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Synthesis of polyaramids in γ-valerolactone-based organic electrolyte solutions†

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The current synthetic procedures for polyaramids mainly involve the use of amide solvents such as *N*-methylpyrrolidone and *N*,*N*-dimethylacetamide. However, these solvents are suspected to be teratogenic and are considered 'Substances of Very High Concern' by the European Commission. Here we propose a benign alternative solvent system: an Organic Electrolyte Solution (OES) consisting of γ-valerolactone (GVL) and a small amount of the ionic liquid 1-methyl-3-octylimidazolium chloride, [C$_8$MIm][Cl]. Three commercially relevant polyaramids were synthesized: poly-*p*-phenylene terephthalamide (PPTA), poly-*m*-phenylene isophthalamide (PMIA) and copoly(*p*-phenylene/3,4′-diphenylether terephthalamide) (ODA/PPTA). PMIA was successfully synthesized in the OES containing [C$_8$MIm][Cl] in a molar fraction of x_{IL} = 0.043, achieving an inherent viscosity of η_{inh} = 1.94 ± 0.064 dL g^{-1}, which is on par with the current industrial standard and the benchmark lab scale synthesis. The reaction mixture could also be directly used for the wet spinning of polyaramid fibers, and all components of the solvent could be recycled in good yields by a series of evaporation and distillation steps. ODA/PPTA could be synthesized, but only rather low inherent viscosities were achieved. The reaction mixture was too viscoelastic to be spun by our small-scale spinning setup. PPTA always instantly precipitated and could not be synthesized from a [C$_8$MIm][Cl]/GVL OES. α-Picoline, the organic base which was added to capture the released HCl during the reaction, was found to play a pivotal role in the polymerization reaction. By undergoing an acid–base reaction with HCl, it forms a protic ionic liquid *in situ* which increases the solubility of the polymer.

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Introduction

Since their development in the 1960s, polyaramids (aromatic polyamides) have become a staple amongst the high performance polymers.[1–4] They display several desirable properties including a high chemical and thermal resistance, a high strength/mass ratio and non-flammability. These properties make them suitable to serve in a wide range of applications such as protective clothing, material reinforcement, ballistic protection, fiber optics and in aviation/aerospace technology. Currently, three types of polyaramids are produced commercially on a large scale: (1) poly-*p*-phenylene terephthalamide (PPTA), (2) poly-*m*-phenylene isophthalamide (PMIA) and (3) copoly(*p*-phenylene/3,4′-diphenylether terephthalamide) (ODA/PPTA). However, the production of these polyaramids entails some difficulties. Their melting points are well above their degradation temperatures, so it is impossible to synthesize or process these polymers from the melt.[5] Polyaramids thus need to be synthesized and processed from solution. This is again complicated by the fact that they are exceptionally difficult to dissolve in most conventional organic solvents. The large number of amide functionalities can form intermolecular hydrogen bonds between the amino and carbonyl groups. Furthermore, the rigid aromatic backbone limits the mobility of the amide functionalities, preorganising them for neatly packed and very efficient hydrogen bond networks.

To dissolve polyaramids, the intermolecular hydrogen bond network needs to be broken up. For PPTA, this is done by using a mixture of *N*-methyl-2-pyrrolidone (NMP) and CaCl$_2$ as the solvent for synthesis.[6] The chloride anions provided by CaCl$_2$ can interact with the amino groups, thus interrupting the intermolecular hydrogen bond network. Although this binary solvent system cannot make a thermodynamically stable solution of PPTA, it can delay precipitation long enough to let the polymerization proceed until a high average molar mass is achieved. A thermodynamically stable solution is required for processing. Thus, PPTA is dissolved in concentrated sulfuric acid, which protonates the amide functionalities, creating a net positive charge on the chains and making them repel each other.[7] PMIA and ODA/PPTA are both more

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soluble than PPTA as a result of their respective structures. PMIA is *m*-oriented, which results in a less efficient orientation of the amide groups, whereas ODA/PPTA has had some flexibility introduced to the chain by adding ether linkages. Both polymers can be synthesized in NMP without the addition of $CaCl_2$, and the synthetic solutions can be used directly for the spinning of fibers.[8,9]

The production of polyaramids is heavily dependent on the use of NMP. However, this solvent has been placed on a 'Substance of Very High Concern' (SVHC) list by the European Commission, because of its suspected teratogenic properties.[10] This makes NMP subject to potential restrictions for use in industry, and so a new benign solvent is needed. PMIA can alternatively be produced *via* an interphase polymerization, using water and THF as a biphasic solvent system.[11] However, this type of polymerization offers poor control of local monomer stoichiometry, leading to significantly broader molar mass distributions. Also, because PMIA is precipitated during the polymerization process, it is impossible to directly spin it from the synthetic solution, and it nevertheless needs to be separated and redissolved in NMP. Another strategy has been to make the polyaramids more soluble in other solvents by altering their chemical structure.[12,13] However, these altered polyaramids are made from more complex (and thus more expensive) monomers, and their properties do differ from the original polyaramids.

In recent years, efforts have been made by our laboratory and others to explore the potential of ionic liquids (ILs) as alternative solvents for polyaramids, both for dissolution[14–17] and synthesis.[18–21] ILs are solvents which consist entirely of ions, which means they can act in a similar fashion to the NMP/$CaCl_2$ solvent system. Indeed, it was found that only ILs with strongly coordinating anions such as Cl^-, AcO^- or PO_4R^- are suitable solvents for polyaramids, as these are required to interrupt the intermolecular hydrogen bonds. For synthesis, only ILs with a chloride anion can be used, as the other anions will cause side reactions. Although ILs do seem to have potential as alternative solvents, they do have some severe disadvantages which can make them less suitable for large scale polymerizations.[22,23] Firstly, ILs are generally very hygroscopic and they readily absorb moisture from the atmosphere.[24] This means that the ILs must be thoroughly dried prior to their use in polyaramid synthesis, as moisture will precipitate the polymer and react with the acyl chloride monomers and terminate the reaction. Secondly, ILs also tend to be very viscous, which can cause problems such as slow reaction kinetics, poor homogeneity and engineering issues. Thirdly, ILs are currently much more expensive than conventional molecular organic solvents. This is mostly due to the small scale at which they are currently being produced, but it is a problem nevertheless.

All of the above-mentioned issues can be resolved by diluting the IL with a cosolvent, creating what is generally referred to as an *organic electrolyte solution* (OES). Adding a cosolvent can lead to a drastic reduction of the viscosity,[25] and the lower relative IL content makes the overall solvent less hygroscopic, easier to dry, and less expensive. This strategy of mixing ILs and cosolvents has successfully been applied to the field of cellulose dissolution, where it has resulted in higher solubilities and faster dissolution kinetics.[26–29] OESs were also proven to be suitable solvents for the synthesis of PPTA and for processing PMIA into porous films.[30,31] However, these applications still relied on the addition of amide solvents such as NMP or DMA. Recently, we have shown that OESs based on γ-valerolactone (GVL) are excellent solvents for PMIA and ODA/PPTA, and that they can be used for wet spinning polyaramid fibers.[32] GVL was found to work synergistically with ILs, even surpassing the solubility of polyaramids in the pure ILs. More importantly, GVL is a very attractive solvent for large scale industrial applications because of its green character, as it is a renewable biomass-derived solvent that has a low toxicity and is readily biodegradable.[33–35] The addition of GVL to ILs for the dissolution of polyaramids makes the whole process more economically and ecologically feasible at an industrial scale.

This paper explores the potential of these GVL-based OESs as solvents for the synthesis of polyaramids. All three of the above-mentioned polyaramids are synthesized in OESs, and the inherent viscosities obtained from the polymerizations are compared to the benchmark values from polymerizations performed in NMP. The influence of several parameters such as the molar composition of the OES, the organic base added to scavenge HCl, the type of IL and the polymer concentration are investigated. Finally, the possibility to directly spin fibers from the reaction mixtures is assessed, along with a method for recyclability of the components of the OES solvent.

Experimental

Products

The ionic liquids were purchased from IoLiTec (Heilbronn, Germany). Isophthaloyl chloride (≥99%), α-picoline (lonza quality, ≥99%), Pd/C 5% loading, *N*-methylpyrrolidone extra dry (99.5%), 2,6-dichloro-4-nitropyridine (97%) and terephthaloyl chloride (+99%) were purchased from Sigma-Aldrich (Diegem, Belgium). 3-Nitroaniline (98%), extra dry *N*,*N*-dimethylformamide (99%), sulfuric acid (96%), aniline (99.8%), benzoyl chloride (99%), triethylamine (99%), 1-methylimidazole (99%), *p*-phenylenediamine (>99%), 4-dimethylaminopyridine (99%) and γ-valerolactone (98%) were purchased from Acros Organics (Geel, Belgium). *m*-Phenylenediamine (99%) was purchased from Chem-Lab (Zedelgem, Belgium) and 3,4-oxydianiline (95%) was purchased from Fluorochem Limited (Hadfield, UK). [2-Me-HPyr][Cl] used as IL in polymer synthesis was recovered from the recycling experiments. *p*-Phenylenediamine (99+%), 3,4-oxydianiline (95%) and *m*-phenylenediamine (99%) were purified extensively prior to use. γ-Valerolactone and α-picoline were dried using molecular sieves (4 Å) until the water content was below 50 ppm. The ionic liquids were dried on a vacuum line operating at 0.6–1.0 mbar until the water content was less than 200 ppm. All other chemicals were used as received, without any further purification. The synthesis and characterization of the aramid oligomers, as well as the purification methods for the diamines are described in the ESI.†

Instrumentation

The water content was measured on a Karl Fischer coulometer (Mettler-Toledo DL39). The inherent viscosity of the polyaramids was determined using a certified calibrated Ubbelohde 10–100 $mm^2\ s^{-1}$ (0.1 K) capillary viscometer from ESI† analytics in a Lauda thermostated water bath. The short path evaporator used in the recycling experiments was the glass oven B-585 Kugelrohr (Büchi). The ^1H NMR spectra (300 MHz) were measured on a Bruker Avance 300 MHz spectrometer. The NMR spectra were analyzed using TopSpin 4.0.2 software.

Polymerization procedures

Poly-*m*-phenyleneisophthalamide (PMIA). After extensive drying, the ionic liquid and cosolvent were mixed in appropriate ratios to obtain an OES with the desired IL molar fraction. The OES (40 g) was then added to a dried 3-neck flask and flushed with N_2. *m*-Phenylenediamine (1.0 eq., 19.4 mmol, 2.09 g) was added immediately after purification to the reaction mixture under a gentle N_2 flow. An overhead stirrer (4 cm collapsible two-blade impeller fitted in a Cowie universal stirrer guide) was then placed on the flask under N_2 flow, and the reaction mixture was stirred at a rate of 200 rpm. When the *m*-phenylenediamine was dissolved, the solution was then put on an ice bath and α-picoline (2.1 eq., 40.7 mmol, 3.79 g) was added using a syringe. The stirring rate was increased to 500 rpm and isophthaloyl chloride (1.0 eq., 19.4 mmol, 3.94 g) was added. The viscosity of the reaction mixture rapidly increased, creating a thick white/yellow gel. The reaction was allowed to proceed for 2 more hours. The reaction mixture was transferred to a beaker filled with water and broken up into a powder using an immersion blender. The polymer was filtrated, washed with water, further purified *via* 12 h of Soxhlet extraction with water and finally dried overnight in a vacuum oven at 50 °C.

Copoly(*p*-phenylene/3,4′-diphenylether terephthalamide) (ODA/PPTA). After extensive drying, the ionic liquid and cosolvent were mixed in appropriate ratios to obtain an OES with the desired IL molar fraction. The OES (40 g) was then added to a dried 3-neck flask and flushed with N_2. *p*-Phenylenediamine (0.5 eq., 4.25 mmol, 0.46 g) and 3,4-oxydianiline (0.5 eq., 4.25 mmol, 0.85 g) were added immediately after purification to the reaction mixture under a gentle N_2 flow. An overhead stirrer (4 cm collapsible two-blade impeller fitted in a Cowie universal stirrer guide) was then placed on the flask under N_2 flow, and the reaction mixture was stirred at a rate of 200 rpm. When the diamine monomers were dissolved, the solution was put on an ice bath and α-picoline (2.1 eq., 17.8 mmol, 1.66 g) was added using a syringe. The stirring rate was increased to 500 rpm and terephthaloyl chloride (1.0 eq., 8.50 mmol, 1.73 g) was added under a N_2 flow. The viscosity of the reaction mixture increased over the course of 15–30 minutes, creating a thick yellow gel. The reaction was allowed to proceed for 4 more hours. The reaction mixture was transferred to a beaker filled with water and broken up into a powder using an immersion blender. The polymer was filtrated, washed with water, further purified *via* 12 h of Soxhlet extraction with water and finally dried overnight in a vacuum oven at 50 °C.

Poly-*p*-phenyleneterephthalamide (PPTA). After extensive drying, the ionic liquid and cosolvent were mixed in appropriate ratios to obtain an OES with the desired IL molar fraction. The OES (40 g) was then added to a custom-made cylindrical reaction vessel fitted with an anchor stirrer and flushed with N_2. This type of reaction vessel was used because it was more suitable for stirring and breaking the reaction mixture as it turned into a crumble.[36] *p*-Phenylenediamine (1 eq., 13.5 mmol, 1.46 g) was added immediately after purification to reaction vessel, and the reaction mixture was stirred at 200 rpm. When the diamine monomer was dissolved, the solution was put in an ice bath and α-picoline (2.1 eq., 28.4 mmol, 2.64 g) was added using a syringe. The stirring rate was increased to 500 rpm and terephthaloyl chloride (1.0 eq., 13.5 mmol, 2.74 g) was added. The stirring rate was further increased to 1000 rpm, and stirring continued for 20 more minutes. The reaction mixture was transferred to a beaker filled with water and broken up into a powder using an immersion blender. The polymer powder was thoroughly washed with water, further purified *via* 12 h of Soxhlet extraction with water and finally dried overnight in a vacuum oven at 50 °C.

Determination of the inherent viscosity

Dried polyaramid (0.1 g) was dissolved in 20 mL of concentrated sulfuric acid (96%) to obtain a solution with a concentration of 0.5 g dL^{-1}. An Ubbelohde capillary viscometer, placed in a water bath at 25 °C, was used to measure the flow times of pure sulfuric acid (t_{solvent}) and of the polyaramid/sulfuric acid solution (t_{solution}). From these flow times, the relative viscosity of the solution (η_{rel}), and subsequently the inherent viscosity (η_{inh}) were calculated as an estimate measure for the average molar mass of the polyaramid (eqn (1) and (2)).

$$\eta_{\text{inh}} = \frac{\ln \eta_{\text{rel}}}{c} \tag{1}$$

$$\eta_{\text{rel}} = \frac{t_{\text{solution}}}{t_{\text{solvent}}} \tag{2}$$

where c is the concentration, and t_{solution} and t_{solvent} are the flow times of the solution and solvent, respectively.

Results and discussion

The general reaction scheme for the synthesis of polyaramids is shown in Fig. 1. The polymerization proceeds *via* a polycondensation reaction between aromatic diamines and aromatic diacyl chlorides. The released HCl is captured by an organic base such as α-picoline. Because this is a polycondensation reaction, high molecular weights can only be obtained if the monomers are present in near perfect stoichiometric balance and of very high purity.[37] Therefore, weighing and adding the

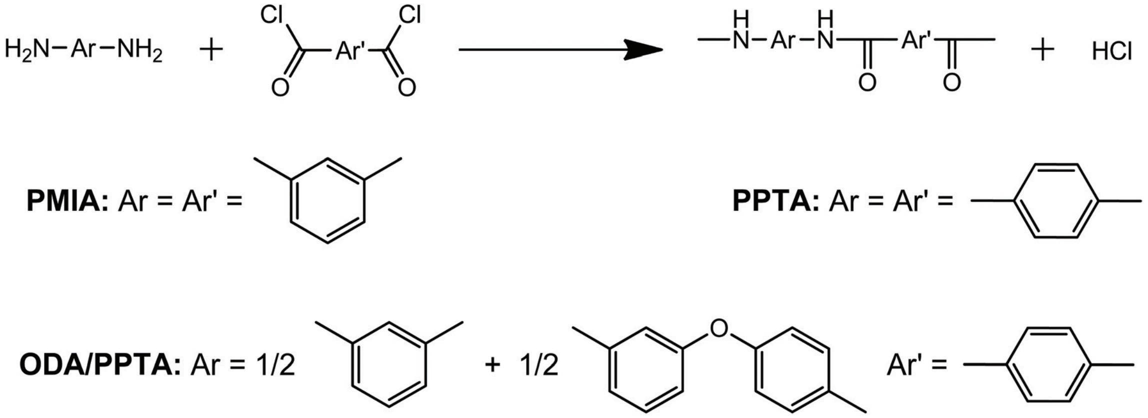


Fig. 1 General reaction scheme for the polycondensation between aromatic diamines and aromatic diacyl chloride to obtain polyaramids. The released HCl is preferably scavenged by adding an organic base such as α-picoline.

monomers must be done with great care. Furthermore, the monomers are chemically very reactive. The diacyl chlorides can react with water present in the reaction mixture and diamines slowly oxidize upon contact with atmospheric oxygen. It is therefore important ensure that the solvent is thoroughly dried, and the diamines are purified extensively directly before use. The purification procedures for the diamines are provided in the ESI.† Specific synthetic procedures for each of the polyaramids are described above. All polymerizations followed these exact procedures unless mentioned otherwise. Procedures for the benchmark syntheses can be found in our previous work.[32]

Benchmark polymerization reactions in NMP

The industrial standards for the inherent viscosities for PMIA, ODA/PPTA and PPTA are $\eta_{\text{inh}} = 2$ dL g^{-1}, $\eta_{\text{inh}} = 2$–3 dL g^{-1} and $\eta_{\text{inh}} = 5$–6 dL g^{-1}, respectively.[4,38] However, these polymerization reactions are very sensitive to several parameters such as stirring efficiency, temperature control, water uptake, monomer purity, weighing errors, *etc*. All these parameters are difficult to control on a small lab-scale reaction setup, meaning that there might be a difference in solvent performance compared to industrial scale setups. Therefore, before using OESs as synthetic solvents, benchmark reactions were performed to more accurately compare the performance of the OESs *versus* NMP under the same reaction conditions. PMIA could reliably be synthesized using our setup, with an average inherent viscosities of $\eta_{\text{inh}} = 2.06 \pm 0.08$ dL g^{-1}, which matches the industrial standard. However, the industrial processes generally add aniline as a chain stopper to have more control over the reaction. The fact that we 'only' reach a benchmark value of about 2 dL g^{-1} without the use of chain stoppers does mean that our lab scale reaction setup underperforms with respect to the specialized industrial setups. The synthesis of ODA/PPTA proved far less reliable than the synthesis of PMIA. A total of 14 polymerizations was performed, out of which the average inherent viscosity was only $\eta_{\text{inh}} = 1.53 \pm 0.33$ dL g^{-1}, with the lowest and highest obtained values being 1.08 dL g^{-1} and 2.45 dL g^{-1} respectively. The reason for this large error margin is probably twofold. Firstly, during this synthesis there was a certain room for human error in weighing and addition of the monomers. This reaction uses three different monomers rather than two, and the smaller amount of monomers used in terms of mass amplifies any weighing inaccuracies. Secondly, over the course of the reaction, the reaction mixture had the tendency to become very viscous, turning into a viscoelastic gel that crept up the shaft of the stirrer (Fig. 2). This phenomenon is known as the Weissenberg effect and it makes efficient stirring impossible.[39] These factors make it difficult to achieve high average molecular weights for ODA/PPTA on our small lab-scale setup. Nevertheless, most of the inherent viscosities

Fig. 2 Weissenberg effect in a polymerization reaction of ODA/PPTA.

were in the range of 1.45–1.55 dL g^{-1}. This is significantly less than the industrial standard, but it is the most appropriate reference to which we can compare the performance of the OESs.

The final polymer PPTA could be synthesized more reliably and matched the industrial standard with an average inherent viscosity of 5.17 ± 0.12 dL g^{-1}. Again, improving the reaction conditions by upscaling and using more specialized equipment can likely increase the inherent viscosities obtained for most of the performed polymerizations. However, larger scale experiments were beyond the scope of this work.

Polyaramid synthesis in [C_8MIm][Cl]/GVL

Next, the syntheses of these polyaramids (PMIA, ODA/PPTA and PPTA) were performed using OESs as solvents. The OESs used in these initial experiments were mixtures of the IL [C_8MIm][Cl] and organic cosolvent GVL in varying mixing ratios (Fig. 3). This combination of compounds was selected because [C_8MIm][Cl] has already shown potential in the synthesis of PPTA,[18,30] and because GVL is well-known for its green properties. Furthermore, our previous work has shown that [C_8MIm][Cl]/GVL OESs have among the highest solubilities for polyaramids. The inherent viscosities of the obtained polymers are plotted *versus* molar fraction of [C_8MIm][Cl] in the OESs (Fig. 4). The inherent viscosities for the industrial standards and the obtained benchmark values are displayed as horizontal lines. For PMIA, only the reaction with the maximum inherent viscosity was repeated in triplicate, yielding a standard deviation of 0.064 dL g^{-1}. For ODA/PPTA, multiple reactions around the maximum were repeated and the variation in the results is displayed. For PPTA, no triplicates were performed because of the poor performance of the OESs in these polymerization reactions.

Pure GVL (x_{IL} = 0.0) turned out to be a mediocre solvent for PMIA synthesis, with the polymer having an inherent viscosity of only η_{inh} = 0.78 dL g^{-1}. After a short period of time, the polymer precipitated from the reaction mixture, preventing the polymerization reaction from proceeding. However, addition of small amounts of IL rapidly increased the inherent viscosities of the polymers. A maximum was reached at x_{IL} = 0.043, achieving an inherent viscosity of η_{inh} = 1.94 ± 0.06 dL g^{-1}, which is on par with the benchmark and the industrial standard. Further increasing the IL content of the OESs resulted in declining inherent viscosities, eventually reaching η_{inh} = 0.35 dL g^{-1} for the pure IL. Even though pure [C_8MIm][Cl] is an excellent solvent for PMIA, it turned out to be a poor medium for synthesis, because ILs have some drawbacks that can substantially impact the polymerization process. Firstly, there is the typical high viscosity of ILs, which causes slow monomer dissolution, poor homogeneity of the reaction mixture and slow reaction kinetics. Secondly, ILs (especially imidazolium

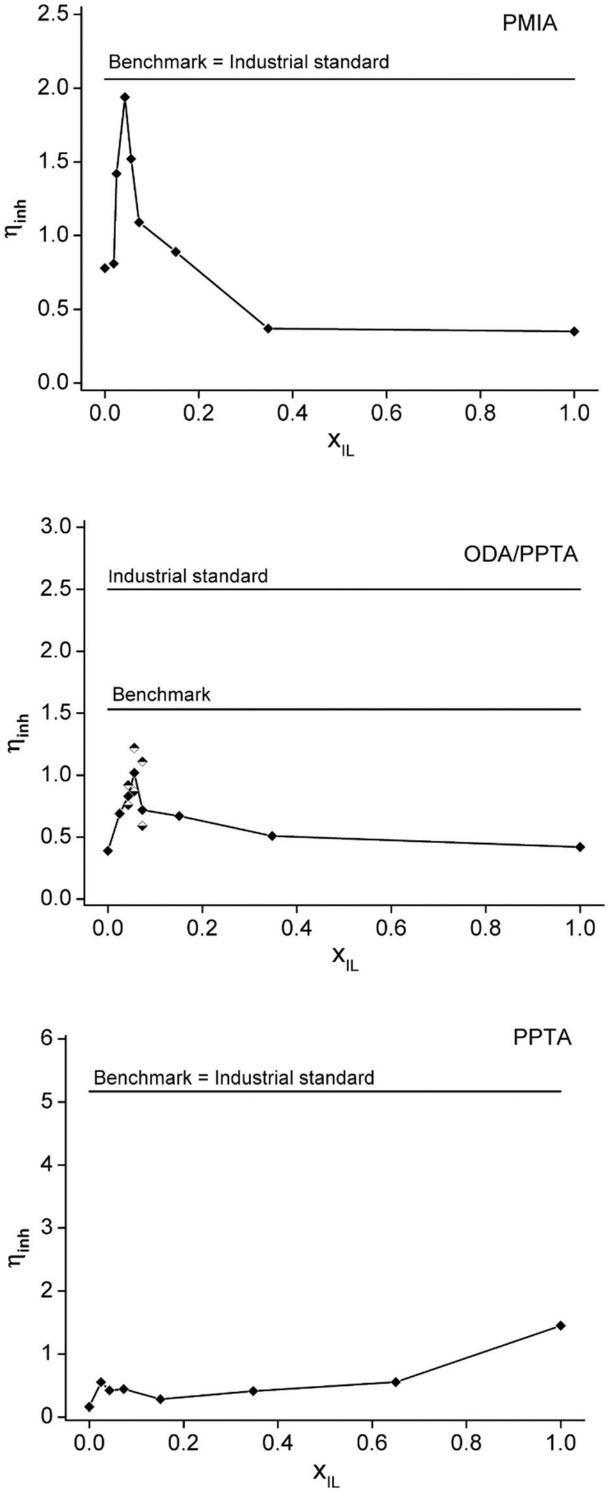
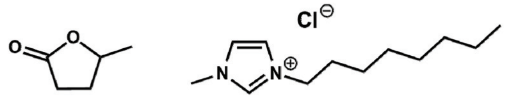


Fig. 4 Inherent viscosities of the polyaramids obtained from polymerizations performed in [C_8MIm][Cl]/GVL as a function of the IL molar fractions of the OES.



GVL **[C_8MIm][Cl]**

Fig. 3 Chemical structures of GVL and [C_8MIm][Cl]. The chemical structures of other ILs used in this work are provided in the ESI.†

chlorides) are very hygroscopic. Even though all compounds were thoroughly dried prior to the polymerization reaction, some contact with the atmosphere is unavoidable using this small lab-scale reaction setup. The solvent can readily absorb moisture during these short periods of contact, which can deactivate the acyl chloride monomers and reduce the solubility of the polymer. This explains why the increase in IL content in the synthesis solvents led to a decrease in the inherent viscosities obtained. However, some IL is still needed because PMIA is not soluble in pure GVL. The chloride anions of the ionic liquid are required to interact with the amide NH groups so as to prevent intermolecular hydrogen bonding between the polymer chains. It seems that a delicate balance must be maintained with respect to the amount of IL that has to be added to the OES. A small amount of IL is required to keep the polymer in solution, while at the same time not adding too much so as to minimize the above-mentioned drawbacks, resulting in an optimal IL molar fraction of $x_{\mathrm{IL}} = 0.043$.

For ODA/PPTA the plot has a similar shape. Again we see an initial increase of the obtained inherent viscosities with increased IL content, reaching a maximum at very low x_{IL}, followed by a sharp decline. The reactions around the maximum were performed in triplicate, owing to the variability in the results from the benchmark reaction. The results are again fairly scattered, with the maximal inherent viscosity being $\eta_{\mathrm{inh}} = 1.22$ dL g^{-1}. However, most reactions yielded inherent viscosities much below the benchmark value of $\eta_{\mathrm{inh}} = 1.53$ dL g^{-1}. Several reasons can be given for these poorer results. Firstly, the diacyl chloride monomer terephthaloyl chloride (TDC) is poorly soluble in GVL. In the initial stages of the reaction, only the small amount of TDC that is dissolved can partake in the polymerization. The heat released from this exothermic reaction ultimately causes the rest of the TDC to dissolve, but this means the reaction mostly occurs well above the optimal temperature range. This is important because at higher temperatures some terminating side reactions can occur.[40] Secondly, as was the case for PMIA, there is the delicate balance between the pros and cons of adding ILs to the OES. ODA/PPTA is simply not soluble enough for synthesis in the lower x_{IL} ranges. Our previous work has shown that ODA/PPTA is highly soluble in the x_{IL} range of 0.2–0.6,[32] but in this range all the above-mentioned drawbacks of ILs are highly pertinent. Using more specialized equipment that allows for more efficient heat dissipation and the addition of TDC in a molten state can alleviate the first issue of poor solubility of TDC. However, solving the issue of poor ODA/PPTA solubility will probably require a different IL/co-solvent combination. The co-solvent should have sufficient solubility of TDC at low temperatures, and the overall OES needs to have an improved solubility of ODA/PPTA compared to GVL/[C_8MIm][Cl].

The graph for PPTA did not display a maximum at low IL molar fractions. The reaction mixture formed a precipitate nearly instantly in all solvents except in the pure IL. PPTA is notoriously difficult to dissolve and is only known to form thermodynamically stable solutions in highly acidic or basic solvents, which are unsuitable for synthesis.[41–43] Even the growing PPTA oligomers are hardly soluble in ILs.[14] However, this low solubility is not necessarily a big problem for this reaction, as the current industrial solvent system NMP/$CaCl_2$ cannot dissolve PPTA either. The synthesis of PPTA proceeds differently compared to that of PMIA or ODA/PPTA. The solvent does not function by forming stable PPTA solution, but rather by delaying precipitation as long as possible to prolong the potential reaction time, leading to higher molecular weight polymers. In this respect, the high viscosity of ILs is actually a benefit, slowing down precipitation and forming a gel-state in which the polymer can still react if stirred properly.[18,30] Because of this polymerization mechanism, the reaction has to proceed very rapidly, which is not possible due to the poor solubility of TDC in GVL. This poor solubility caused an even bigger problem at lower IL molar fractions. The unreacted TDC flakes would get coated in insoluble PPTA oligomers, effectively terminating the reaction. Overall, it is evident that GVL is not a suitable co-solvent for the synthesis of PPTA. Again, an alternative co-solvent should have sufficient solubility of TDC at low temperatures. Furthermore, a good distribution of TDC needs to be achieved by rapid stirring and perhaps adding the monomer in a molten state. This ought to prevent the coating of unreacted TDC flakes, and allow for a rapid polymerization reaction in a gel-state.

In situ ionic liquid formation

The highest inherent viscosity for PMIA was obtained using an OES with an IL molar fraction of $x_{\mathrm{IL}} = 0.043$. This is actually a very low IL content, one at which PMIA should not be soluble in the concentration we used for the synthesis.[32] Furthermore, despite the fact that pure GVL is completely unable to dissolve any PMIA, it was still able to keep the growing polymer in solution for a while. This is because [C_8MIm][Cl] is not the only IL present in the reaction mixture. During the polycondensation reaction between the amine and acyl chloride groups, HCl is released. This HCl is scavenged by the base α-picoline, creating a protic IL, 2-methylpyridin-1-ium chloride ([2-Me-HPyr][Cl]), *in situ* as is displayed in Fig. 5. This protic IL is always present in a one-to-one ratio with the amide bonds of the polymers and should definitely have an impact on the solubility. Liu *et al.* made a similar discovery in their work on the synthesis of the polyaramid poly–(benzimidazole–terephthalamide).[44,45] They found that the addition of imidazole or sodium acetate to scavenge *in situ* the released HCl greatly increased the solubility of their polyaramids.

To study the impact of the *in situ* IL formation, three *meta*-oriented oligomers were synthesized to emulate a growing PMIA polymer chain. The oligomers used were: (1) a diacyl

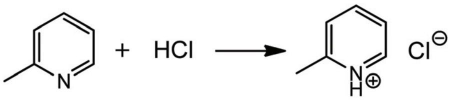


Fig. 5 *In situ* formation of the protic ionic liquid [2-Me-HPyr][Cl] by scavenging HCl by α-picoline.

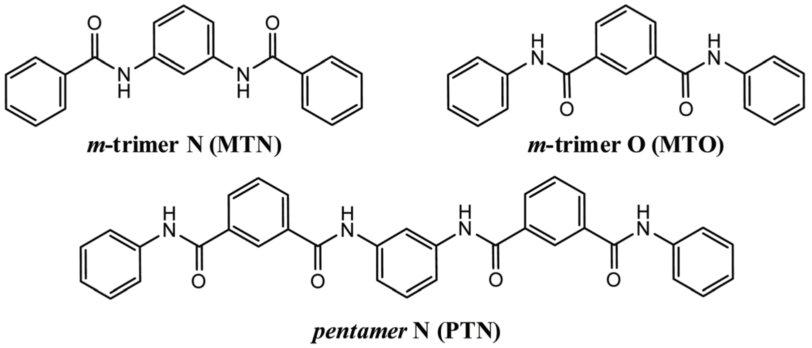


Fig. 6 Chemical structures of polyaramid oligomers.

chloride-centred trimer (MTO), (2) a diamine-centred trimer (MTN), and (3) a diamine-centred pentamer (PTN) (Fig. 6). The solubility of 10 wt% of these oligomers was tested in pure GVL, the OES [C$_8$MIm][Cl]/GVL with IL molar fraction x_{IL} = 0.043 and in the same OES also containing [2-Me-HPyr][Cl] in a molar fraction of $x_{[\text{2-Me-HPyr}][\text{Cl}]}$ = 0.092, similar to the reaction mixture after full conversion of the monomers. The results of these solubility tests are shown in Fig. 7. Pure GVL was unable to dissolve any of the oligomers. The OES was able to dissolve MTO, but MTN formed a cloudy solution, and the pentamer PTN was found to be insoluble. These findings already indicate that neither GVL nor the OES with x_{IL} = 0.043 can keep a growing polymer chain in solution. However when [2-Me-HPyr][Cl] was added, all the oligomers were completely soluble, indicating that this *in situ* formed IL provides the majority of the dissolving capacity of the solvent. This explains why only a small amount of [C$_8$MIm][Cl] is required for a successful polymerization reaction. This initial small amount of [C$_8$MIm][Cl] is enough to keep some dimers and trimers in solution during the early stages of the reaction. This allows for the *in situ* formation of [2-Me-HPyr][Cl], which gradually increases the dissolving capacity of the reaction mixture, keeping the growing polymer chain in solution.

Further evidence of the essential role of the *in situ* formed IL was found by performing polymerization reactions by using different organic bases or no added base at all. The bases used were 4-dimethylaminopyridine (DMAP), 2,6-dichloro-4-nitropyridine and 1-methylimidazole. DMAP was used as it is a much more basic pyridine derivative than α-picoline, and it is often used as a catalyst for amidation reactions.[46] 2,6-Dichloro-4-nitropyridine on the other hand is a much less basic pyridine derivative because of the electron-withdrawing nitro and chloro functionalities. No measured value for its pK_a could be found in the literature, but we can assume that it is less than 1.6, as that is the pK_a value of 4-nitropyridine which does not have the chloro substituents. Finally, triethylamine and 1-methylimidazole were used as they are both more basic than α-picoline, but will form an ammonium chloride and imidazolium chloride *in situ*, respectively, rather than a pyridinium chloride. Results of the polymerizations are summarized in Table 1.

When no base was added, early precipitation of the reaction mixture occurred, terminating the polymerization prematurely. No base means no *in situ* IL formation, and a reduced solubility. Furthermore, if no base is present the HCl can protonate

Table 1 pK_a values and inherent viscosities of PMIA synthesized in [C$_8$MIm][Cl]/GVL x_{IL} = 0.043 with different bases

Base	pK_a	η_{inh}
α-Picoline	6.0	1.94
1-Methylimidazole	7.0	0.80
4-Dimethylaminopyridine	9.7	0.79
Triethylamine	10.8	0.66
None	—	0.14
2,6-Dichloro-4-nitropyridine	<1.6	0.12

Fig. 7 Solubility tests of polyaramid oligomers. Left: solubility in only GVL, centre: solubility in [C$_8$MIm][Cl]/GVL OES with x_{IL} = 0.043, right: OES also containing [2-Me-HPyr][Cl]. Solubility of the oligomers increases from left to right.

the diamine monomers, which can slow down or perhaps even terminate the polymerization reaction. Precipitation of the reaction mixture was again observed when 2,6-dichloro-4-nitropyridine was added as a base. This pyridine derivative is not only a weaker base than α-picoline, but it is also a weaker base than the diamine monomer, which has a pK_a of 5.1. This means that the monomer is protonated preferentially over the base, giving a situation which is similar to using no base at all. 4-Dimethylaminopyridine is a stronger base than α-picoline, but it was not completely soluble in the reaction mixture, resulting in a lower inherent viscosity. Triethylamine and 1-methylimidazole are also stronger bases than α-picoline, but also these bases yielded poorer results. Evidently, the pK_a of the base is not directly correlated to the inherent viscosity of the polyaramids obtained, as long as the basicity is high enough to effectively scavenge all the HCl. The inherent viscosities obtained for the different bases follow the trend: α-picoline > 1-methylimidazole > triethylamine. This trend is in accordance with that of the solubility of polyaramids in pyridinium chlorides > imidazolium chlorides > ammonium chlorides.

Influence of altering the ILs and the polymer concentration for PMIA synthesis

Considering the fact that the *in situ* formed IL [2-Me-HPyr][Cl] seems to be chief driving force for dissolution of the polymers, OESs were made from ILs other than [C_8MIm][Cl] to investigate how this would influence the obtained inherent viscosities: [C_4MIm][Cl] which has a shorter side chain compared to [C_8MIm][Cl], rendering it cheaper and less energy intensive to produce; [C_6Pyr][Cl] which has a pyridinium cation instead of an imidazolium; and finally the *in situ* formed IL [2-Me-HPyr][Cl] itself was tested, as using this as an IL would greatly simplify any post-reaction recycling steps. Several PMIA polymerization reactions were performed in the lower x_{IL} range around the optimum for [C_8MIm][Cl]/GVL, the results of these reactions are displayed in Fig. 8.

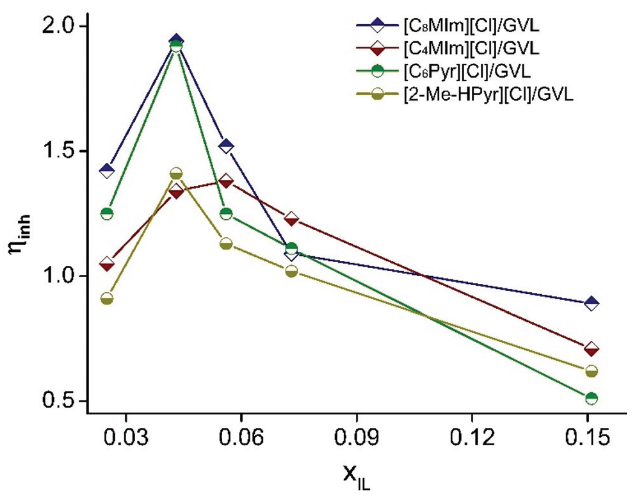


Fig. 8 PMIA polymerization reactions in several IL/GVL OESs.

The other ILs all yielded the same shape of curve as [C_8MIm][Cl], showing a maximum at low x_{IL}. The OES [C_6Pyr][Cl]/GVL achieved a maximum inherent viscosity of 1.92 dL g^{-1}, reaching the benchmark value and rivaling [C_8MIm][Cl]/GVL. The OESs made from [C_4MIm][Cl] and [2-Me-HPyr][Cl] achieved lower maximal inherent viscosities, at 1.38 dL g^{-1} and 1.41 dL g^{-1}, respectively. Interestingly, a longer alkyl chain length in the cation led to higher inherent viscosities. A similar trend was observed in our earlier work on the synthesis of PPTA in IL/NMP mixtures.[30] Cations with a longer alkyl chain length can more effectively shield different polymer chains *via* steric hindrance. Furthermore, longer alkyl chains may also reduce the hygroscopicity and the viscosity of the solvent. However, although the ILs with longer alkyl chains did give better results, these other ILs should not be discarded. As mentioned above, upscaling and using more specialized equipment can lead an improvement of the results. Thus, although the OES [2-Me-HPyr][Cl]/GVL underperforms compared to NMP, it might still be worthwhile to optimize the reaction for this solvent at an industrial scale, as this would greatly simplify the purification and recycling of the solvent.

In all our syntheses of PMIA, the monomers were added in an amount such that the final polymer concentration would be 10 wt%. However, current synthetic and spinning procedures use a polymer concentration of 20 wt%, because faster production can be achieved at a lower cost in this way. We therefore performed several polymerization reactions in the [C_8MIm][Cl]/GVL OES around the optimal IL molar fraction, using a polymer concentration of 20 wt%. We expected that this would lead to decreased inherent viscosities, as the solubility limit of the OES might be surpassed. However, we actually observed a gradual increase in inherent viscosity for almost all IL molar fractions, and the peak was much broader making the IL/cosolvent balance less delicate compared to 10 wt% (Fig. 9). The fact that we did not observe any polymer precipitation is a result of the *in situ* IL formation mentioned above.

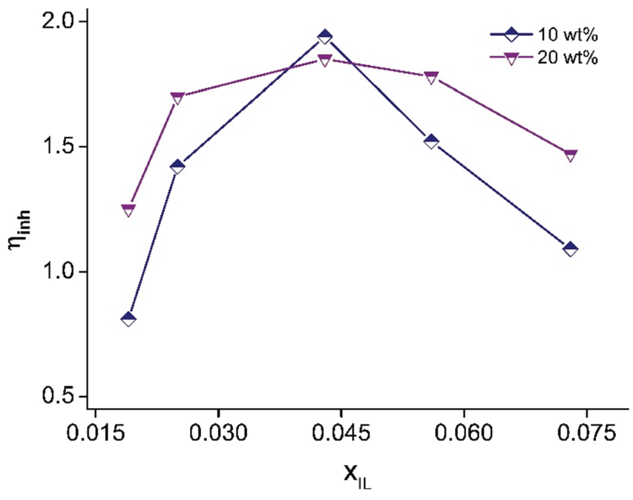


Fig. 9 Inherent viscosities of PMIA polymerization reaction performed at 20 wt% *vs.* 10 wt% polymer concentration.

As the polymer concentration was increased, the amount of α-picoline was also increased by an equal amount. This means more IL was generated *in situ* and the dissolution capacity of the solvent increased. Moreover, increasing the polymer concentration has the advantage that some of the issues related to small-scale polycondensation reactions are mitigated. As the monomers were added in larger amounts, the magnitude of the effect of weighing/addition inaccuracies is decreased. Furthermore, the amount of water absorbed from the atmosphere remains the same, while the amount of acyl chloride has been doubled. As a result there is less water present relative to the amount of acyl chloride. This means that the negative impact of monomer impurity, as a result of the side reaction between water and the acyl chloride, on the inherent viscosity is reduced. So it is not only possible but beneficial to perform the synthesis at the same concentration as in the current industrial procedures. Furthermore, this experiment may serve as a demonstration that upscaling can indeed lead to better results for polycondensation reactions.

Direct spinning and solvent regeneration

In our previous work we have shown that it is possible to create PMIA and ODA/PPTA fibers from GVL-based OESs through wet spinning.[32] From an economical point of view, it would be beneficial to be able to spin the polymer directly from the synthetic solution, and to be able to purify and recycle the solvent after spinning. Therefore, polymerizations of PMIA were performed using an $[C_8MIm][Cl]$/GVL OESs with a molar fraction of $x_{IL} = 0.043$ and a polymer concentration of 10 wt% and 20 wt%. After the polymerization reaction was finished, the reaction mixtures were allowed to settle for about 30 minutes to allow air bubbles to escape. The reaction mixtures were then transferred to a syringe, from which a fiber could be spun using a syringe pump and a 3D-printed coagulation bath and winding apparatus (Fig. 10). The spinning occurred at room temperature and the coagulation bath contained distilled water. Both reaction mixtures were readily spinnable, giving uniform white fibers that could easily be pulled from the coagulation bath with the winding setup. Characterization of the mechanical properties of the fibers was beyond the scope of this work, but this experiment gives the proof-of-principle that this environmentally friendly OES can be used for both synthesis and the direct spinning from the reaction mixture. This is a great improvement from an environmental and economical viewpoint compared to the current industrial syntheses using harmful solvents such as NMP or DMA, or the interphase type polymerizations which require precipitation and redissolving in NMP at a later stage.

ODA/PPTA could not be spun directly after synthesis. The reaction mixture was not a liquid, but rather a viscoelastic gel that was very difficult to handle. When trying to transfer this gel to a syringe it would start to break up as it absorbed moisture from the atmosphere, and the polymer would start to precipitate. Even if upscaling and optimizing would result in a higher inherent viscosity for ODA/PPTA, it is unlikely that this reaction mixture could be used for direct spinning.

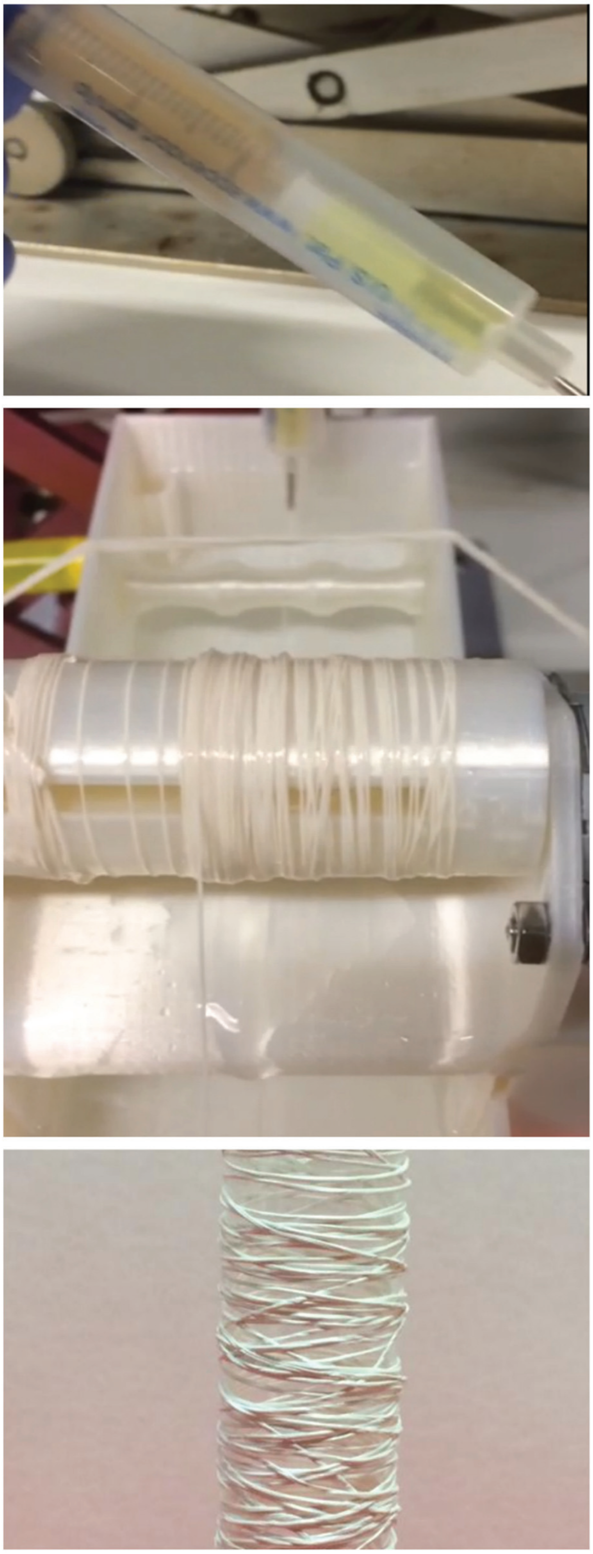


Fig. 10 Direct spinning of PMIA from the reaction mixture. Details on the spinning setup and spinning parameters can be found in the ESI S6.†

After spinning, the content of the coagulation bath was transferred to a round-bottom flask. Water and GVL were evaporated together using a rotary evaporator operating at a temperature of 60 °C and a pressure of 65 mbar. It was necessary to remove water and GVL together because of the presence of ILs. These can increase the boiling point of water closer to that of GVL and making selective removal more challenging.[47] Once removed from the ILs, the GVL and water can easily be separated *via* distillation.[32,48] Finally, in order to regenerate the expensive [C_8MIm][Cl], it needs to be removed from the mixture with [2-Me-HPyr][Cl]. A useful difference between protic ILs and other ILs is the fact that protic ILs can be removed with short path distillation in a Kugelrohr apparatus.[49] The acid–base reaction that forms these protic ILs is reversible, meaning that the protic cation (a conjugate acid) and the anion (a conjugate base) can revert back to the original base (α-picoline) and acid (HCl). These are neutral compounds which can be distilled off. Once condensed, the base and acid react again to form [2-Me-HPyr][Cl] (Fig. 11).

[2-Me-HPyr][Cl] was thus removed using a short path evaporator (Kugelrohr apparatus), operating at a temperature of 100 °C and a pressure of 1 mbar. The progress of the distillation process was monitored by periodically sampling and recording ^{1}H NMR spectra (Fig. 12). After 12 hours, all traces of [2-Me-HPyr][Cl] were removed and [C_8MIm][Cl] was recovered with a yield of 89%. If wanted, the [2-Me-HPyr][Cl] can be converted back into α-picoline by the addition of a stronger base. However, an upscaled version of this short path distillation step will consume a large amount of energy. An ideal situation would be if the polymerization process in [2-Me-HPyr][Cl]/GVL were to be optimized on an industrial scale. This would eliminate the need to separate [2-Me-HPyr][Cl] from another IL. After evaporating water and GVL, the *in situ* formed [2-Me-HPyr][Cl] can be directly used to prepare a new OES.

Fig. 11 Separation of [C_8MIm][Cl] and [2-Me-HPyr][Cl] *via* short path distillation in a Kugelrohr apparatus.

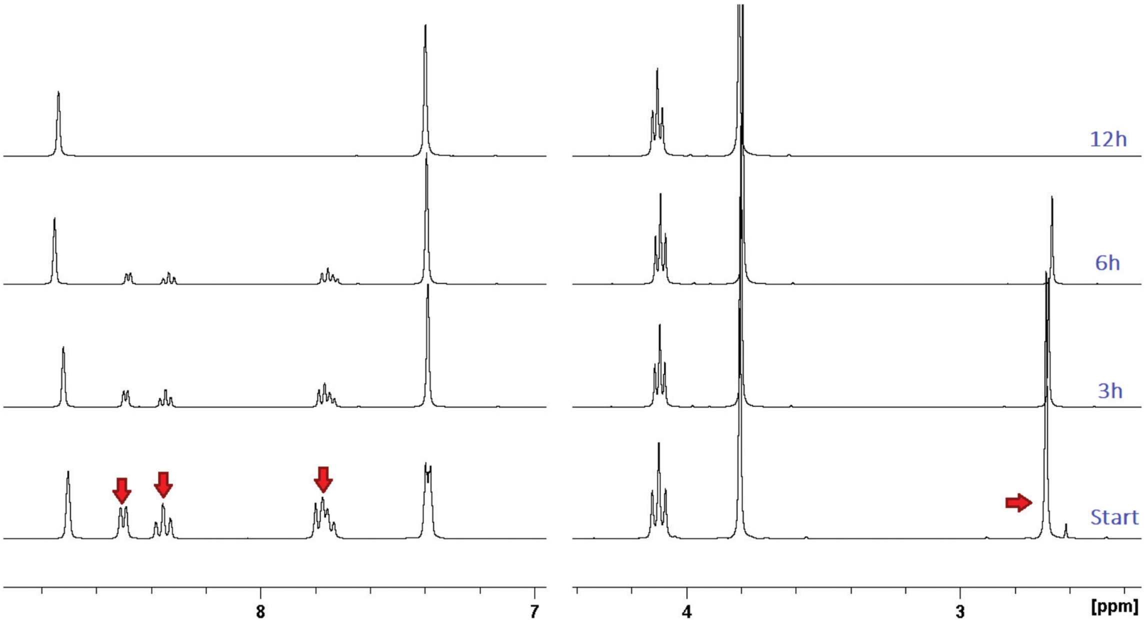


Fig. 12 Separation of [C_8MIm][Cl] and [2-Me-HPyr][Cl] monitored by ^{1}H NMR. After 12h, all the [2-Me-HPyr][Cl] was found to be removed.

Conclusion

The three most commonly produced polyaramids (PMIA, ODA/PPTA and PPTA) were synthesized using GVL-based organic electrolyte solutions (OESs) as benign alternative solvents. The results from these polymerizations were compared to those of benchmark reactions which were performed using the established solvent NMP. The OESs were not suitable solvents for PPTA synthesis, as oligomers instantly precipitated owing to the low solubility of PPTA in these solvent systems. ODA/PPTA could be synthesized in OESs, but the results were mediocre compared to those obtained in NMP. The poor results can be attributed to the low solubility of the diacyl chloride monomer and of ODA/PPTA itself. However, the performance of the OESs was similar to that of NMP in the synthesis of the *m*-aramid PMIA if: (1) the molar fraction of IL in the OES was small, but not zero (x_{IL} = 0.043), (2) α-picoline was added to scavenge HCl and (3) the IL used was either [C_8MIm][Cl] or [C_6Pyr][Cl]. The polymerization reaction was found to be very sensitive to the amount of IL added to the OES. The IL has properties that can be both beneficial (increased solubility) and disadvantageous (high viscosity and hygroscopicity) for the polymerization reaction and a very delicate balance exists between these factors. This balance became less delicate when the polymer concentration in the reaction was increased from 10 wt% to 20 wt%, resulting in a broader tolerance for IL content in the OES. The organic base added to the reaction mixture to scavenge HCl is also an important factor in the polymerization reactions. This base forms a chloride IL *in situ* which partakes in the dissolution process of the polymer. α-Picoline thus outperformed other bases, as this forms a pyridinium chloride IL ([2-Me-HPyr][Cl]), which is known to be a strong solvent for polyaramids. The reaction mixtures could directly be used for wet spinning fibers without the need for isolating and redissolving the PMIA polymer. Furthermore, it was possible to separate and recycle the components of the OES from the coagulation bath, making these solvent systems promising candidates to replace NMP in PMIA synthesis and processing.

Conflicts of interest

There are no conflicts of interest to declare.

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