have a contribution to the interactions with the PPTA polymer, but they could act as plasticizers during the gel formation process.[42] Those gels do not fall apart into a solid crumble and facile stirring is possible during the entire reaction (Figure 5).

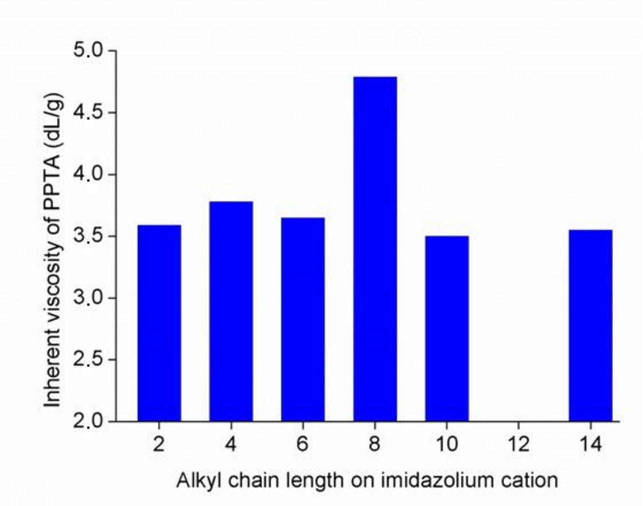


Figure 4. Resulting inherent viscosities (dL/g) of PPTA from polymerization experiments containing imidazolium chloride ionic liquids with different alkyl chain lengths. When [C_8MIM][Cl] was used, the molecular weight of PPTA stood out in terms of inherent viscosity compared to the other experiments.

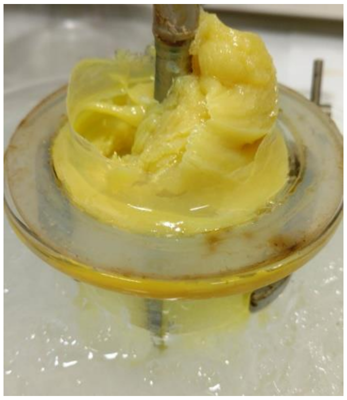
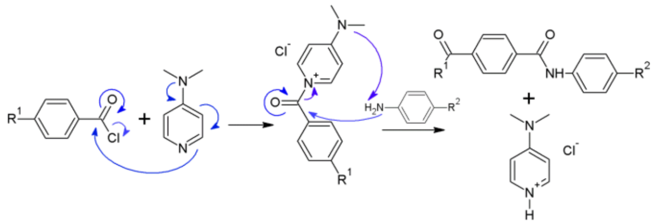


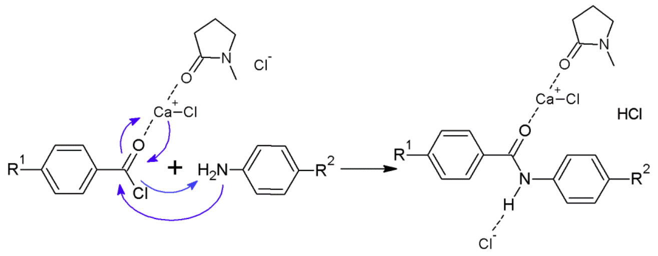
Figure 5. Reaction mixture after a polymerization reaction in a [C_8MIM][Cl]/NMP solvent mixture. The long alkyl chain on the imidazolium cation results in a softer gel that does not crumble at the end of the reaction.

As the [C_8MIM][Cl]/NMP reaction mixture gave the best results, more experiments were performed. First, the same reaction was performed in a cylindrical reaction vessel with an anchor stirrer. However, unlike the benchmark tests, this method did not result in an increase in inherent viscosity. Secondly, in the same reaction vessel, a reaction was performed without the addition of a base. Unfortunately, only PPTA polymer with a rather low inherent viscosity was obtained (0.96 dL/g). This could be explained by the fact that α-picoline besides its function as an acid neutralizer also functions as a nucleophilic catalyst in the condensation reaction via a similar reaction path as is known for 4-dimethylaminopyridine (DMAP) (Scheme 3).[43;44]



Scheme 3. Proposed reaction scheme of a condensation reaction catalyzed by 4-dimethylaminopyridine (DMAP).

However, a polymerization with NMP/$CaCl_2$ without the addition of α-picoline as a base did result in PPTA with reasonably high molecular weights. This is ascribed to the highly coordinating nature of the Ca(II) cation which interacts with the oxygen atoms of the carbonyl functional groups present in the reaction mixture.[45-47] By interacting as a Lewis acid towards terephthaloyl chloride, the Ca(II) ions activate the acid chloride for reaction with *p*-phenylenediamine (Scheme 4). This activation is beneficial for coupling longer oligomers, because reactant mobility at that stage of the reaction is reduced. The lack of a Lewis acidic cation in NMP/IL reaction mixtures means that polymerizations are best performed in the presence of α-picoline, which besides its function as acid neutralizer also functions as a coupling catalyst.



Scheme 4. Proposed reaction scheme for the condensation reaction in NMP/$CaCl_2$ without the presence of a Brønsted base. By coordination of the carbonyl functional group with the Lewis acidic calcium cation, the carbon of the carbonyl functionality becomes even more attainable for nucleophilic attack.

3.3 Polymerization in [C_8MIM][Cl]/cosolvent mixtures

As [C_8MIM][Cl] was by far the best ionic liquid for the polymerization reactions with *N*-methylpyrrolidone as cosolvent, it was used in additional polymerization experiments using other cosolvents. Furthermore, [C_8MIM][Cl] is a room-temperature IL and is in contrast to $CaCl_2$ soluble in all concentrations in a variety of polar and nonpolar solvents such as various amides, acetone, acetylacetone, acetonitrile, dichloromethane, 1,2-dichloroethane, chloroform, toluene, tri-*n*-butyl phosphate, propylene carbonate and dimethyl sulfoxide. Only ethyl acetate, diethyl ether, tetrahydrofuran and hydrocarbon solvents were found to be non-solvents for [C_8MIM][Cl]. First of all, polymerization reactions were performed using [C_8MIM][Cl] in other amide solvents. By doing this, it can be checked if comparable results are obtained with solvents similar to NMP. Next, a whole range of other solvents combined with [C_8MIM][Cl] was tested and finally, some selected solvents in different concentrations with [C_8MIM][Cl] were tried out. Notice that all these solvents have different molecular masses. The monomer concentration was changed according to the solvents molecular mass in order to maintain the same molar ratio between monomers and solvent compared to the benchmark experiments.

Polymerization of PPTA was performed in mixtures of [C_8MIM][Cl] and other amide solvents in a 25/75 mass ratio. Both known and synthesized amide solvents were tested. Since the molecular mechanism behind the teratogenicity of NMP is not fully understood yet, it is not known to which extent these other amide solvents will exhibit similar toxic properties. Unfortunately, *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc) and tetramethylurea (TMU) were also deemed teratogenic after tests with mice and frogs.[48] However, no data of the teratogenicity of dimethylimidazolidinone (DMI) could be found in the literature and this compound has already been presented as a replacement for the very carcinogenic hexamethylphosphoramide.[49] Chart 2 shows the amide solvents that were used in the polymerization experiments and Table 3 presents the inherent viscosities of the PPTA polymers that were obtained from these reactions.

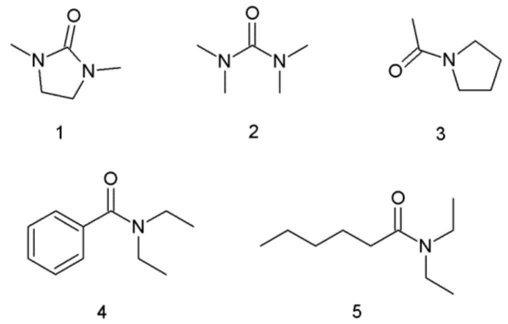


Chart 2. Different amide solvents used in combination with [C8MIM][Cl] as solvents for the polymerization of PPTA: 1. dimethylimidazolidinone, 2. tetramethylurea, 3. *N*-acetylpyrrolidine 4. *N,N*-diethylbenzamide, 5. *N,N*-diethylhexanamide.

Table 3. Molecular weight indicated as the inherent viscosity of PPTA polymer obtained from a low-temperature polycondensation reaction in a 25 wt% [C_8MIM][Cl] and 75 wt% amide solvent mixture.

Entry	Amide solvent	Inherent viscosity (dL/g)
29	Tetramethylurea	3.40
30	dimethylimidazolidinone	2.45
31	*N*-acetylpyrrolidine	2.30
32	*N,N*-diethylbenzamide	1.81
33	*N,N*-diethylhexanamide	n.p[a]

[a]no polymerization occurred, because *p*-phenylenediamine was not soluble in the solvent mixture.

All polymerizations of [C_8MIM][Cl] with an amide solvent caused gel formation of the reaction mixture. However, the molecular weight of the resulting PPTA polymers was not as high as for those obtained with NMP/[C_8MIM][Cl]. Since it was not sure if these solvents also posed potential health risks, no further experiments to improve the inherent viscosity of PPTA were performed.

It was suggested that the ability to produce high molecular weight PPTA in NMP/$CaCl_2$ mostly relies on the free chloride anions present in solution and that the amide solvent mainly functions as a carrier for the dissolved salt.[8] Since ILs show a much larger flexibility in dissolution in common organic solvents compared to $CaCl_2$, this assumption could be easily tested by performing polymerization experiments using a 25 wt% of [C_8MIM][Cl] in various other organic solvents (Table 4).

Table 4. Molecular weight indicated as the inherent viscosity of PPTA polymer obtained from a low-temperature polycondensation reaction in a 25 wt% [C_8MIM][Cl] and 75 wt% of a cosolvent.

Entry	**Cosolvent**	**Inherent viscosity (dL/g)**
34	tri-*n*-butylphosphate	1.43
35	Acetonitrile	0.53
36	Acetylacetone	0.52
37	Dichloromethane	0.49
38	Acetone	0.47
39	Toluene	0.37
40	methyl acetoacetate	n.p[a]
41	propylene carbonate	n.p[a]
42	α-picoline	n.p[b]

[a]No polymerization occurred, because terephthaloyl chloride was not soluble in the solvent mixture. [b]No polymerization occurred, because *p*-phenylenediamine was not soluble in the solvent mixture.

Unfortunately, polymerization reactions in reaction mixtures containing [C_8MIM][Cl] and a non-amide solvent always resulted in premature precipitation of the polymer and no gel formation, thus no higher molecular weights of PPTA could be obtained (Table 4). Clearly, the solvent has an additional role other than merely keeping cations and anions in a mobile and dissolved state. The solvent must not interfere with the interaction of the ILs with the growing polymer chains and perhaps must even aid the process of gel formation. Interestingly, the inherent viscosity of PPTA obtained after polymerization using tri-*n*-butyl phosphate (entry **34**) stood out from the other solvents tested. In fact, to the best of our knowledge, such molecular weights of PPTA obtained from a non-amide solvent have not yet been reported in literature.

Since the use of non-amide solvents in the reaction mixture negatively influenced the solvent strength for PPTA polymerization, it was tried to perform polymerization experiments that contained a much higher concentration of [C_8MIM][Cl] in the solvent mixture. Of course, this implied that reactions must be performed in a reaction solvent with a much higher viscosity and this influences the dissolution kinetics and the uniform distribution of the acid chloride in the reaction mixture. However, even a small amount of a cosolvent can lower the viscosity of an IL drastically.[50-52] Zhang *et al*. discovered that internal cooling can be applied by adding an immiscible low-boiling solvent such as pentane and liquid nitrogen to NMP/$CaCl_2$ as internal coolant.[53;54] This solvent absorbs the reaction heat released during polymerization by evaporation and keeps the temperature in the reaction vessel within the optimal range. In our case, dichloromethane (DCM) was added as low boiling solvent to [C_8MIM][Cl]. Dichloromethane which is soluble in this IL, would then act as internal coolant and cosolvent for lowering the viscosity. Several experiments were performed using this method (Table 5). Again, the monomer concentration was changed according to the solvents molecular mass in order to maintain the same molar ratio between monomers.

Table 5. Molecular weight indicated as the inherent viscosity of PPTA polymer obtained from a low-temperature polycondensation reaction in varying concentrations of dichloromethane (DCM) and [C_8MIM][Cl].

Entry	**[C_8MIM][Cl]/DCM (wt%/wt%)**	**Solvent viscosity at 25°C (cP)**	**Inherent viscosity (dL/g)**
43	50:50	23	0.95
44	75:25	265	1.11

When these polymerization reactions were started by addition of terephthaloyl chloride, slow dissolution of the acid chloride was observed, followed by a very steep increase in solvent viscosity as dichloromethane evaporated in the gas stream of nitrogen. Nevertheless, premature precipitation of PPTA did occur. However, raising the IL content in the reaction mixture did prolong the polycondensation reaction until precipitation occurred at a later stage.

Finally, some polymerization reactions were performed in solvent mixtures with an even higher concentration of [C_8MIM][Cl], i.e. a 90:10 mass ratio. In that case, solvent viscosity was so high that rapid and homogeneous dissolution of the acid chloride was not guaranteed. To partly circumvent this issue, terephthaloyl chloride was added to the reaction mixture as a melt (Table 6).

Table 6. Molecular weight indicated as the inherent viscosity of PPTA polymer obtained from a low-temperature polycondensation reaction in a 90:10 (wt%/wt%) [C_8MIM][Cl]/cosolvent mixture.

Entry	Cosolvent	Solvent viscosity at 25 °C (cP)	Inherent viscosity (dL/g)
45	*N*-methylpyrrolidone	1593	2.36
46	tri-*n*-butyl phosphate	1836	1.86
47	acetonitrile	1432	1.45

Promising results were obtained by using [C_8MIM][Cl] as solvent in combination with small amounts of cosolvent. These reactions were only possible by adding terephthaloyl chloride in the molten state, as solid flakes of the acid chloride will never dissolve rapidly enough in the time frame of the polymerization reaction. It must be noted that viscosities were measured at 25 °C, the viscosity increases exponentially to levels that are not measurable with the viscometer by lowering the temperature. Most importantly, no precipitation of PPTA polymer was observed and the reaction mixture was obtained as a gel. When the solvent mainly consisted of [C_8MIM][Cl], it was possible to synthesize PPTA with an inherent viscosity as high as 1.86 dL/g, without the use of any amide solvent (entry **46**). The fact that a gel was formed is an interesting feature for [C_8MIM][Cl], which proves that the characteristics of both cation and anion enable a polymerization process that is closely related to the polymerization process in a NMP/$CaCl_2$ solvent mixture. Further research is needed to investigate if these solvents have the potential to produce PPTA with even higher inherent viscosities. After all, it could be that higher molecular weights of PPTA are inhibited due to the highly viscous solvent.

3.4 Polymerization mechanism of PPTA

It is assumed that high molecular weight PPTA cannot be completely dissolved in a neutral solvent at concentrations that are ideal for polycondensation reactions. In order to keep the reaction ongoing, precipitation of the growing polymer chains during the reaction is prevented by a series of interactions that takes place between the solvent/salt mixture and the PPTA polymer. In this way, the solvent particles impede the different PPTA chains in coagulating and polymerization is continued in a gel-state. From the many polymerization experiments that were performed, more insights were gained in what requirements a solvent should fulfill in order for the reaction mixture to form a gel and to successfully polymerize PPTA with reasonably high molecular weights.

First of all, as was seen in the initial screening experiments using different ILs diluted in NMP, a coordinating anion is of prime importance. A coordinating anion functions as a Lewis base that will occupy the H-bonds of the secondary amide functional groups of the PPTA polymer. With the lack of such interactions, precipitation of low molecular weight PPTA will always occur. However, strong Lewis basicity could also imply a strong nucleophilic character, which is detrimental for the polycondensation reaction because side reactions occur with terephthaloyl chloride. For this reason, the chloride anion is considered the only suitable anion.

Furthermore, the cation in the IL plays a secondary but important role during the polymerization reaction. Polymerization using imidazolium and 2-methylpyridinium chloride ILs in the solvent results in stronger swelling, more extensive gelation and eventually higher molecular weights of PPTA. This observation is in contrast with the fact that ILs with a coordinating cation are not effective in dissolving PPTA oligomers.[24] A weak H-bond donor on the cation is regarded as beneficial during polymerization. In this case, the chloride anion interacts with both the cation and the polymer which helps with the formation of a protective solvent shell around the growing polymer chain. These interactions block different chains in forming intermolecular H-bonds which prevents aggregation and precipitation of the polymer.

The fact that the highest inherent viscosity of PPTA was obtained when using [C_8MIM][Cl] in the solvent mixture can be explained by two reasons. Firstly, longer alkyl chains on the imidazolium cation result in increased sterical shielding from the aggregation of different PPTA polymer chains. An optimum was found for [C_8MIM][Cl] as too long alkyl chain lengths might hinder the mobility of the cation during the reaction. Secondly, the H-bond acidity of an imidazolium cation actually decreases with increasing alkyl chain length due to inductive effects and steric shielding of the cationic center.[55] The cation of [C_8MIM][Cl] might possess the ideal H-bond acidity for an anion to have a balanced interaction between the polymer and the imidazolium cation. In other words, this weakly coordinating cation will interact with the chloride anion but only to such an extent that the chloride anion is still available to form H-bonds with amide functionalities of the polymer. In fact, the Kamlet-Taft parameters of [C_8MIM][Cl] and a secondary amide, e.g. *N*-methylacetamide, show that they have similar H-bond-donating and -accepting properties (Table 7)[56], meaning that all possible H-bonds (cation – anion, cation – polymer, anion – polymer) have similar affinities (Figure 6). This also explains why the use of phosphonium chloride ILs did not result in high inherent viscosities of the resulting polymer as the H-bond strength of this cation is much lower compared to imidazolium cations.[55] A similar reasoning could explain the lower value of inherent viscosity of PPTA when 1-benzyl-3-methylimidazolium chloride ([BzMIM][Cl]) as IL is used (entry 9). The electron withdrawing aromatic ring on the cation makes the imidazolium cation more susceptible for stronger H-bond interactions with the anion. Furthermore, the presence of the aromatic ring could hinder mobility for efficient cation – anion and cation – polymer interactions.

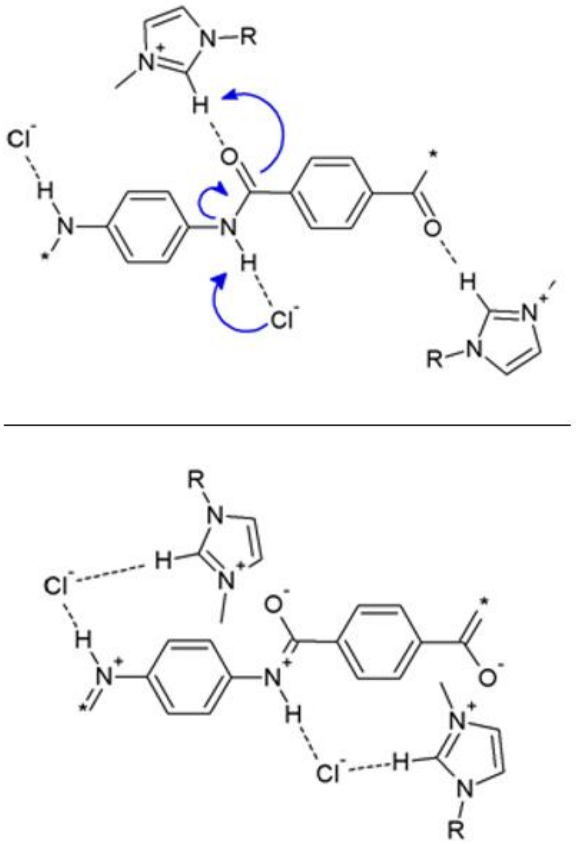


Figure 6. Two proposed interactions of an imidazolium chloride ionic liquid and a PPTA polymer during reaction. Top: Both cation and anion interact with PPTA polymer as hydrogen bond donor and acceptor respectively. Bottom: The aramid polymer is drawn in the imidate resonance form to emphasize ionic interactions.

All observations were made while these ILs were diluted in a cosolvent and in most cases the cosolvent was present in a large excess. The cosolvent will interact with the IL and the polymer which negatively or positively influences the polymerization process. Solvent parameters of ILs and cosolvents used in the polymerization experiments were collected and compared. The Lewis acidicity and basicity, i.e. the electron pair-accepting and donating properties respectively, can be quantified by the Gutmann donor number (DN) and the Gutmann acceptor number (AN)[57] while the hydrogen bond acidity (α) and basicity (β) are described by the Kamlet-Taft parameters (Table 7).[58;59]

Table 7. The α- and β-value from the Kamlet-Taft parameters[56;60-63] and the Gutmann acceptor numbers (AN) and the Gutmann donor numbers (DN) for cosolvents and ionic liquids[57;64;65] used in the polymerization experiments.

Cosolvent	**α**	**β**	**AN**	**DN**
N-methylpyrrolidone	0.00	0.77	13.3	27.3
tetramethylurea	0.00	0.80	9.2	31
tri-*n*-butyl phosphate	0.00	0.80	9.9	23.7
acetonitrile	0.19	0.40	18.9	14.1
dichloromethane	0.04	-0.01	20.4	1
acetone	0.20	0.54	12.5	17
toluene	0.00	0.11	n.d[a]	n.d
Ionic liquid	**α**	**β**	**AN**	**DN**
[C_8MIM][Cl]	0.31	0.98	n.d	69.2
Secondary amide	**α**	**β**	**AN**	**DN**
N-methylacetamide	0.47	0.80	n.d	n.d

[a]n.d: no data was found. [b]To have an indication how the secondary amide functional groups of a PPTA polymer would interact, the solvent parameters of *N*-methylacetamide are also mentioned.

The use of cosolvents with a non-zero α-value or with an acceptor number higher than its donor number result in immediate precipitation of the PPTA polymer. These solvents show a high affinity for the chloride anion, the most active species in PPTA polymerization. They disturb the anion in forming H-bonds with the polymer.

Table 7 also shows that the amide solvents exhibit no H-bond acidity[66] but however show a small tendency to act as Lewis acid. On top of that, they also function as an H-bond acceptor and Lewis base. This means that the solvent could interact in multiple ways with the species present in the reaction mixture (solvent – cation, solvent – anion, solvent – polymer). As reactions using these cosolvents resulted in gelation with PPTA of high molecular weight, it is assumed that these interactions help towards network formation within the reaction mixture. As previously discussed, the cation and anion of [C_8MIM][Cl] have a well-balanced interaction with each other and with the secondary amide bonds of the polymer. This balance in interactions between the different components could well be extrapolated to the cosolvent, if the cosolvent also consists of an amide functionality. In this case, the chloride anion will interact with the labile hydrogen of the secondary amide bonds of the polymer while the cation is able to interact with the chloride anion and amide bonds of both the polymer and the solvent. This means it is theoretically possible to form an aggregation that extends over the whole volume of the reaction mixture (Figure 7).

Interestingly, solvent parameter values between tri-*n*-butyl phosphate and the amide solvents are similar. This means that the same process as discussed above could as well happen when tri-*n*-butyl phosphate is used. Precipitation of PPTA still occurred with a 75 wt% tri-*n*-butyl phosphate and 25 wt% [C_8MIM][Cl] solvent mixture but only at a later stage of the reaction compared to other non-amide solvents (entry **34**).

Further proof that a balance in interactions between all the components must be kept, was found with a mixture of *N*-methylpyrrolidone, tri-*n*-butyl phosphate and [C$_8$MIM][Cl]. A polymerization in a 71 wt%/4 wt%/25 wt % solvent mixture of all components respectively resulted in PPTA with an inherent viscosity of only 0.91 dL/g, a value that is lower than when both cosolvents are used in their pure form.

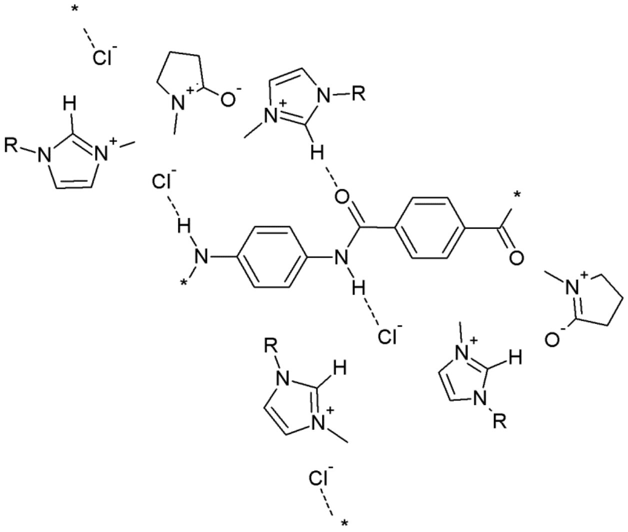


Figure 7. Proposed interactions of a *N*-methylpyrrolidone/imidazolium chloride solvent mixture with a PPTA polymer during a reaction. *N*-Methylpyrrolidone is drawn in the imidate resonance form to emphasize ionic interactions.

4. Conclusions

Ionic liquids were proposed as an alternative and greener medium for polymerization of PPTA as they exhibit a higher ion concentration compared to the *N*-methylpyrrolidone/calcium chloride (NMP/CaCl$_2$) solvent mixture. It was opted to dilute the ILs in a cosolvent in order to diminish their melting points and viscosities. This enabled to follow the synthetic procedure of the industrial polymerization of PPTA. As an initial screening, polymerizations of PPTA were performed in solvent mixtures of IL and NMP in a 25 wt%/75 wt% mass ratio. It was found that coordinating anions are needed to prevent early precipitation of the PPTA polymer but that too nucleophilic anions are prone to side reactions with the highly reactive terephthaloyl chloride. For this reason, only ILs containing chloride anions were deemed suitable for the synthesis of PPTA. PPTA polymer with molecular weights close to the benchmark tests were obtained with 1-octyl-3-methylimidazolium chloride ([C_8MIM][Cl]). Using ammonium and phosphonium chloride ILs resulted in lower molecular weight of PPTA while they showed the highest dissolving capacity towards PPTA oligomers. The reason for this discrepancy in performance is the difference in the mechanics of dissolution and the polycondensation of PPTA. Obtaining a high molecular weight of PPTA during synthesis relies on gelation of the reaction mixture. Gel formation is only obtainable if a network of similar interactions between secondary amide bonds of the polymer, cation, anion and solvent is established. By analyzing the Kamlet-Taft parameters and Gutmann donor and acceptor numbers of various solvents it is clear that the intermediate H-bond acidity of an imidazolium cation is ideal in interacting with both the chloride anion and the carbonyl groups of both amide functionalities of the solvent and the polymer. Tri-*n*-butyl phosphate contains similar solvent parameters as NMP and by using it as a cosolvent together with [C_8MIM][Cl], it was possible to produce PPTA with the highest molecular weight of all the non-amide solvents. In fact, such inherent viscosities of PPTA without the use of HMPA or an amide solvent have not been reported in literature. [C_8MIM][Cl] has proven to be miscible with a variety of solvents in all possible concentrations. Polymerization experiments using [C_8MIM][Cl] diluted with a small amount of tri-*n*-butyl phosphate showed that it was possible to produce PPTA polymer with an inherent viscosity of 1.86 dL/g, with establishing gelation within the reaction mixture. This proves that [C_8MIM][Cl] as IL is a promising candidate in producing PPTA polymers without the use of any amide solvent.

Corresponding Author

*Koen Binnemans; mail: koen.binnemans@kuleuven.be; Tel: +32 16 32 74 46

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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