RAFT-Polymerization of N-Vinyl Pyrrolidone and Methyl Methacrylate for Synthesis of Functional Co-Blockpolymer Binders for Solid Electrolyte Batteries.

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Abstract: This report is a summary of laboratory work done in a research group from the department of polymer chemistry of Uppsala University. The project work was to synthesize functional polymers through [RAFT]-polymerization, based off of N-Vinyl Pyrrolidone [NVP] and continue the "living" polymerization with Methyl Methacrylate [MMA] to create an ion conducting binder to serve in an solid electrolyte battery. With [AIBN] being the radical initiator, that was used in an oxygen free matrix and system, to polymerize the monomer. A reaction of [40:1:0.2] molar equivalents of [NVP]:[RAFT-reagent]:AIBN was the mixture that seemed to be the one combination that worked, thus being the product that the rest of the project was expanded upon. 1g of [NVP] and 50mg of RAFT was added together. After three freeze thaw cycles the 7.8mg of AIBN was added. After RAFT-polymerization aminolysis was performed. The polymerized product, with about 6.5 repeating units, had 0.295g of tri-phenyl phosphine added to it. After three freeze thaw cycles argon and 0.27mL of ethanol-amine, the base, was pipetted into the glass, and finally "Michael Click Addition" to make the desired product. A volume of 0.3137mL of the Michael Click reagent was pipetted into the aminolysis product along with saturated HNaCO$_3$ water solution. However, due to the monomer’s diverse functionality, sensitivity to impurities and instability, also because of synthesized by products, many problems occurred as the synthesis progressed in time. The desired product was not synthesized and further studies has to be made.

Introduction

Batteries are today extremely common. In our machines, cars and in general small everyday apparatuses. Most of these battery cells contain some sort of ion conducting medium or mass. This medium is most commonly made out of a liquid, e.g battery acid H$_2$SO$_4$. When batteries grow old these types of chemicals can be difficult to get rid of, or just leak straight into the environment, which could cause long term damage on our biosphere. One way of erasing this issue would be to exchange the ion conducting medium, the electrolyte, from a liquid to something which could be considered a solid to a solid electrolyte battery. [5]

The ambition behind this project was to test one specific polymeric compound based off of two different monomers, which would be the electrolyte binder later mixed with a lithium salt. One monomer possessing the ion carrying properties and one monomer which would give it more mechanical prop-
erties in terms of rigidity and solidity. If the ambition is executable it could also be possible to give the battery consisting of a solid electrolyte any imaginable form. One example of this would be to remove a vehicle battery and then turn the entire carriage body into a solid electrolyte battery instead.

Figure 1: Structure of used RAFT reagent

RAFT (Reversible addition-fragmentation chain-transfer) polymerization is a technique used for polymerizing e.g vinyl compounds with good control of the chain lengths during the synthesis. It is referred to as a "living" polymerization due to its' inability to terminate mid-synthesis. It is also commonly used for homo-polymer synthesis that perhaps might be the only way to polymerize a certain chemical, such as [NVP], due to its' other functional groups.[6] [3] The RAFT chemical, in this particular case S-Cyanomethyl-N-methyl-N-(pyridin-4-yl)dithiocarbamate (C_{10}H_{10}N_{2}S_{2}), see Figure 1.

The double bond to the sulphur atom will break as the first radical monomer attacks and form a radical intermediate which makes the RAFT chemical very inclined to react with the monomer, then the it forms a new double bond on the second sulphur atom plus a monomer radical. As a new radically charged molecule springs to life it will react with the RAFT chemical once again and the sulphur double bond will switch back. Like a pendulum this continues on and on until the reaction is terminated. [6] See Figure 5 in Appendix.

Because of this the average chain lengths in the mixture will become very similar, giving a low PDI (Poly-Dispersity Index). A low PDI value will be important as the properties of each polymer might differentiate in terms of ion conducting properties or mechanical properties. If the chains have a very diverse length it will be difficult to determine if the chain length is a factor in the conductive capability, or strength, the polymer would have. Also, if a low PDI is achievable it makes it easier to change if another specified length is desired. This method is applied to chemicals such as the N-Vinyl Pyrrolidone [NVP] and the Methyl Methacrylate [MMA] in order to create a block polymer, A-B block based, with functional ligands to carry ions through the system, acting as a functional binder for the battery cell. This was accomplished by using controlled radical polymerization through RAFT polymerization with [NVP] and [AIBN](Azobisisobutyronitrile) as the radical initiating chemical, making that into pNVP (poly-NVP), further commencing aminolysis on the pNVP with Ethanolamine, and then using a dihalogenated compound to "Click" (1:1 ratio between reagents with no by-products) them together with a reaction step called "Michael Click Addition", or in this case "Thiol Michael Click Addition". It is insensitive to oxygen and air which makes water a good solvent in this step as the monomer makes the whole polymer soluble in water. [7] The reagent, see Figure 2, is 4-bromo-2-(2-(buta-1,3-dien-2- yloxy)ethoxy)-4-methylpent-1-ene dihydrate
(C\textsubscript{10}H\textsubscript{15}O\textsubscript{4}Br). Lastly, pMMA is to be synthesized upon the halogenated edge of the MC-reagent of the chain to create the B-block in the A-B structure through ATRP (Atom Transfer Radical-Polymerization).

![Figure 2: Structure of used Michel Click reagent](image)

The final product shown in the figure, see Figure 3, displays the structure of the compound which would be the end goal of the entire synthesis and project.

![Figure 3: The wanted product showing the A- and B-block polymeric structure](image)

**Methods**

Many of the terms used in this report, common terminology associated with polymer chemistry, need an introduction as well. DP, or "Degree of Polymerization", is a term that describes the amount of repeating units of monomer within the propagated chain. [2]

\[
\text{DP} = \frac{M_n}{M_0}
\]

\(M_n\) is the number average molecular weight and \(M_0\) is the molecular weight of the given polymer.

**Nuclear Magnetic Resonance (NMR)**

This technique is very established in laboratories which handle organic molecules of some sort. The machine uses a very strong magnetic field to detect atoms such as carbon or hydrogen which makes it possible to identify the injected sample. When the magnetic field turns on the atoms, e.g hydrogen, will all be pulled in the same direction and then released again to point in the direction it had prior to the field actuation point that time. "Like tiny compass needles" [4] they go from pointing south to then all of them pointing north. For hydrogen there are only two energy states, a high one and a low one; it can either align in the magnetic field (lower) or against it (higher). Depending on how magnetized the proton would be is determined by its’ surrounding atoms and how it bonds with them. The machine calculates the level differences of nuclei and from that a proton NMR spectra can be drawn. [4] The Y-axis conveys the intensity of said proton shifts and the X-axis shows the ppm (parts per million). Peaks below 4ppm can be considered to be protons which are relatively saturated and above 4ppm the protons can be considered to be unsaturated. [4]
Experimental

The aminolysis was preformed to preserve the functionality of the sulphur as a thiol in order to make the reaction with the Michael-Click reagent. The sulphur from the thiol and the double bond of the MC-reagent would then react instantly with no by-products into a water soluble compound.

All reactions were followed with proton NMR samples in order to characterize and make sure that the right characteristics were present at all times to make the correct product. The solvent used for all samples was CDCl$_3$. Important to note is that when the baseline fluctuates a lot around all the "unsaturated" peaks around and below 4 ppm it is a strong indicator of having polymeric character in the analysed mixture.

Recrystallization of [AIBN] (Azobisisobutyronitrile)

To start off the project a new batch of fresh and recrystallized [AIBN] was required in order to reduce the risk of having impurities corrupting the polymerization. A saturated methanol solution of [AIBN](raw) and was stirred with a magnet stirrer in an E-flask for about 20 minutes after the solution could not dissolve any more of the [AIBN]. The solution was poured through a filter to remove the excess raw, non-recrystallized [AIBN]. A small vial filled with the recrystallized product stood in the fridge to slowly create new crystals, and the crystals were then filtered off again, put in a vial and placed inside a vacuum oven to get rid of all the methanol solvent.

Synthesis of pNVP

Step 1: The initial monomer (NVP), see Figure 4, was first distilled from a large round flat bottom flask (250mL), to get rid of the NaOH inhibitor from the reagent, two times, with hydroquinone(C$_6$H$_6$O$_2$) added to stabilize the monomer as it easily creating dimers at higher temperatures, to ensure that it was clean. Purity was investigated with NMR. Due to the instability of the purified reagent it was put in a freezer during times of no usage and defrosted every time before usage. Also the RAFT reagent and [AIBN] was kept in either a freezer and/or a fridge to reduce decay or degradation.

![Figure 4: Structure of N-Vinyl-Pyrrolidone[NVP] into [pNVP]](image)

Step 2: First off was a concept reaction of a polymer with low molecular weight. The goal was to have an average $M_W$ $10 000$ g mol$^{-1}$ (or a DP (degree of polymerization) of about 100 repeating units. To achieve this the molar equivalents were calculated. See Table 1. Another synthesis with different molar equivalents was synthesized as well. See Table 2. The reaction with a higher molar equivalence of (NVP) stood over night to let the polymerization go to about 60-70% in order to achieve a $M_W$ between $60 000$ and $70 000$ g mol$^{-1}$.

A magnet stirrer and RAFT-agent was added to a nitrogen flask. In order to be able
to calculate conversion with NMR two drops of 1-propanol as an internal standard to determine the percentage of conversion. No solvent was used as the reaction was made as a bulk reaction. Freeze thaw cycles were carried out to remove the oxygen from the system’s matrix, which otherwise would terminate the reaction from the start. Argon was injected to serve as a coating when the stopper was pulled off, to protect the mixture from air, as the AIBN initiator was added. The argon and the air that might have run inside the nitrogen flask was removed with vacuum and new argon was injected to preserve the inert properties.

Step 3: The nitrogen flask containing the NVP-mixture was set in an oil bath with a set temperature of 60°C. The rate of conversion could be determined through taking proton NMR samples with a syringe through the rubber stopper seal without introducing air to the system.

Step 4: To terminate the reaction DCM was added to dissolve and quench the reaction. Further the synthesized product was precipitated into an e-flask of diethyl ether. The precipitate had a very bright white colour and was filtrated through a Büchner funnel with a very fine filter paper. The product was set to dry in a vacuum oven for at least 10 hours. (Side note: The pNVP with 40 molar equivalents remained in the nitrogen flask for further synthesis to not lose any product as the amount of reagents to begin with was initially very small).

Aminolysis of pNVP

After the polymer product (pNVP) had been washed and separated, and the average $M_W$ of the polymer as well as number of repeating units (DP) was calculated, the (pNVP) was added to a new nitrogen flask (though, the exception for the reaction of the mixture which was done in the smaller quantity (See Table 1 was the only one that was made due to lack of time) From the estimated average DP and $M_W$ a new table of molar equivalents was created in order to prepare the aminolysis. See Table 4. The base used in the aminolysis and refereed to in Table 4 was Ethanol amine, and the phosphine was triphenol phosphine, used as a reducing agent to minimize the chance of creating any S-S bonds in the mixture as we want to maintain the functionality of the sulphur as a thiol.

Step 1: First the phosphine was added to the mixture and dissolved. Freeze thaw cycles were preformed to remove the air from the system. Argon was injected and the rubber septa was removed carefully and the base pipetted down into the mixture. The system was put on stirring in room temperature for two hours.

Step 2: After stirring for two hours the product was precipitated into diethyl ether. The powdered product was then filtrated through a Büchner funnel with a filter to separate the finished product from the unreacted chemicals still left inside the nitrogen flask. The clean product was put in a glass flask for storage. The product from [pNVP 40], see Table 1, was weighed to 0.214 g which corresponds to 0.001 124 5 mol of the MC-reagent.

Michael Click (MC) addition of pNVP

The ratio between the reacting compounds in the MC-reaction was 1 to 1, thus the same molar equivalents were used. The product
from the aminolysis was added to a glass flask, some water and base (NAHCO₃) sat. was added to activate the thiol group and dissolve the polymer. Lastly the MC-reagent was pipetted into the mixture. It was set to stir for one hour in room temperature. The oily product was dissolved in methanol and rolled in three times with a rotovapour-apparatus. First round bottom flask rolled away the H₂O, and then the two following to remove the methanol left inside the mixture. It was approximated that the density of the MC-reagent was 1.0.

Synthesis of pMMA
The procedure for synthesis of (pMMA) was approximately the same as for the (pNVP). A table for the molar equivalents was created to calculate the correct amounts. See Table 6.

Results

Review of Distillation of NVP
The first step of the synthesis was the distillation of [NVP]. The boiling point of [NVP] lies between 90–92 °C, and it was found that the optimal conditions for distillation were 92 – 95 °C and 8 – 10mbar. As the distillation went on it changed colour. The round bottom flask, with a flat bottom to increase the surface area to prevent shock boiling, was initially filled to about 1/3 of the flask. The non-matching boiling points could be because of the stabilizing agent in the flask of [NVP] from Sigma Aldrich, which is NaOH. Also, the possibility to create dimers is very high, which further influences the fluctuation in the systems boiling point.

The [NVP] with the inhibitor NaOH had a very yellow colour, but as the chemical was distilled the colour disappeared and got colourless. A proton NMR sample was prepared with CDCL₃ as solvent. It was found that peaks between 5ppm and 6ppm is a strong indicator of the distillate containing dimers, see Figure 6. In general the NMR spectra was bad overall. The fronting of the earlier peaks, between 1ppm and 4ppm, could be a sign of polymerization as it had been boiled without an additional stabilizer. The product was distilled once again and Hydroquinone to stabilize the system as vinyl compounds often tend to polymerize at high heat very easily. The proton NMR sample which was taken after showed no signs of anything else but the clean monomer, see Figure 7. The peaks between 5ppm and 6ppm had disappeared completely.

Before distillation had been carried out filtration was an alternative method to clean the monomer from the basic inhibitor but proved to be less effective.

Review of Synthesis of pNVP
During this synthesis there were many tries in order to identify what was wrong initially. The first conclusion that was made was that the flask of [NVP], which was opened a few months before this project commenced, probably had gone ”sick” or begun to degrade. The earliest synthesises of [pNVP] did not work at all. It all remained a yellow coloured and very watery solution. The proton NMR samples showed a very strange spectra, which from it was concluded that many side reactions had happened.
Table 1: Molar Equivalents For Synthesis of pNVP 40

<table>
<thead>
<tr>
<th></th>
<th>NVP</th>
<th>RAFT</th>
<th>AIBN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eqv</td>
<td>40</td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>mass</td>
<td>1g</td>
<td>50mg</td>
<td>7.8mg</td>
</tr>
<tr>
<td>Volume</td>
<td>1mL</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

Table 2: Molar Equivalents For Synthesis of pNVP 450

<table>
<thead>
<tr>
<th></th>
<th>NVP</th>
<th>RAFT</th>
<th>AIBN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eqv</td>
<td>450</td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>mass</td>
<td>6.26g</td>
<td>19mg</td>
<td>2.8mg</td>
</tr>
<tr>
<td>Volume</td>
<td>6mL</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

After working past that, purchasing a new [NVP] from Sigma, and doing everything thoroughly it was found that after a successful synthesis of [pNVP], with 40 molar equivalents see Table 1, with 1-propanol as an internal standard to calculate conversion (approx.16%), that the amount of repeating units only were about 6.5, which gave an average molecular weight of the polymer of about 721 g mol$^{-1}$. This was a lot shorter and lighter polymer than intended, but since it was the first sign of any working synthesis and due to the lack of time it was decided to continue with the aminolysis. The peak integral of the peak which shows up around 7.02-7.13ppm was compared to each other before and after synthesis. See Table 3. The peak integral of the 1-propanol, 0.88ppm, was set to 1, as it would stay the same throughout the synthesis and had a very early peak that does not interfere with any other peaks, which made it easy to identify. See Figure 8 and Figure 9. The very stretched baseline, seen in Figure 9, is a common indicator of polymeric characteristics in the sample.

Table 3: Integral Data and Comparison

<table>
<thead>
<tr>
<th>ppm</th>
<th>Ref. Int.</th>
<th>Synth.Int.</th>
<th>Rat. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.02-7.13</td>
<td>21.12</td>
<td>17.81</td>
<td>84.3%</td>
</tr>
<tr>
<td>0.88</td>
<td>1.00</td>
<td>1.00</td>
<td>*</td>
</tr>
</tbody>
</table>

The comparison between the integrals of the two separate runs led to a realisation that approximately 16% of all of the monomer in the glass had polymerized. Ref.Int. is based off of Figure 8. As "Synth.Int.", based off of Figure 9, from Table 3, was a quenched product it was not possible to put it back for heating and stirring as everything had been terminated due to the introduction of Dichloromethane and oxygen in the system.

Looking at Table 1 it is written that there were 40 molar equivalents of [NVP]. The DP that was sought after was 100 (the average amount of repeating units in a chain), and the molecular weight of [NVP] is 111.14 g mol$^{-1}$, makes the average molecular weight to be 4445.60 g mol$^{-1}$ from taking $40 \cdot 111.14$. As approximately 16% conversion was achieved this gave and average molecular weight of 721 g mol$^{-1}$, the $M_n$, which would give a DP of simply 6.5 repeating units when divided by the molecular weight of [NVP], the $M_0$.

**Review of Aminolysis of pNVP**

The aminolysis was a relatively quick step to perform. Once again as it precipitated into diethyl ether it took to form of a white and very light powder. However, there was still
some product left at the bottom of the nitrogen flask, in which the reaction took place, that had a slight yellow tone. It could be by products, though the proton NMR spectra was difficult to interpret as the polymeric characteristics were still present in the spectra; so it could not be proven if there were any trace amounts of relatively saturated by products because they could be hidden behind the rough base-line. In either case a product was made which could be assumed to be the right product based off of the observation of no proven amounts of by products.

Table 4: Molar Equivalents for Aminolysis of pNVP

<table>
<thead>
<tr>
<th></th>
<th>pNVP</th>
<th>Base</th>
<th>Phosphine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eqv</td>
<td>1</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>mass</td>
<td>0.1568g</td>
<td>0.2748g</td>
<td>0.295g</td>
</tr>
<tr>
<td>Volume</td>
<td>*</td>
<td>0.27mL</td>
<td>*</td>
</tr>
</tbody>
</table>

Review of Michael Click Addition of pNVP

This step did not go as planned at all. The idea was that the polymer made was supposed to be soluble in water, but in this case the mixture of the product after aminolysis [pNVPam] and water only turned into a beige sludge. It refused to dissolve. Though it was given extra time to perhaps dissolve still it refused to. It could be so that there actually were quite a high amount of by product left from the aminolysis in the filtered products. After it was rolled with the roto-vapourizer three times, where two of them were with added methanol, the cloudy suspension was still present afterwards. It became a think dark yellow oil. The fact that there was any sought product inside could not be proven either. No available deuterium-containing solvent that could dissolve the oily product hindered the study of this to the point where it was just assumed to be the wrong product and thrown in the waste. The proton NMR showed absolutely no sign of any successful synthesis, probably because of the insoluble compounds which also were present in the mixture. See Figure 10.

Table 5: Molar Equivalents for Thiol Michael Click Addition of pNVP

<table>
<thead>
<tr>
<th></th>
<th>pNVPam</th>
<th>Michael Click</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eqv</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>mass</td>
<td>0.214g</td>
<td>0.3137g</td>
</tr>
<tr>
<td>Volume</td>
<td>*</td>
<td>0.3137mL</td>
</tr>
</tbody>
</table>

Review of Synthesis of pMMA

Judging from the result one can absolutely say that it was successful in regards of creating [pMMA]. Letting it stand over a whole night, however, was a mistake as it polymerized to 99.9%. To make the desired product the reaction had to be quenched after a given time to maintain the end group functionality, but if the reaction goes to a 100% it terminates and kills all functionality. See Figure 5. In this case that happened and created a very hard piece of plexiglass. This could not be used in any further experiments in the project because of that reason.
Table 6: Molar Equivalents For polymerization of MMA

<table>
<thead>
<tr>
<th></th>
<th>pNVP</th>
<th>Base</th>
<th>Phosphine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eqv</td>
<td>1</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>mass</td>
<td>0.1568g</td>
<td>0.2748g</td>
<td>0.295g</td>
</tr>
<tr>
<td>Volume</td>
<td>*</td>
<td>0.27mL *</td>
<td></td>
</tr>
</tbody>
</table>

Conclusion

From all of these steps it can be concluded that most of the lab-work ended in a non-success, mostly because of the lack of time. The envisioned molecule was not made, and there were many small stops within the project as the monomer [NVP] was such a troublesome chemical to work with. [3]. The cited article no [3] brings this problem up as well. Much time which could have been spent on working was instead placed on trying to make the [NVP] work properly, or as intended in the first place. A lot of clean up, trail and error and also queues for machinery made the project very time inefficient. Of course, given enough time it would probably have ended with a correct product.

As stated, the monomer [NVP] was difficult to work with, and when it comes to the monomers purity is extremely important as trace amounts of anything that contains species with good ion carrying properties, or can make ions easily, will terminate the reactions in the glass. The best way to deal with this was to distil the monomer at least two times to remove all the unwanted molecules which, among other effects, cause termination.

When doing this reaction in a bulk, without a proper purification step, there seem to be a high risk of leaving in potential by products during reaction steps. Taking a closer look at the aminolysis it could be debated that the reason why the thiol mixture was not water soluble completely could be because of the lack of purifications steps, such as filtering or precipitation. The reaction which got the furthest in this project was, though, in fact the vessel containing the bulk reaction material. The chance of a "non-contaminated" product is probably a lot higher if each step is done separately and not just added to the same glass like the most successful reaction was. Doing each step separately would be recommended because of this.

Further Studies

Continuation of this project is necessary to reach the desired goal. If the given time of this project would have been double, to 18 weeks instead of 9 weeks, the problems would most likely have been solved and the rest would be assumed to roll downhill. Outside of the scope further studies with other monomers instead of [NVP] would be interesting to compare with when the ion conductivity tests would commence to get some sort of perspective on how functional the monomer actually is. Further a PDI (poly dispersity index) analysis would be a good idea to evaluate a more exact average molecular weight of the synthesized material and to observe the average chain length in the system. It would give a good measurement of control which RAFT is said to have. [1]

Another aspect worth looking into would be the ratio of [pNVP] and [pMMA] needed to make the material rigid enough to work as a solid electrolyte, combined with the lithium salt. E.g if a longer chain of [pMMA]
would not only affect the rigidity of the material but also if it would change the ion conductivity of the electrolyte as a whole. The same goes for length of [pNVP], if it chain length is extremely crucial or not.

References


Appendix

Abbreviations

NVP: N-Vinyl-Pyrrolidone
MMA: Methyl Methacrylate
pNVP/pMMA: Poly-NVP/MMA.
AIBN: Azobisisobutyronitrile
DP: Degree of polymerization
PDI: Poly Dispersity Index
RAFT-: Reversible Addition-Fragmentation Chain Transfer-
MC-reagent: Michael Click-reagent
ATRP: Atom Transfer Radical-Polymerization
DCM: Dichloromethane
Figure 5: RAFT mechanisms for the polymerizing systems.
Figure 6: NMR Spectra of Distilled NVP Containing Dimers and Other Impurities
Figure 7: NMR Spectra of Distilled and Purified NVP
Figure 8: NMR Spectra of Reference NVP with PropOH as Internal Standard
Figure 9: NMR Spectra of Reference poly-NVP with PropOH as Internal Standard
Figure 10: NMR Spectra of Final Product after Thiol Michael Click Addition