LTH - PERSTORP AB

Isocyanate-free polyurethane from cyclic carbonates

Synthesis, application and evaluation

Christoffer Wallerek

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Kent Sörensen
Perstorp AB

Patric Jannasch
Examinator, LTH

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Abstract

Polyurethane is a widely used polymer with a lot of different applications due to its versatility and often resilient properties. The polymer is often prepared as a two component system consisting of polyols and isocyanates and can be cured at relatively low temperatures. Even though the formed polymer is hazardless the isocyanate used in the manufacture is dangerous in itself, but even more so is the often used precursor phosgene. Large quantities of phosgene and isocyanates are handled in the production of isocyanates and pose a threat to the environment and the people working with the production, and to great extent the application works. There is however a relatively new and "greener" alternative to commercially available polyurethane which is based on cyclic carbonates and amines. This NIPU (Non-Isocyanate PolyUrethane) production and comparison to commercial PU are the main focus of this master thesis. From the available literature NIPU is commonly prepared from 5-membered cyclic carbonates. But via internal competence and research from Perstorp AB and from Lund University a possible way to prepare a more reactive 6-membered monomer cyclic carbonate to be cross-linked with amines were formed.

As a primary objective a polymer with an acrylate skeleton and cyclic functionality would be cross-linked with isophorone-diamine and compared with a similar acrylate-polyol polymer cross-linked with isophoronediisocyanate (IPDI). If the primary objective would prove too difficult, a crosslinking between a di-cyclic carbonate (di-TMPC) and polyether amines (Jeffamines) should be evaluated as films. The synthesis and final products were to be analyzed with gas chromatography, FT-IR, GPC and standardized film evaluation methods. The monomer was to be prepared via acrylate-esterification of tri-methylol-propane (TMP), followed by carbonation with di-methyl-carbonate (DMC). The cyclic carbonate with acrylate functionality would then be polymerized before being cross-linked with amines to create a multifunctional polyurethane polymer.

The esterification process started with TMP being ring-protected with acetone before being transesterified. Later, the acetone group was removed to allow for carbonation. The three first synthesis steps were relatively simple in their set-up and a product purity of 93.67 % were obtained. The carbonation proved more complicated and several approaches were tried. The most effective way for preparing the precursor for the cyclic product was an enzymatic approach with N435, an enzyme kindly provided from Novozyme. At a reaction time of 45 h at 60 °C an estimated mass content of 53% of single coupled monomer were achieved. The other methods included a higher temperature thermal reaction, hydroxide catalyzed, DBTDL catalyzed and enzymatic processes at lower temperatures. All other methods besides the enzymatic approach yielded no product or precursor mass content of over 10%. The primary objective were put on hold in favor of the secondary aim.

The secondary approach encountered problems with solubility of the di-TMPC and the Jeffamines which resulted in the lack of the polymer reactions necessary for film evaluation. The two solvents (cyclohexanone and methylethylketone) used to try and overcome this problem did not solve the di-TMPC effectively enough despite raised temperature and sufficient time. Several DSC-scans did however confirm some exothermic reactions occurring at room temperature and an almost instantaneous reactivity at the melting point of di-TMPC. FT-IR was used to confirm the presence of urethane bonding and the cyclic carbonate decomposition in a series of scans.

There are still different monomers to be evaluated to compare system and physical data for the pure cyclic carbonate in the future.

Sammanfattning

Polyuretan är en allsidig och utbrett använd polymer tack vare dess mångsidighet och tålighet. Polymeren är oftast tillverkad genom ett tvåkomponentsystem bestående av polyoler och isocyanater som kan härdas vid relativt låga temperaturer. Trots att den bildade polymeren är ofarlig är isocyanaterna, och framför allt dess synteskemikalier inklusive fosgen, farliga för både miljön, arbetarna vid tillverkningen och framför allt applikationsarbetarna. Det finns dock ”grönare” alternativ till de konventionella isocyanaterna som är baserade på cykliska karbonater som tvärbinds med aminer för att skapa en isocyanat-fri polyuretan (NIPU). Denna polyuretans tillverkning och egenskaper jämfört med konventionella system är denna masteruppsats huvudmål. Enligt den allmänna litteraturen skapas denna NIPU oftast med 5-ringade cykliska karbonater. Perstorp AB har dock tillsammans med Lunds universitet hittat ett möjligt sätt att framställa en mer reaktiv 6-ringade cyklisk karbonat för att tvärbindas med aminer.

Den första målsättningen är att jämföra en polymer tillverkad med akrylatskelett och cyklisk funktionalitet som sedan tvärbundits med isoforon-diamin med ett mer konvetionellt polyakrylat med alkohol-funktionellt polymer som tvärbundits med isoforon-diisocyanat. Om målsättningen skulle bli onåbar skulle polymeren av en di-cyklisk 6-talig karbonat (di-TMPC) och polyeteraminer (Jeffaminer) utvärderas som filmer med standardiserade tester. Syntesen och de erhållna slutprodukterna skulle utvärderas med gaskromatografi, FT-IR, GPC som komplement till de standardiserade testerna för polymerena. Den cykliska monomeren skulle skapas genom en akrylat-esterifiering av tri-metylol-pentan (TMP) som sedan skulle karboneras med di-metyl-karbonat (DMC). Den cykliska karbonaten med akrylatfunktionalitet skulle sedan polymeriseras innan polymeren tvärbinds med aminer för att skapa en multifunktionell polyuretan.

Förestringsprocessen startade med ett ringskydd på TMP-molekylen med en aceton-koppling innan omföresteringen. Ringskyddet spjälkades sedan av för att monomeren skulle kunna karboneras. Dessa tre första syntessteg utfördes utan några större problem och en renhet på 93.67% erhölls. Karboneringen visade sig vara besvärligare och ett flertal tillvägagångssätt testades. Den mest effektiva var en enzymatisk påkoppling av DMC för att skapa ett förstadie till den cykliska produkten. Detta gjordes med enzymet N435 som vänligen skänktes av Novozyme. Vid en reaktionstid på 45 h med en reaktionstemperatur på 60 ℃ uppmättes en masshalt av den enkel-kopplade monomeren till 53%. De andra metoderna innefattade termisk påkoppling vid högre temperatur, hydroxid katalysering, DBTDL katalysering samt enzymatiska processer vid lägre temperatur. Ingen utom den enzymatiska processen lyckades producera en masshalt på förstadiet eller den cykliska produkten på över 10%. Målsättningen övergavs till förmån för den andra ansatsen, tvärbindandet av jeffaminer och cykliska karbonater.

Den andra ansatsen hade problem med lösligheten mellan di-TMPC och Jeffaminerna vilket resulterade i uteblivandet av polymerisering som var nödvändig för filmutvärdering. De två lösningsmedlen (cyklohexanon och metyl-etyl-keton) som testades lyckades inte lösa upp karbonaten tillräckligt effektivt för filmdragning trots förhöjd temperatur och långa lösningstider. Ett flertal DSC-skanningar konfirmerade dock exotermiska reaktioner mellan karbonaten och Jeffaminerna även vid rumstemperatur och en nästan ögonblickligen reaktion då karbonaten smälte. FT-IR användes sedan för att validera bildandet av uretanbindningar och ringöppning av karbonaten. Det finns dock fortfarande andra monomerer som kan användas för att skapa ett jämförelsebart system samtidigt som fysisk data för den rena cykliska och akrylerade monomeren kan tas fram.

Acknowledgements

I want to extent my gratitude to all those who have helped me and showed understanding while I completed this master thesis.

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List of symbols and abbreviations

PU – PolyUrethane
NIPU – Non-Isocyanate PolyUrethane
TMP - TriMethylolPropane
TMPC - TriMethylolPropaneCarbonate
di-TMPC – di- TriMethylolPropaneCarbonate
FT-IR – Fourier Transform- Infra Red
GSC - Differential Scanning Calorimetry
MS – Mass Spectrometer
GC – Gas Spectrometer
NMR – Nuclear Magnetic Resonance
IPDA – Iso-Phorone-di-Amine
IPDI – Iso-Phorone-di-Isocyanate
MEK - MethylEthylKetone
DMC – Di-Methyl Carbonate
TMPA - TriMethylolPropaneAcetonid
TMPAMMA - TriMethylolPropaneAcetonid MonoMethAcrylate
TMPCMA – TriMethylolPropane Carbonate MethAcrylate
TMPMMA –TriMethylolPropane MonoMethAcrylate
TMPMMA-DMC - TriMethylolPropane MonoMethAcrylate coupled with one DMC
TMPMMA-di-DMC - TriMethylolPropane MonoMethAcrylate coupled with two DMC
DBTDL – Di-Butyl-Tin-Di-Laurate

Introduction

Polyurethane is a widely used polymer with a high molecular weight. There are several ways to alter the polymer functionality which makes it a very versatile product in thermosetting polymers amongst others. The thermosetting properties are due to the three-dimensional network and size of the final polymer and can be enhanced with secondary functional groups in the polymer. Polyurethane is used for anything from cast elastomers, structural foam to insulation in house construction and very commonly in car upholstery, coatings and adhesives.

Polyurethane is often produced by a two-component polymerization of alcohols and isocyanates which both can have several functional groups. The usage of the many functional groups is the basis for the wide variety of applications for polyurethane. The polymer can be either a hard solid plastic, flexible plastics, created as rigid or soft foam, varnishes and gels which are all used in multiple ways.

The polymer is very stable and harmless. It is even used in kitchenware, often as an adhesive. The hazard and possible contamination risks stems from the production of the isocyanates, with phosgene as a reagent, and from the application of the two component systems. There is much to be won in safety and environmental aspects if such reagents can be avoided without sacrificing the stability and desired properties of the polymer. There is research which shows that reacting cyclic carbonates with amines create a urethane bond. The most commonly used cyclic carbonate compounds are 5-membered ones but this master thesis aims to create a comparative polymer by using 6-membered cyclic carbonates.

Since the field of 6-membered cyclic carbonate non-isocyanate polymers is relatively uncharted, the primary goal would be to firstly synthesize the acrylate-cyclic carbonate monomer. The second step includes the polymerization of the acrylic group with other commonly used acrylate monomers to create an acrylic skeleton, and to lastly cross-link the cyclic carbonate functional groups with IsoPhorone-Di-Amine (IPDA). The polymer is then compared with a similar system of an acrylic polymer with alcohol functionality which is cross-linked with IsoPhorone-Di-Isocyanate (IPDI) by film evaluation.

The secondary goal would be investigated if the primary goal would be deemed unobtainable during the experimental or synthesis stages. It would include the investigation of cross-linking a di-cyclic carbonate with polyether polyamines as films.

Perstorp is always striving to improve existing coatings and create innovative solutions to new problems and is thus very interested in improving both the quality and the environmental effects of both the production and the final polyurethane coating. The NIPU technology could potentially create better coating systems but also greatly reduce the amount of dangerous precursors used in both the synthesis and the application processes. Cyclic carbonate of TMP can be a new large product for Perstorp and that has the advantage of being a down-stream product from the existing TMP production platform.

Challenge

There are ongoing trends in the modern world to achieve “greener” more environmentally friendly production processes. Since there are quite some risks with the production of commercial polyurethane combined with the large production volume, there is a need for alternative production methods.

The main problem in the production and handling of the precursors of the polyurethane is the isocyanates which are toxic. There is thus a production related risk to both the environment and workers at the production of the components for the polyurethane and the application site. Once cured, the produced polyurethane is considered harmless and can even be used in kitchenware. Polyurethane is also commonly used as a two component, spray applied, coating on cars, trains, airplanes etc, which is a health concern for the application workers which may be exposed to the dangerous chemicals despite wearing protective equipment.

By avoiding the usage of isocyanates, and thus the use of phosgene, the major processing risks can be eliminated. The majority of the risks comes while working with isocyanates during application. Even small quantities can produce significant effects such as asthma, dermatitis, irritation or burns to the eyes, nose and throat. Workers may also become permanently sensitized to isocyanates and have severe allergic reactions to any exposure of isocyanates.

Objectives

The master thesis has a primary and a secondary objective if the primary would be impossible to complete.

The primary objective of this master thesis is to synthesize a polyacrylate system with a cyclic carbonate functionality and then to crosslink the polymer with an amine, such as isophorondiamine to prepare a polyurethane polymer. The polyurethane polymer is then to be compared to a polyacrylate system with an alcohol functionality cross-linked with isophorone-di-isocyanate. The two polyurethane systems are to be evaluated as coatings with standard measurement tests.

If the primary objective is not reached another amine-cyclic carbonate system can be evaluated. Di-functional cyclic carbonate can be cross-linked with Jeffamines and film-evaluated. The used Jeffamines can be seen in Figure 18 and 19 with the di-cyclic carbonate shown in Figure 17.

Master thesis outline

The main outline of the master thesis is as follows:

Part 1 presents background information regarding polyurethanes and the master thesis objectives and aims.

Part 2 provides further and more detailed information regarding the polymer structure and the commercial systems synthesize routes.

Part 3 contains the overall processes, material and synthesizes performed over the course of the master thesis.

Part 4 reveals the details of the different synthesis steps for the involved monomer.

Part 5 include the details of the testing of the crosslinking of di-TMPC and Jeffamines.

Part 6 summarize the results from all the different synthesizes and experiments.

Part 7 presents the conclusions and the discussion regarding all synthesis steps and analyses made.

Part 8 include the future work proposes that is needed to further approach the NIPU goals of the thesis.

Background

Commercial polyurethane

Polyurethane is very versatile and is thus used in many applications and industries such as insulation foam in the construction industry or flexible foam for padding in seating and mattresses. As depicted below in Figure 1 there is relatively a low amount of polyurethane that is used for coating purposes in terms of relative mass. However, polyurethane stills plays a major role for the coating industry with its versatility and thus good properties for special applications and overall hard-wearing capabilities.

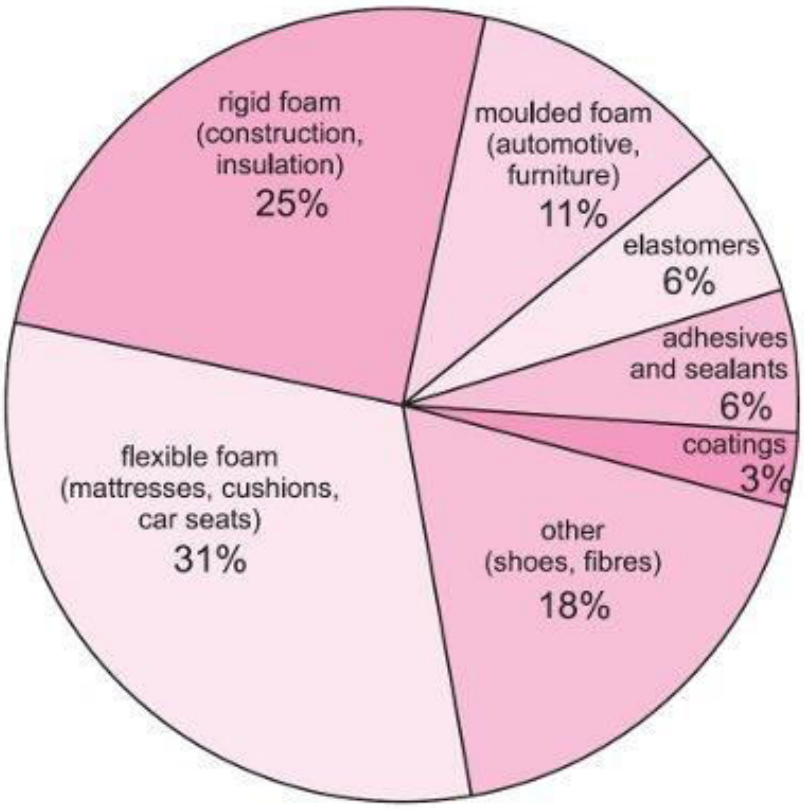


Figure 1, Uses of commercial polyurethane [1]

Since polyurethane is used in so many ways and can be modified to suit other needs the market for polyurethane is ever growing with approximately 4.7% annually with an estimated production of 13 650 ktons 2010.[2]

Synthesis of commercial polyurethane

Commercial polyurethane is often produced as a two component system and is cured over time after mixing. Polyurethane is a polymer consisting of segments interlinked with urethane bonds as shown below in Figure 2. The urethane bond comes from an isocyanate group interlinking with an alcohol group which bonds irreversibly. This property makes the polyurethane a thermosetting polymer and makes it a useful for coatings, adhesives and sealants.

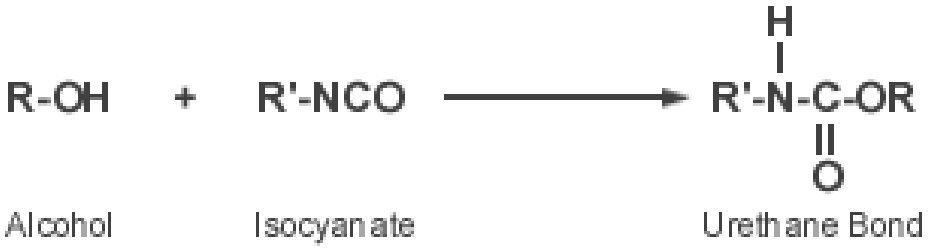


Figure 2, Commercial polyurethane synthesis

The health and environmental concerns that usually comes with polyurethane is often attributed to isocyanates and the synthesis of them. The commercial systems often follows Figure 3 and thus involve the very toxic gas phosgene. The produced isocyanate does also present toxic threats but the formed and cured polymers neutralizes the toxicity and the final polyurethane is deemed non-toxic and can be used in kitchenware.

The risks of exposure comes thus from either gas leakage of phosgene, leakage or spillage of isocyanates but foremost from the application part of the two-component system. Since the application is often in a more open system and spray applied it is harder to properly contain and guarantee that the workers remain un-exposed to the substances although ventilation is used as in spray booths.

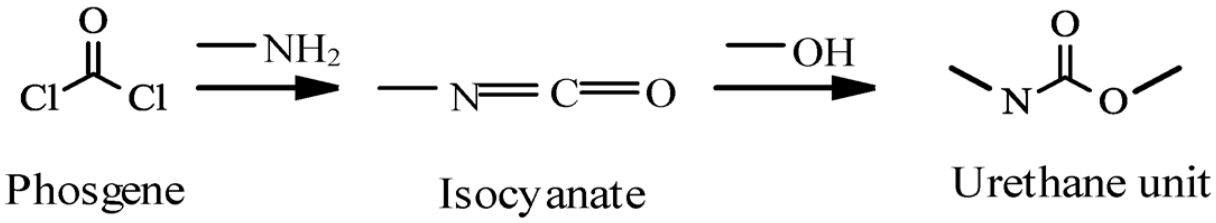
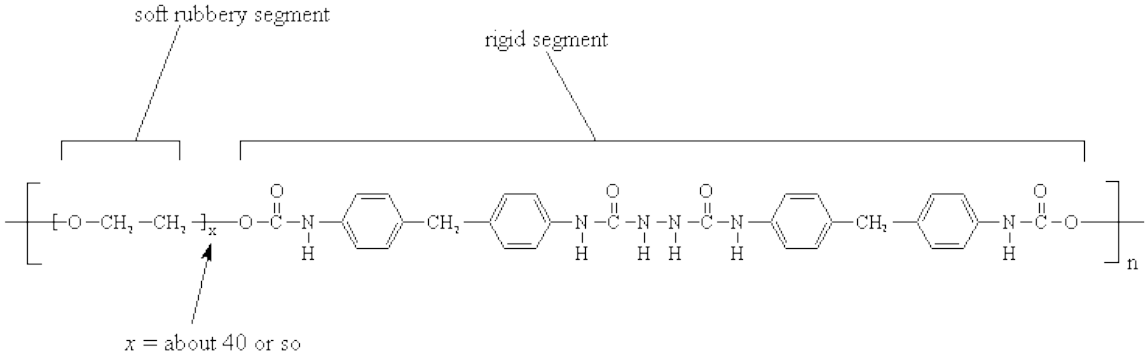


Figure 3, Phosgene used in commercial polyurethane synthesis [3]

Structure of commercial polyurethane

As discussed earlier there are many uses for polyurethane and it can be attributed to the versatility of the polymer structure and functional groups of the components or precursors of the polymer system.

Naturally the functionality regarding the bonding groups need to be at least two for a polymer to form. There are also a lot of different functional groups that can be used (R and R') which gives the created polymer its different properties. Due to the fact that there are so many different and highly specialized functional groups available, polyurethane is just as versatile as the versatility of the available functional groups. There is nothing that hinders the usage of several functional groups per component either which created multifunctionality within the polymer. An excellent example of the usage of different function groups to create a special property is spandex, the structure is shown in Figure 4.



Spandex has a complicated structure, with both urea and urethane linkages in the backbone chain.

Figure 4, Multifunctionality in polyurethane[4]

As a two-component system there are a lot of different ways to integrate functionality but one of the most common ways are using polyols with polyacrylate, polyester, polyether or polycarbonate functionality which gives the crosslinked final polymer very different properties due to the included polyol functionality.

Isocyanate-free polyurethanes

There are other ways of creating the urethane bond than using isocyanates. This is usually done by having a two-component system with cyclic carbonates and functional poly/oligoamines. The major advantage of this approach is the opportunity to bypass the usage of isocyanates and thus phosgene and other major health risks. The health and environmental concerns are also the driving force behind research projects which focuses on the creation of NIPU (Non-Isocyanate PolyUrethane).

Since there are many different cyclic carbonates which can be used there are also a lot of potential versatility with NIPU compared to traditional PU. The majority of the carbonates used to make NIPU in laboratory studies, and even more so in patents, have been 5-membered rings as opposed to the generally more reactive 6-membered rings [5] which will be used in this master thesis. There is virtually no commercially available 6-membered cyclic carbonates yet [3]. The functional groups coupled to the cyclic carbonates are interchangeable and can usually be used for both five and six-membered ring without any compatibility problems.

A notable difference between NIPU and commercial PU is the addition of a hydroxyl group besides the urethane bond which is created by the splitting of the cyclic carbonate as shown in Figure 5. The effects of the additional functional group have been investigated and there are indications of improved hydrolytic stability, increased chemical resistance and a lower permeability [6][7].

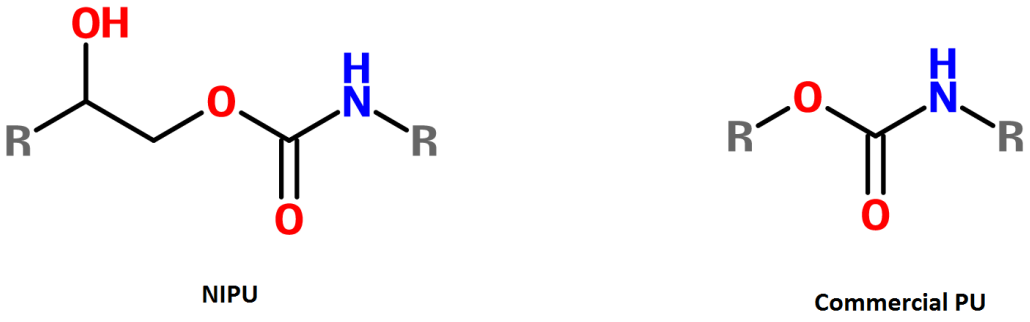


Figure 5, Difference in conventional polyurethane bond and NIPU

There are however some problems regarding the compatibility of cyclic carbonates and amines regarding their miscibility and reactivity. These problems can sometimes be managed with temperature increases, solvents and radiation but it is not a universal fix. Some mixtures are not miscible until the cyclic carbonate melts at which point the reaction is often too fast for application to be commercially valid.

Synthesis of cyclic carbonates for NIPU production

Cyclic carbonates can be synthesized via a multitude of different processes but the ones most commonly used for making 5-membered cyclic carbonates are catalyzed insertion of carbon dioxide to oxiranes or direct oxidation as a pre-step as shown in Figure 6.

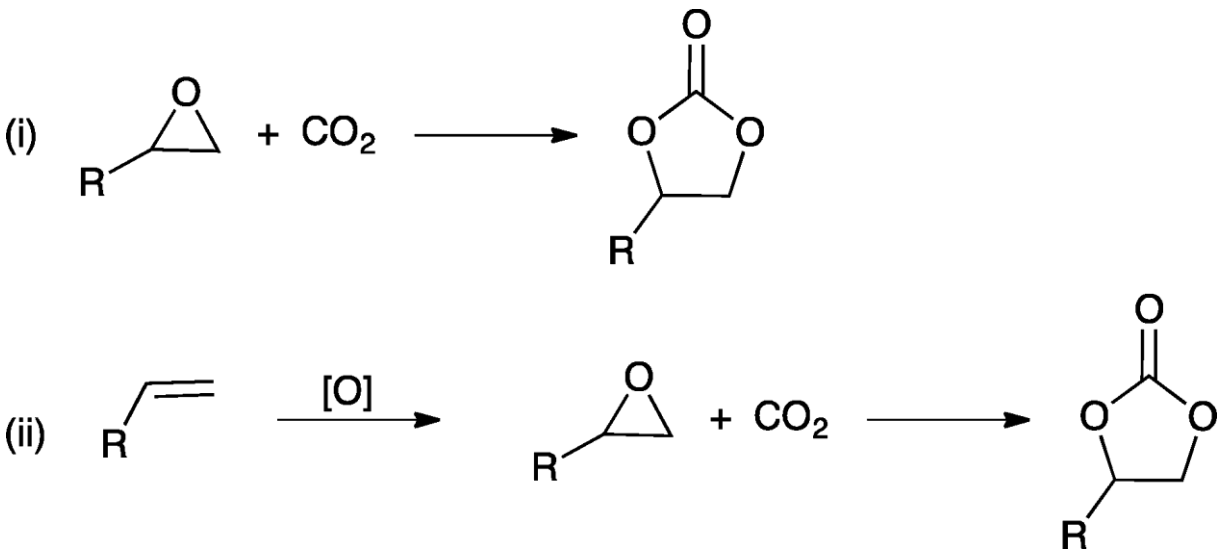


Figure 6, commonly used synthesis routes for creating 5-membered cyclic carbonates [8]

While this being the favored commercial process for 5-membered rings there was little literature available to creating the desired 6-membered cyclic carbonate monomer in a laboratory scale. Figure 7 describes the overall process of the synthesis which was created in the early stages of the master thesis. The details of the synthesis process are discussed in the synthesis section of the report. There are reports of the much more common 5-membered cyclic carbonate (propylene carbonate methacrylate PCMA) being readily made [9] but there is also few patent reports for creating the sought after monomer. [10]

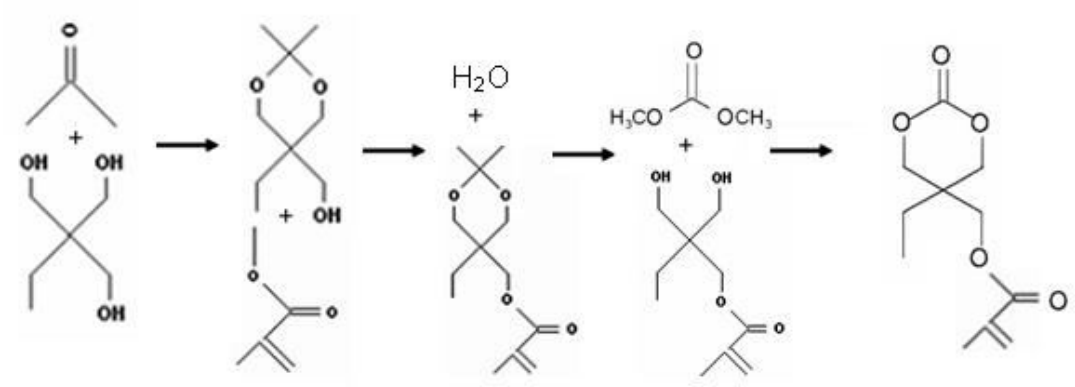


Figure 7, Overall, condensed monomer synthesis route

Synthesis of NIPU by crosslinking with amines

Cyclic carbonates can react with amines as described in Figure 8 and create a urethane bond. The overall reactivity and reaction speed along with miscibility complications are often the problems with NIPU synthesis. It is therefore impediment to investigate the miscibility and reactivity of the chosen system.

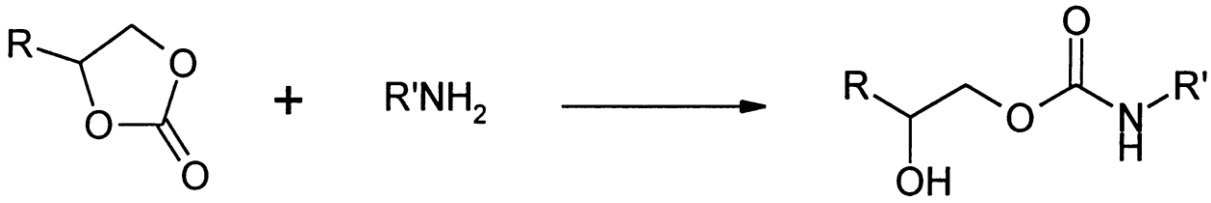


Figure 8, NIPU bonding with cyclic carbonate and amine group [11]

Amine reactivity

There have been many studies on the reactivity between cyclic carbonates and amines, and it is claimed that 5-membered cyclic carbonates can react with aliphatic and aromatic amines, alcohols thiols and carboxylic acids [12]. Perstorp AB have conducted reactivity tests regarding different amines with 6-membered cyclic carbonates and the reaction rates are very much dependent on the position of the amine group, where primary amines react fastest and sterical hindered groups or amines with other electron donating groups have a lower reactivity, as seen in Figure 9.

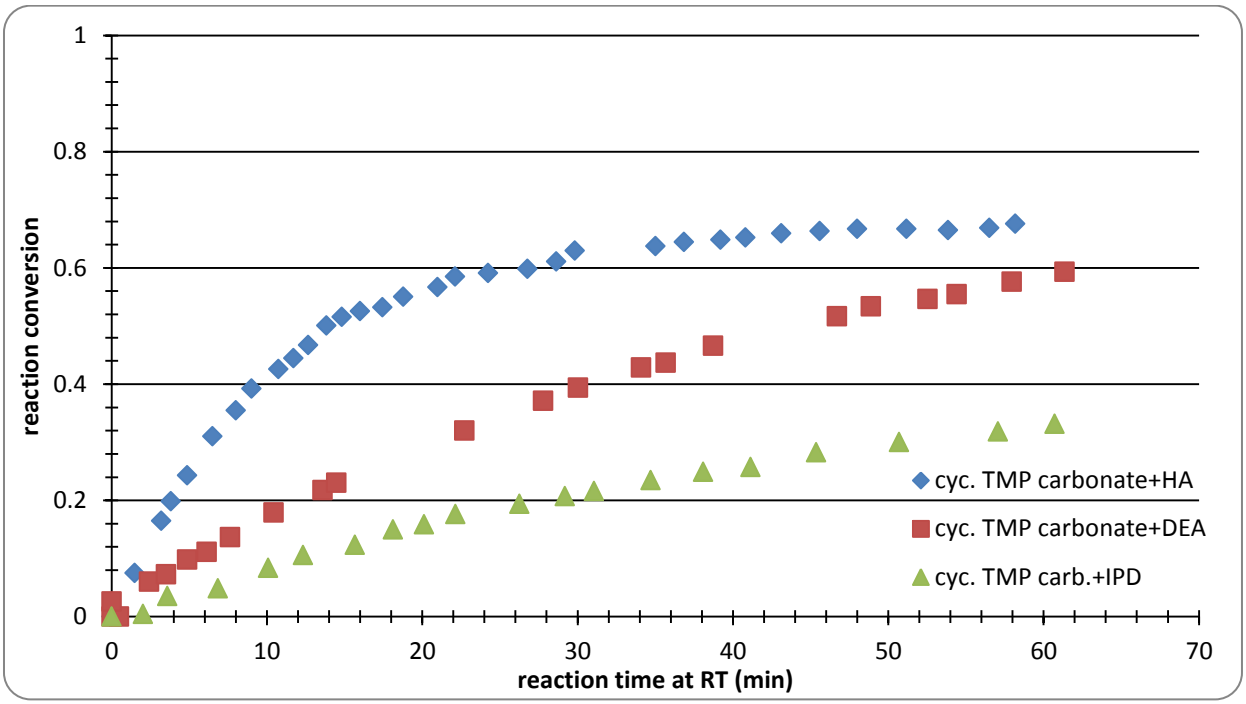


Figure 9, Amine reactivity with cyclic carbonates [13], blue (HA) hexylamine, red (DEA) di-ethyl-amine and green (IPD) isophoronediamine

The reactivity differences are also very dependent on the other functionalities of the amine, whereas some electron-donating functional group lowers the reactivity of the amine groups so much that there is virtually no reaction despite increased temperature, electron-withdrawing groups increases the reactivity.

The structure and size of the amine are also very important as there is steric hindrance which slows the reaction speed significantly for larger amines.

NIPU functionality

As any two-component system both the used components can add different functionality into the end product. The functional groups can be added to either components but it is sometimes easier to create functional monomers with specific functional groups with one the components than the other. It is therefore of great importance to have both functionality in both the cyclic carbonate and the amine.

There are many ways to create functional group-coupling and different methods have their own advantages. There are currently studies regarding polyamine structures for multi-functioning NIPU [14] as shown in Figure 10.

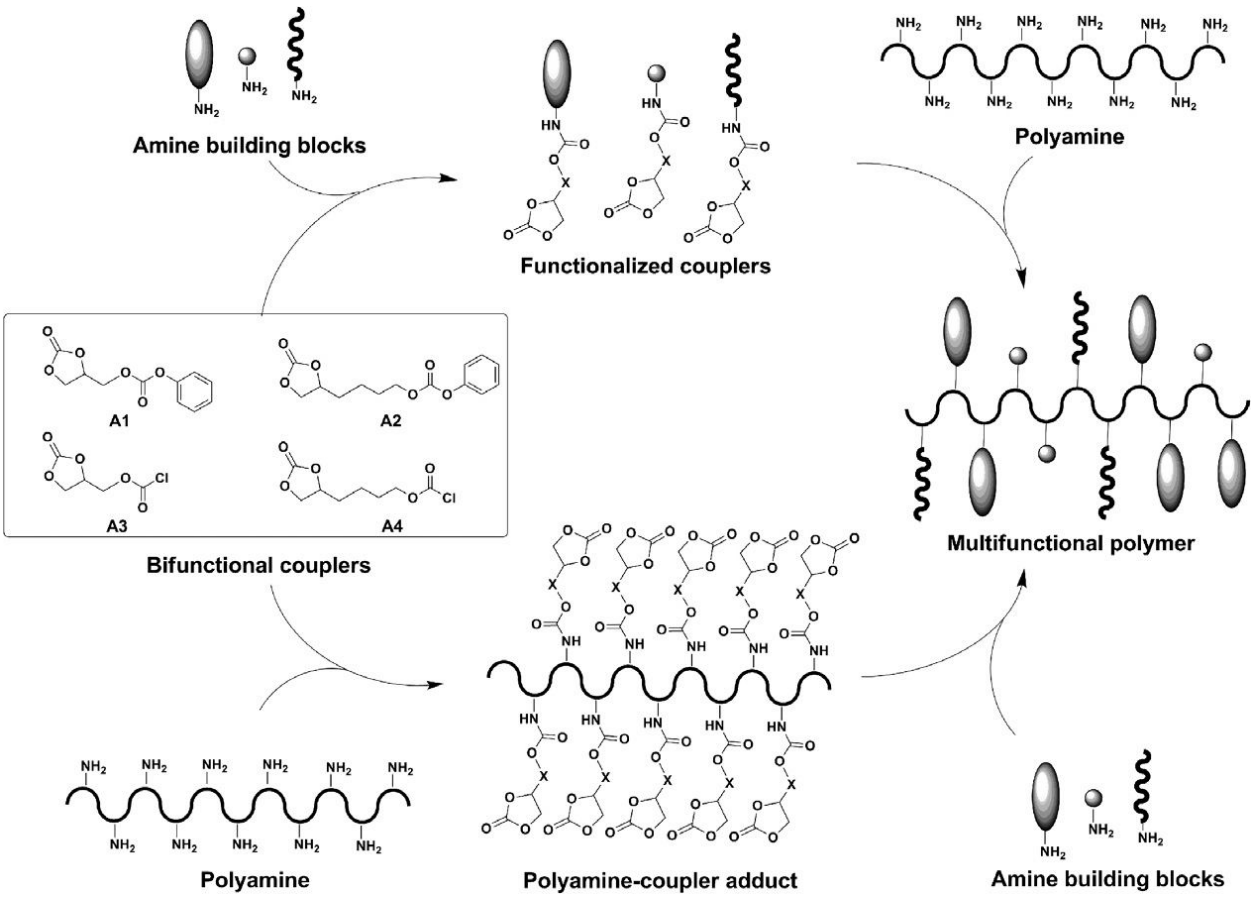


Figure 10, Multifunctional polyurethane synthesis routes [14]

The multifunctional macromolecules can also be created with cyclic carbonate functionality. As discussed earlier the proposed comparable systems are polyacrylic polymers with the NIPU having an acrylic skeleton with poly-cyclic carbonate functionality as shown in Figure 11 and which can later be cross-linked by smaller and less steric hindered amines to form the final polymer of cross-linked macromolecule.

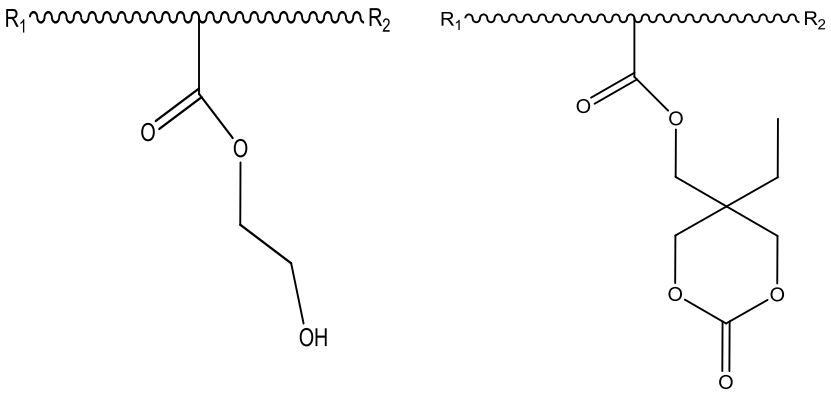


Figure 11, Comparison of the two acrylic polymers which will be cross-linked and compared [15]

Synthesis and characteristic evaluation

Differential scanning calorimetry (DSC) is often used to measure temperature and thus enthalpy changes in a sample during reactions or heating. The DSC can give information about what temperature the glass transition temperature is reached by recording a change in heatflow. This is most useful when dealing with polymers. The DSC can also give information about the reaction, if it is exothermic or endothermic and by what degree. It is also possible to determine roughly how the reaction rate is affected by temperature changes.

The DSC have been used frequently in reports studying NIPU synthesis and should be used in the master thesis as a way of determining both the glass transition temperature and at what temperature the curing or crosslinking reaction begins. These are important data for the different applications, such as two component coatings which would preferably be cured at ambient temperatures.

Fourier transform infrared spectroscopy (FT-IR) is a very useful and powerful tool as an analyzer both in-situ and of the final product since the instrument can monitor and distinguish between specific bonds, molecules and groups. This makes this method excellent for following a reaction where a specific molecule can be seen consumed and another targeted (or unwanted) product is formed. FT-IR could also be used to roughly calculate the yield and selectivity of a certain reaction. The method is also considered rather cheap, fast and effective. FT-IR should be used to verify and a roughly estimate the composition in the synthesis and in the evaluation of the final product. It has been used repeatedly and are able to give adequate information about the given reactions and products for the master thesis.

Gas chromatography (GC) can be used to analyze smaller molecules which need to be evaporated or otherwise carried in a gas stream which passes into a column which separates different molecules by interacting with the carried compounds and not the carrier gas. The GC is a good tool for getting further information about a sample composition if it is able to evaporate and separate the sample content. The precision and versatility of a GC can be improved by connecting the outlet of the column to a mass spectrometer. Gas chromatography is not widely used in these types of reactions and is not really of interest unless any previous methods have failed to obtain adequate enough data.

A mass spectrometer (MS) ionizes the sample and analyzes the fragments to calculate the different parts such as functional groups, bonds, specific atoms and such. It is quite common to include a mass spectrometer to a GC for the increase in analytical strength. But since the MS is as useful as the GC in these areas it shouldn't be necessary to run any testing through a MS.

Nuclear magnetic resonance (NMR) is widely used to investigate properties of a large array of different organic molecules in both solutions and solid forms. NMR can give the user detailed information regarding the samples structures, dynamics and the chemical environment of the studied molecules.

Product characteristics evaluation

The final product should be mechanically and chemically tested after being studied and the chemical composition have been confirmed. There are standardized testing procedures available at Perstorp

AB and American Society for Testing and Materials (ASTM) provides some mechanical property testing that have been used to review and evaluate coating properties.

A MethylEthylKetone (MEK) test can be carried out as a ball peen hammerhead wrapped with MEK soaked tissue being moved back and forth over the coating that is up for testing. These motions are usually counted and carried out until either a set amount of motions have been completed or the coating has been removed from the test panel. A similar test could be relevant in the master thesis if the chemical and mechanical resistance of the final applied coating would be of interest.

A non-yellowing property is very important to clear coatings since the discoloring would spoil the underlying color. Therefore a photo stable coating formulation is often necessary when creating clear coatings. The most common way to see the effect of prolonged exposure to natural light is to radiate the test surface with UV-light and measure the yellowing effect.

This could also be of interest if the NIPUs created were to be used in any kind of coating formulations that would require a certain degree of clarity or color preservation. Since this is probably the case an UV-light test should be issued to the final product to measure the effect on both the ordinary NIPU and the NIPU with acrylic functionality since there have been records of increased photo stability with the incorporation of acrylic groups in the polymers.

The pure hardness of the coating describes the ability to withstand scratching which is a key point for clear coatings to automotives. A coating which scratches easily soon becomes ineffective. Some sort of hardness or scratch testing is therefore essential for the produced NIPU in the master thesis. This can be done by an ASTM device or a similar tool at Perstorp AB.

Shear and tensile strength, impact resistances etc. of the NIPU products are in some ways measurements of the toughness of the material and should in some cases be examined. There are several ways of determining the physical properties of polymers at Perstorp AB and the standardized testing should be adequate for evaluation.

The gloss of the coating could be an important aspect as the coating could be required to have a high gloss. There should be gloss testing on the final applied products in the master thesis and any standardized testing routine at Perstorp AB should provide sufficient data.

Methods and material

Synthesis routes of monomer TMPCMA

The synthesis of the monomer was achieved by a four-step synthesis scheme as shown in Figure 12 again. The last cyclization step proved difficult and thus many varieties were tried with varying results.

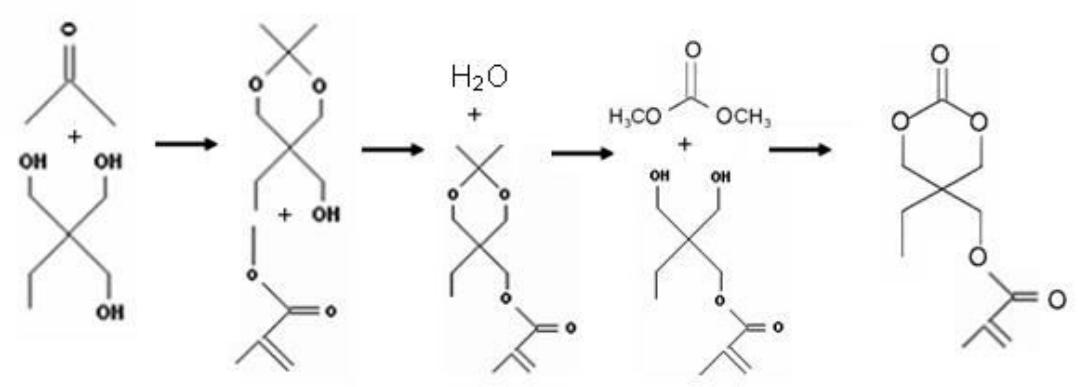


Figure 12, Synoptic synthesis route for the cyclic monomer

The synthesis can be described by four distinct steps, Figure 13, 14, 15, and 16 respectively, which are all illustrated above with inter-reaction purification. All steps were repeated several times and the presented numbers are representative for all of the successful trials.

Ring protection of TMP with acetone

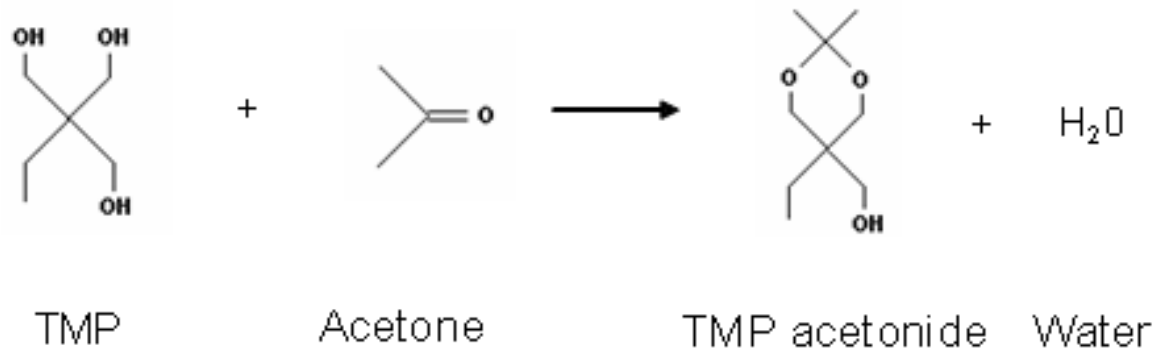


Figure 13, Ring protection of TMP with acetone [16]

TMP (1100 g), acetone (714.2 g) and catalyst, methane sulfonic acid (9.07 g) were charged in 2 liters 4-neck flask equipped by reflux condenser, stirrer, N_2-flow and temperature control and heat was supplied by an electric mantel.

To easily dissolve TMP in acetone the temperature was increased to 55 °C. The reaction was carried out with a reactor temperature of 72 °C for 70 minutes. The mixture was slightly yellow.

The synthesis composition were roughly:

Acetone 22 wt-%, TMP 24 wt-% and TMP acetonide 45 wt-% and ~3 wt-% produced water.

The solution cooled in the reactor to 40 °C before 70.6 g of 10 wt-% NaOH –solution was added. The reactor was then mixed for 10 minutes. The reaction mixture was evaporated as soon as possible as water may remove the ring protection and thus lower the reaction yield. When evaporating the solution it should become hazy, this is due to salt being precipitated when the water is removed. These particles could be removed by filtering (pressure filtering was necessary due to the high viscosity). The solution was clear and slightly yellow after the filtration. Further purification was done by vacuum distillation. The entirety of the reaction mixture could be loaded and distilled. This was carried out in a larger stationary distillation apparatus with a reflux unit.

1498.8 g of product mixture was loaded. The temperature was increased to 130 °C in the reactor, the top column gas phase temperature was kept at 85 °C (± 3°C) whilst the pressure was 1 torr. Fractions were taken continuously until the top temperature rose drastically. This was when the TMP were becoming more dominant in the gas phase. This was achieved after about 3 hours of distillation.

An initial small fraction was taken as it contained leftover water and acetone and 702 g distillate was obtained. The last fraction was not used as it had been contaminated with TMP.

Transesterification

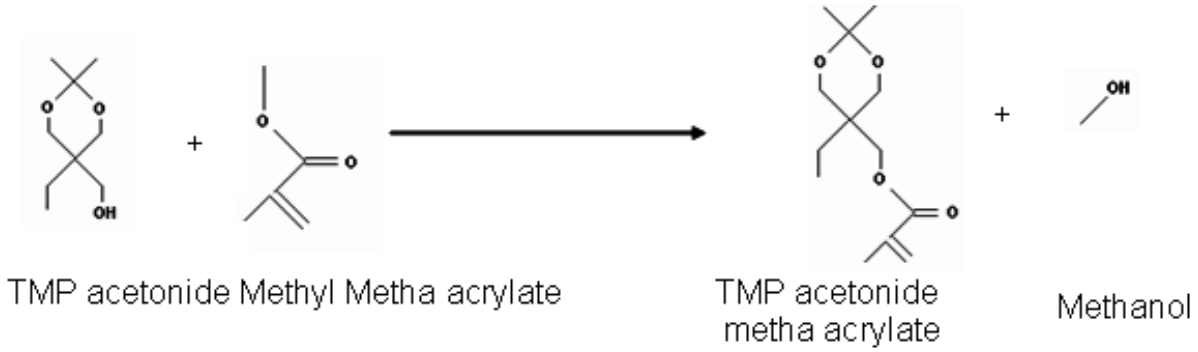


Figure 14, Transesterification of TMPA with MMA [16]

300 g of the previously acquired solution, 192 g methyl methacrylate and 1,26 g phenothiazine, used as an acrylate polymerization inhibitor, was added to a stationary distillation unit with reflux, steel net packed column and a top column temperature indicator. The reactor had a magnetic stirrer, feeding inlet from a pump, temperature control coupled electric heating mantle and nitrogen bubbling.

The reactor was heated to 140 °C with a full reflux and 3,6857 g tetra isopropyl titanate, which was used as the transesterification catalyst, was added only when the top temperature reached 92.5 °C.

An additional 192 g methyl methacrylate was added through the feeding inlet over the course of the reaction. Start the pumping after about 1 hour after the addition of catalyst. Maximum addition speed should be 2 ml/minute.

The top temperature drops due to the formation of methanol and the reflux was adjusted to keep the temperature at a couple of degrees below 70 °C. Only start the reflux unit when the top temperature is at 65°C or lower. The reaction is over when the top temperature rises to over 80-100°C and doesn't fall back down. This should take about 3-4 hours.

73 grams of distillate were obtained whereas the theoretical maximum amount of methanol were 67 grams. The remaining reaction mixture was evaporated and was darker in color than before the synthesis.

Ring-opening

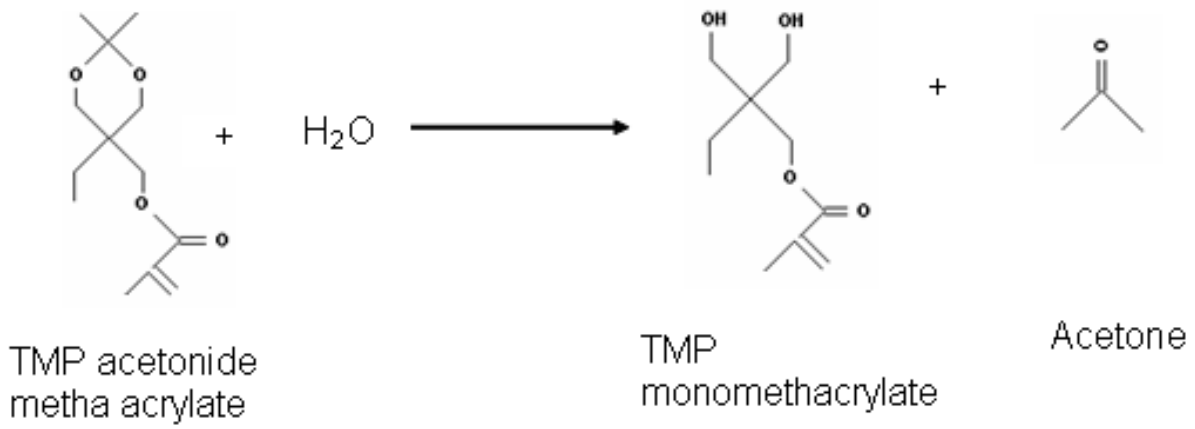


Figure 15, Ring opening of TMPA-MA [16]

418.9 g TMPA-MA, 209.6 g water and 41.8 g Amberlyst 15, an acid functional ion-exchange resin catalyst, was loaded into a reactor equipped with stirring, temperature indicator, air bubbling and a vigreux column.

The reactor was heated by an electrical heating mantle to 72 °C and the reaction mixture was kept at said temperature for 1 hour.

The resulting solution was filtered and evaporated, 306.5 g obtained.

A second procedure for ring-opening starts with 200 g of product mixture (directly from acrylation), 200 g of 50 wt-%-ethanol mixture and 20 g of Amberlyst 16 that were loaded into a 500 ml three neck flask. Flask was equipped by short vigreaux (20 cm) column, air bubbling and temperature control unit. The mixture was heated to 70-75 °C and some acetone was distilled out during reaction. Acrylate is very sensitive for water and some hydrolysation had happened during ring opening and evaporation. TMP monomethacrylate purity was 93.63% after filtration.

Cyclization – Creating cyclic carbonates

The general cyclization principle in an enzymatic process is shown in Figure 16 and has been previously tested with very promising results [17], in the cyclization synthesis the enzyme N435 was used as it have been used by other researchers with promising results. [17] [18]

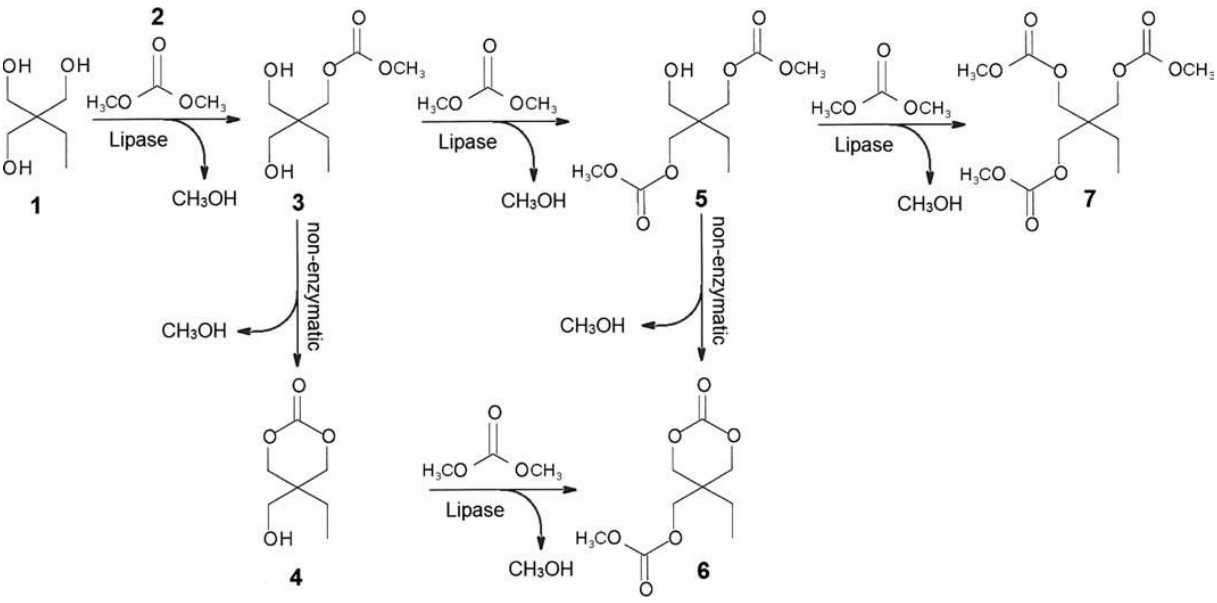


Figure 16, Lipase based cyclization of TMP with DMC [17]

The only difference from the Figure above was the starting material, which have an acrylate group instead of a hydroxyl group.

Enzymatic process

54.9 g TMP-MMA, 489.9 g dimethyl carbonate (DMC), 219,8 g 4Å molecular sieves (just enough to be completely covered by the liquid) and 9.9 g Novozyme N435 were loaded in a 1 liters 4-neck flask equipped with stirrer and temperature control. The reactor temperature was kept at 60 °C with an electrical mantle for 18 and 105 hours. Further testing with the same amounts of reactants was conducted with a reactor temperature of 40 °C for 7 hours.

High temperature cyclization step

The carbonation was carried out in a 300 ml steel Parr reactor equipped with a stirrer, thermometer, pressure release valve, pressure indicator and sample drain. The reactor was heated by an electrical mantle with an automatic temperature control unit. The reactor was loaded with all the components and was then sealed. The stirrer was not active during the processes described below.

Non-enzymatic process

11.3 g TMP-MMA, 100.6 g dimethyl carbonate (DMC) and 150.3 g 4Å molecular sieves were loaded. The reaction temperature was 150 °C for 30 hours. The reaction was monitored after 10 and 30 hours.

Hydroxide catalyzed

15 g TMP-MMA, 142.3 g dimethyl carbonate (DMC), 0.06 g NaOH(aq) (50 w/w-%) and 160.0 g 4Å molecular sieves were loaded and the reactor was heated to 140 °C. A sample was taken after 17 and 89 hours.

12 g TMP-MMA, 107.7 g dimethyl carbonate (DMC), 0.3 g $NaOH_{(aq)}$ (50 w/w-%) and 160.0 g 4Å molecular sieves were loaded and the reactor was heated to 140 °C. A sample was taken after 17, 41 and 140 hours.

DBTDL catalyzed

14 g TMP-MMA, 131.8 g DMC were covered by 4Å molecular sieves in the parr reactor and the temperature were raised to 120°C for 19 h before adding 0.3 ml DBTDL. The temperature was raised to 165°C but fluctuated and had peak temperatures of up to 180°C.

High temperature post-enzymatic process

113.6 g of the end product from the enzymatic process described above and 108 g 4Å molecular sieves were loaded. The reaction temperature was set to 135 °C for 12 hours.

Crosslinking of di-TMPC and Jeffamines

Di-TMPC (shown in Figure 17) is an ether bonded double cyclic functional carbonate which can be crosslinked twice (due to the two carbonate groups) with amines.

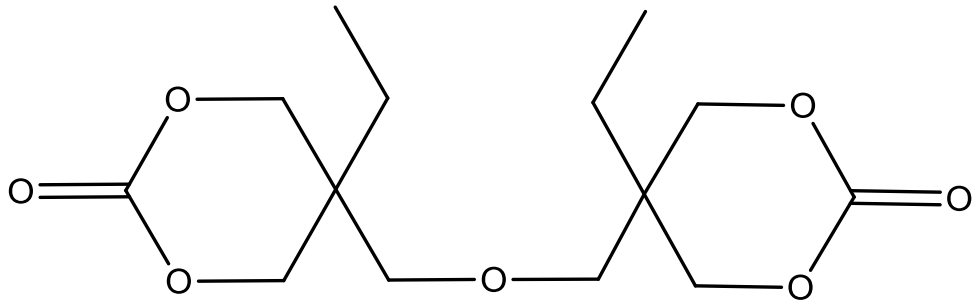


Figure 17, Di-TMPC

Jeffamines are polyether amines sold by Huntsman. They are varying in size but are almost always containing primary amine groups connected to a polyether backbone. The jeffamines used (T-403 and EDR-176) are shown in Figure 18 and 19.

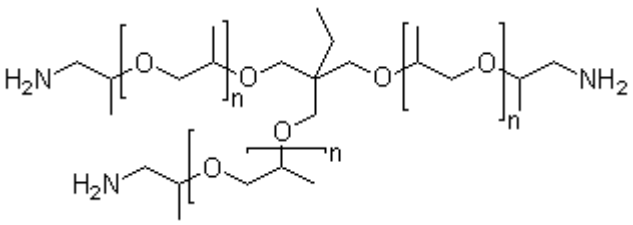
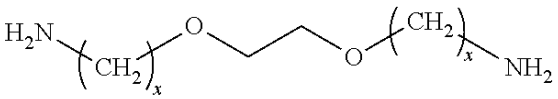


Figure 18, Jeffamine T-403, n=5-6, with a total molar weight of approximately 440.



JEFFAMINE®	x	MW
EDR-148 (XTJ-504)	2.0	148
EDR-176 (XTJ-590)	3.0	176

Figure 19, Jeffamine EDR-176

Solubility and polymerization testing

Initial testing regarding solubility, polymerization rate and curing temperatures were conducted before any plates could be produced for further testing.

4.86 g T-403 and 0.97 g EDR-176 Jeffamines were mixed with 6.67 g di-TMPC at room temperature, there was no phase-interface but also almost no solubility. 17.88 g cyclohexanone was added after several minutes of stirring and observation. The mixture was stirred vigorously for several minutes.

After 45 minutes 8.82 g of the previous prepared and freshly stirred mixture was extracted and mixed with 12.90 g cyclohexanone at room temperature. A sample was placed in an oven at 80°C for an hour.

Another solubility mixture was prepared with 0.51 g di-TMPC, cyclohexanone were added until moderate solubility occurred (21.71g) and until almost all di-TMPC was solved (30.44g).

A heat enhanced solubility mixture started with 2g of both cyclohexanone and di-TMPC which was gradually heated with an electric mantle. The undissolved grains of di-TMPC disappeared at 80°C but the mixture was misty with very small di-TMPC flakes. The mixture was heated to over 110°C but the mixture was never clear. As the mixture was cooled grains of di-TMPC precipitated very rapidly until the mixture had the same appearance as it did in room temperature, grainy and slightly yellow. The test was repeated but with the same results.

4.35 g of di-TMPC was mixed with 3.19g of T-403 and 0.64g ERD-176 at room temperature and was then slowly heated with manual rigorous stirring while under observation. The grainy mixture was turning increasingly viscous as the temperature went over 40°C and at 90°C the grains seemed to shrink while the viscosity increased greatly. At 95°C the polymerization was total with grains locked into the polymer.

A long-time solubility test mixture was prepared with 2.24g di-TMPC, 172g T-403 and 0.33g EDR-176. The mixture became somewhat viscous at room temperature while stirring. There was no change in appearance and obvious properties over 48 h at room temperature.

Another solubility test mixture was prepared using 2.24 g di-TMPC and 8.96g MEK at room temperature. There were no large grains but a very prominent haziness. Adding another 11.3 g MEK did not seem to increase the solubility, only a possible dilution the haziness somewhat.

DSC and FT-IR

A Jeffamine mixture was prepared for DSC and FT-IR analysis by mixing 2.566g EDR-176 and 6.447g T-403 (functionality 2.5 with respect to the amine groups).

A DSC capsule was prepared with 11.06mg di-TMPC and 8.64mg of the Jeffamine mixture prepared earlier. A gradient DSC was run with a starting temperature of 25°C and an end temperature of 145°C with a 5°C increase each minute. The sample was then removed from the capsule and was scanned with FT-IR.

Another DSC-gradient run with the same gradient specifics were run on a sample with only 7.25mg di-TMPC.

While using the same gradient method as above a sample of 3.87mg di-TMPC and 3.02mg Jeffamines was mixed and stored at 25°C for 10 h before being analyzed.

A sample with 11.84mg di-TMPC and 9.61mg Jeffamines were mixed in a DSC capsule and analyzed isothermally at 25°C for 10 hours.

Base curves for di-TMPC and the previous mentioned jeffamine mixture were obtained with FT-IR.

A sample was prepared with the same stoichiometric relation as previously and analyzed each 30 minutes with the FT-IR for 2.5 hours and another scan was made after 24h.

A sample with slightly higher amine functionality (2.66) was prepared and scanned with FT-IR as well.

A reaction mixture that had been stored at room temperature for 10 hours were scanned with FT-IR.

Results

Monomer synthesis results

The distillate composition from the ring protection is shown in below in Figure 20. The quality of the formed product was determined by gas chromatography. The conversion rate of TMP in the ring protection is 59% with a selectivity of 98% to TMPA. The yield before purification is 58% by mass and the overall yield was estimated to 49% as there were some losses of TMPA during all the purification steps, most notably the pressure filtration.

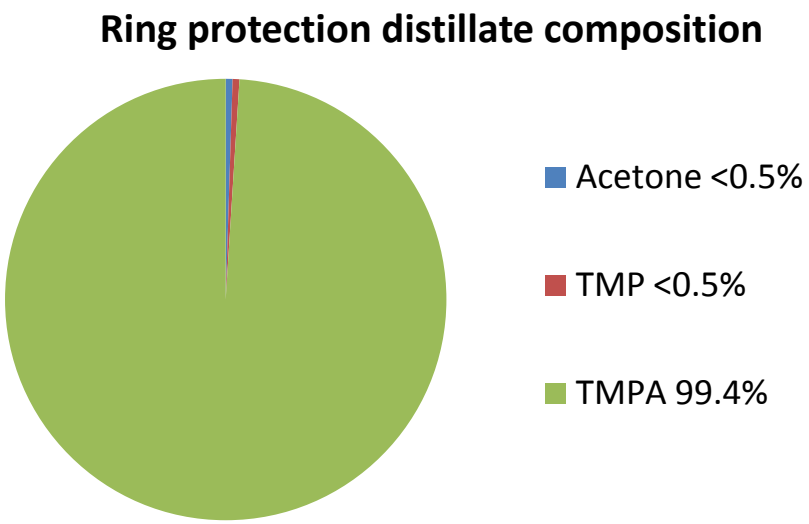


Figure 20, Purity of the synthesized TMPA

The final composition from the transesterification after evaporation is shown below in Figure 21. The composition was yet again determined with gas chromatography. Note that the green portion of the mixture is the desired product. The conversion, selectivity and thus yield of TMPA were all very high, approximately 98% by mass.

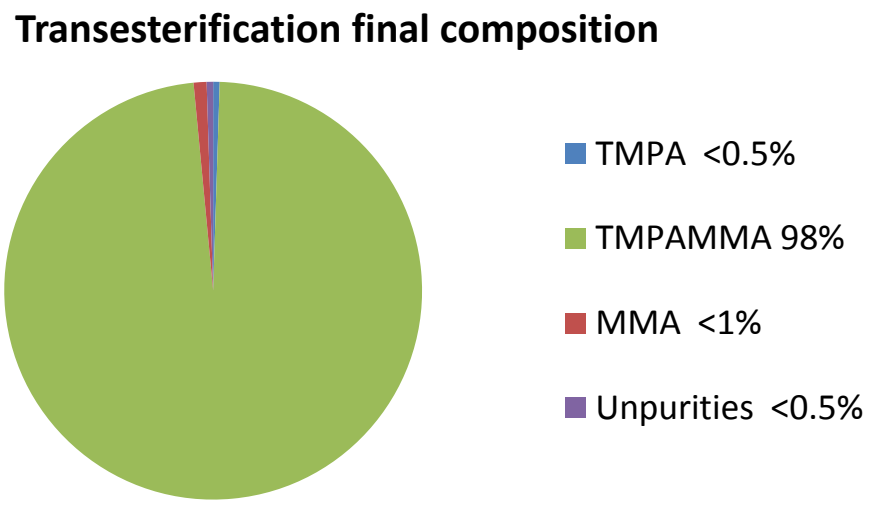


Figure 21, Purity of TMPAMMA after the transesterification

The purity of the product is decreased with each additional synthesis step and after the ring opening of the monomer the purity of the desired product is down to 97.4 % in this last synthesis step as shown in Figure 22. The selectivity is about 100% and the conversion and yield of the TMPA-MMA is 85%.

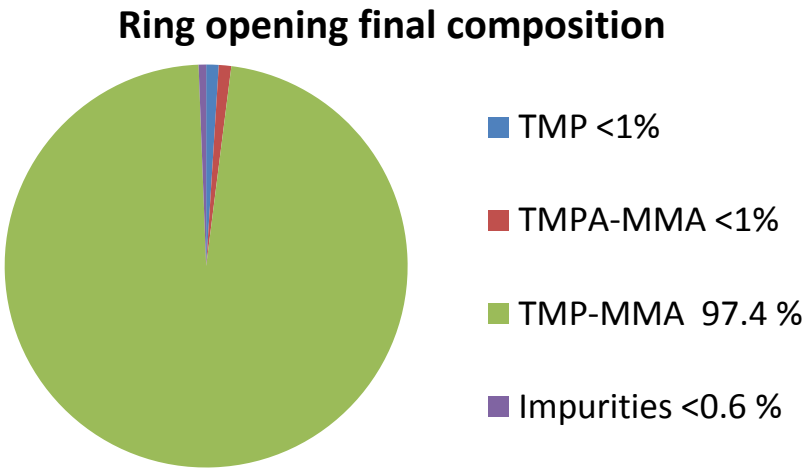


Figure 22, TMPMMA purity after removal of the ring protection

Enzymatic cyclization process

Low temperature enzymatic approaches were initially tested, the reactions were monitored and the composition was determined with gas chromatography as shown in Figures 24, 25 and 26.

The structure of TMPMMA, a single coupled TMPMMA-DMC (the precursor to TMPC-MA) and a dual coupled TMPMA-2xDMC is shown below in Figure 23. The process is otherwise the same as shown and discussed earlier in the cyclization theory section.

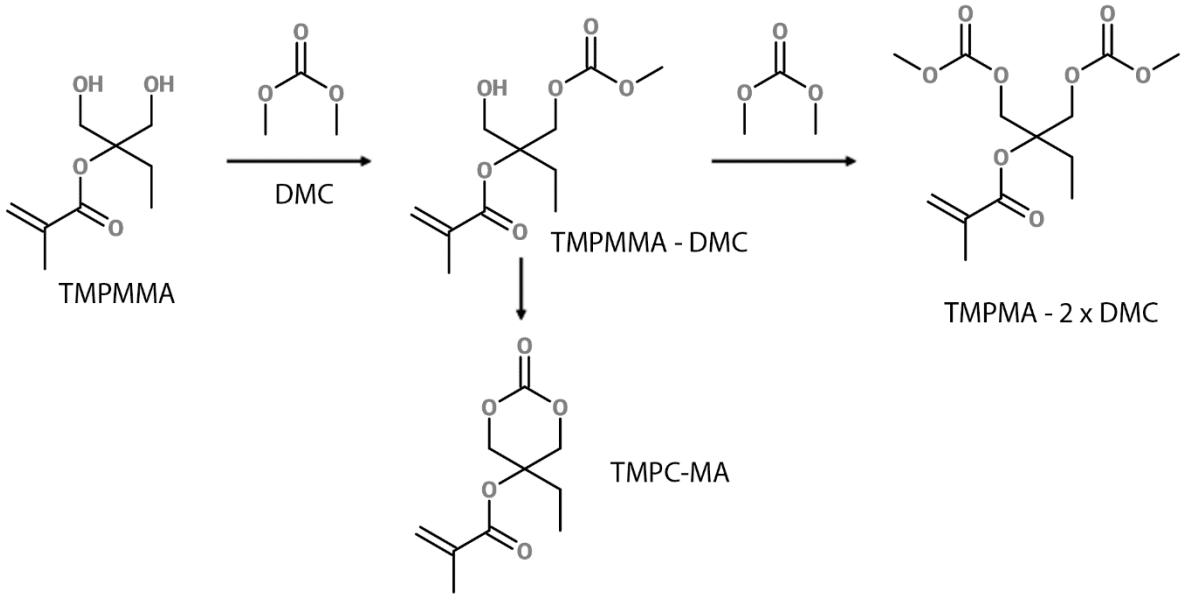


Figure 23, Overview of the cyclization process

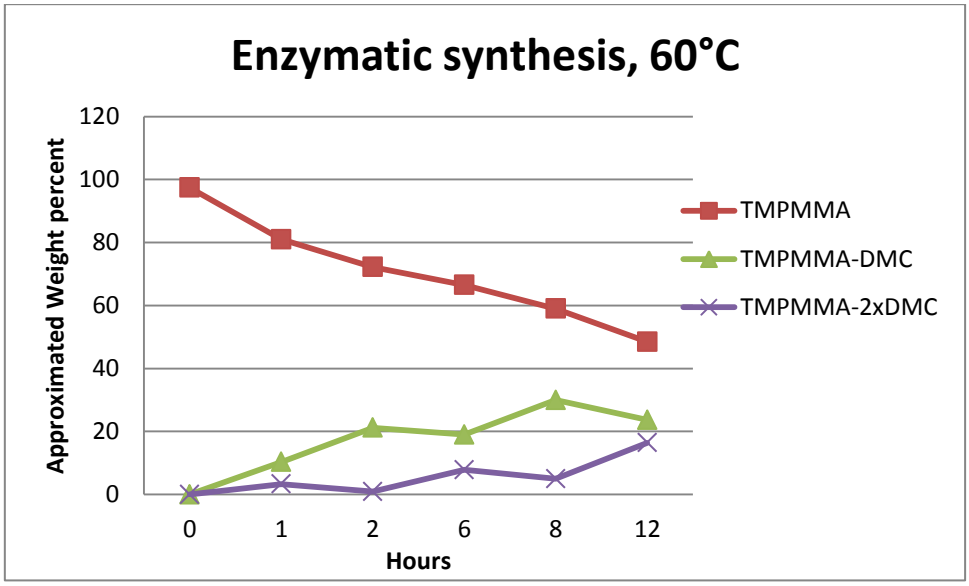


Figure 24, Weight percent of reaction mixture after evaporation

After 18 hours the approximate composition of the evaporated and filtered reaction mixture was;

TMPMMA 46.8 %, TMPMMA-DMC 35.0 % and TMPMMA-di-DMC 12.0 %.

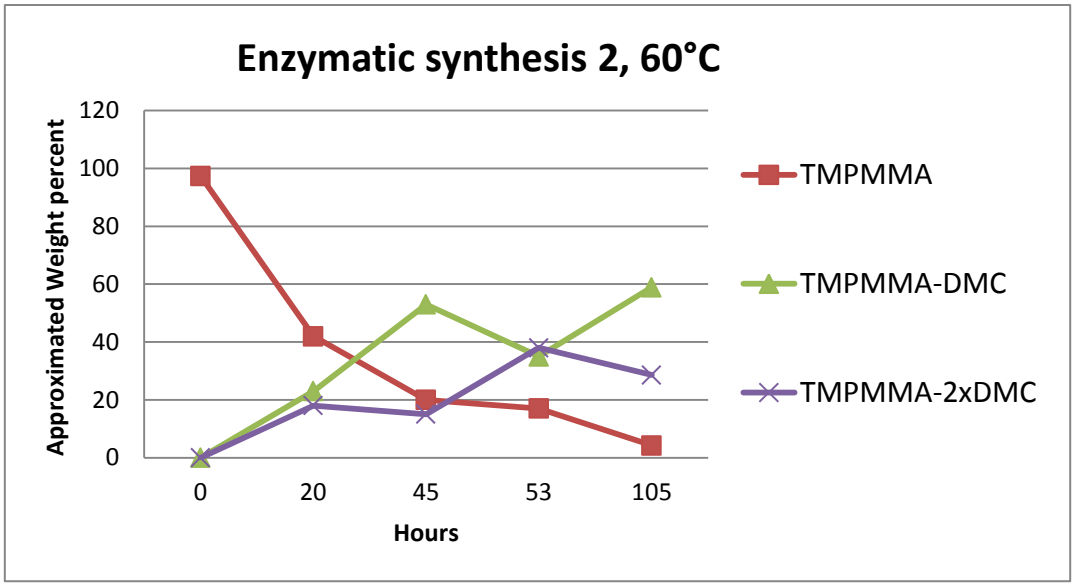


Figure 25, Weight percent of reaction mixture after evaporation

After 105 hours the approximate composition of the evaporated and filtered reaction mixture was;

TMPMMA 4.25 %, TMPMMA-DMC 58.92 % and TMPMMA-di-DMC 28.61 % and suspected 3.61% cyclic product.

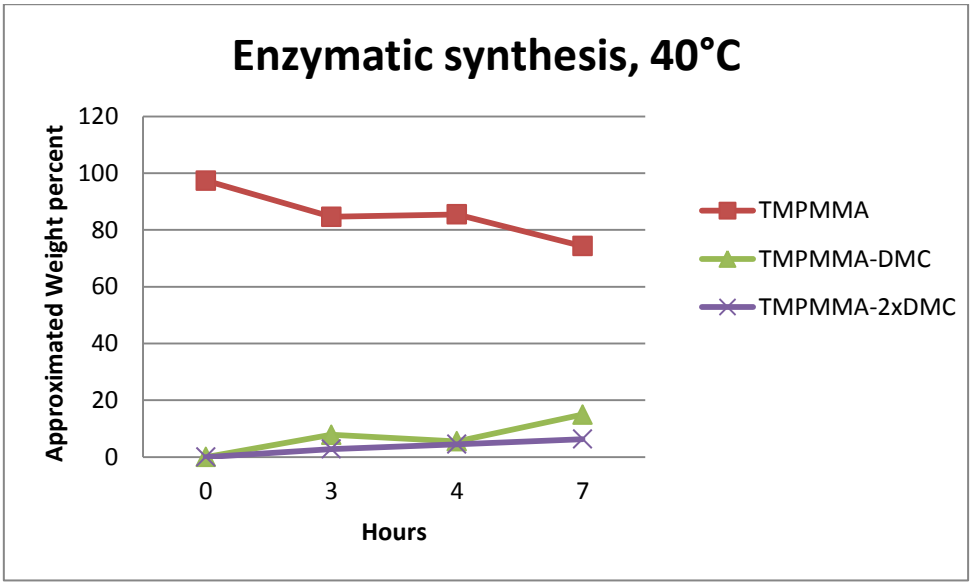


Figure 26, Weight percent of reaction mixture after evaporation

After 7 hours the approximate composition of the evaporated and filtered reaction mixture was;

TMPMMA 74.3 %, TMPMMA-DMC 14.9 % and TMPMMA-di-DMC 6.3 %.

Non-enzymatic

The non-enzymatic high temperature reaction was monitored and the reaction is depicted as a graph in Figure 27 below.

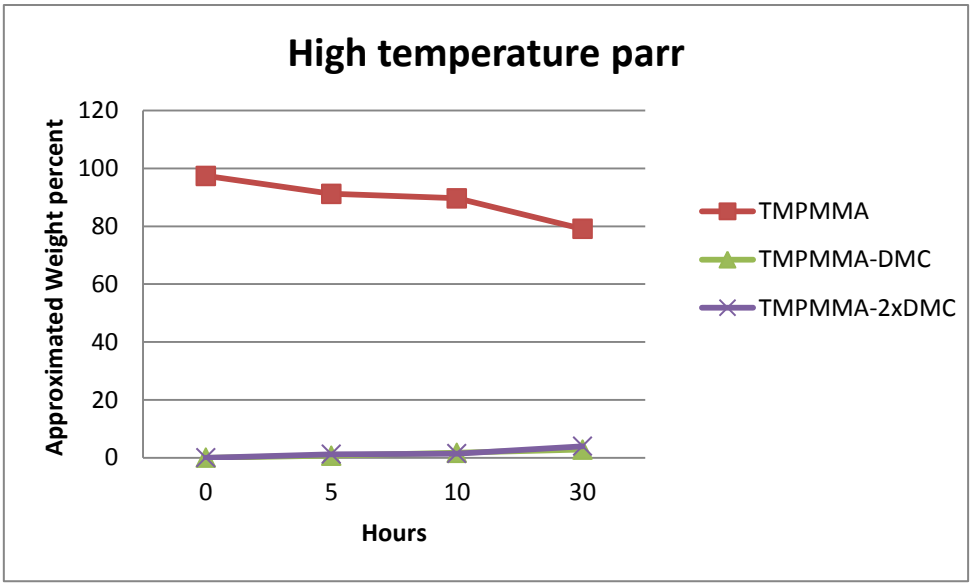


Figure 27, Weight percent of reaction mixture after evaporation

Clarification data for 10 hours;

TMPMMA 89.7 %, TMPMMA-DMC 1.7 %, TMPMMA-di-DMC 1.4 % and an estimate of 0.5 % cyclic TMPMA carbonate.

Clarification data for 30 hours;

TMPMMA 79.1 %, TMPMMA-DMC 2.8 %, TMPMMA-di-DMC 3.95 % and an estimate of 1.4 % cyclic TMPMA carbonate.

Hydroxide catalyzed

A non-enzymatic hydroxide catalyzed high temperature process was evaluated and the composition monitored, the results are presented in Figure 28.

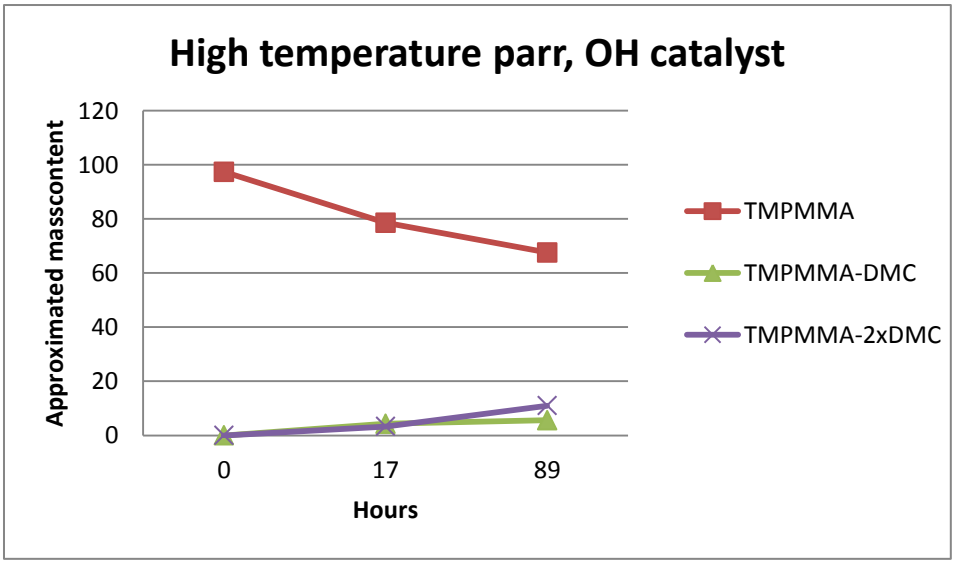


Figure 28, Weight percent of reaction mixture after evaporation

Approximate composition after 89 hours;

TMPMA 67.6 %, TMPMMA-DMC 5 .6%, TMPMMA-di-DMC 11 % and an estimate of 5.4 % cyclic TMPMMA carbonate.

Due to concerns that the molecular sieves were neutralizing the catalyst a second test was conducted with an increased amount of hydroxide as described in the method section. The results are presented in Figure 29.

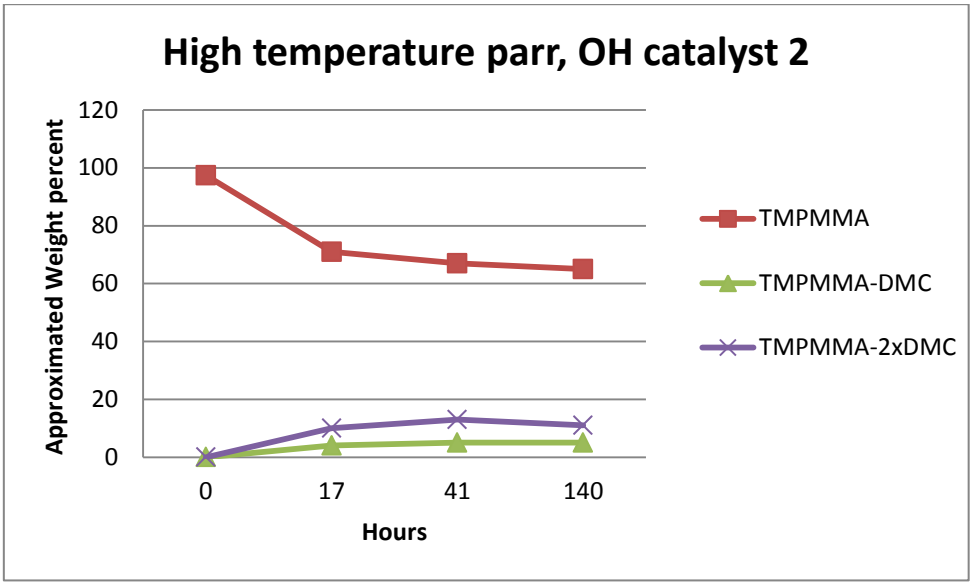


Figure 29, Weight percent of reaction mixture after evaporation

Approximate composition after 140 hours;

TMPMMA 65 %, TMPMMA-DMC 5 %, TMPMMA-di-DMC 11 % and an estimate of 5 % cyclic TMPMMA carbonate.

High temperature post-enzymatic process

The filtered solution from the first enzymatic process were introduced into the parr reactor and the process was studied for 12 hours as shown in Figure 30.

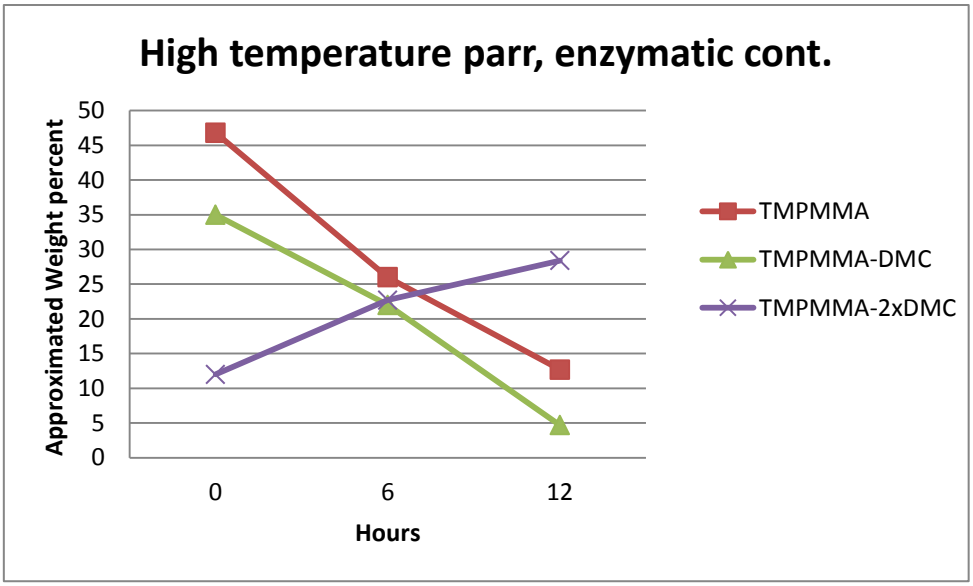


Figure 30, Weight percent of reaction mixture after evaporation

Approximate composition after 12 hours;

TMPMA 12.7 %, TMPMA-DMC 4.7 %, TMPMA-di-DMC 33.6 % with 7.7 % assumed cyclic TMPMA carbonate, the desired product.

DBTDL catalyst

The graph in Figure 31 shows the reaction mixture composition after the addition of the catalyst.

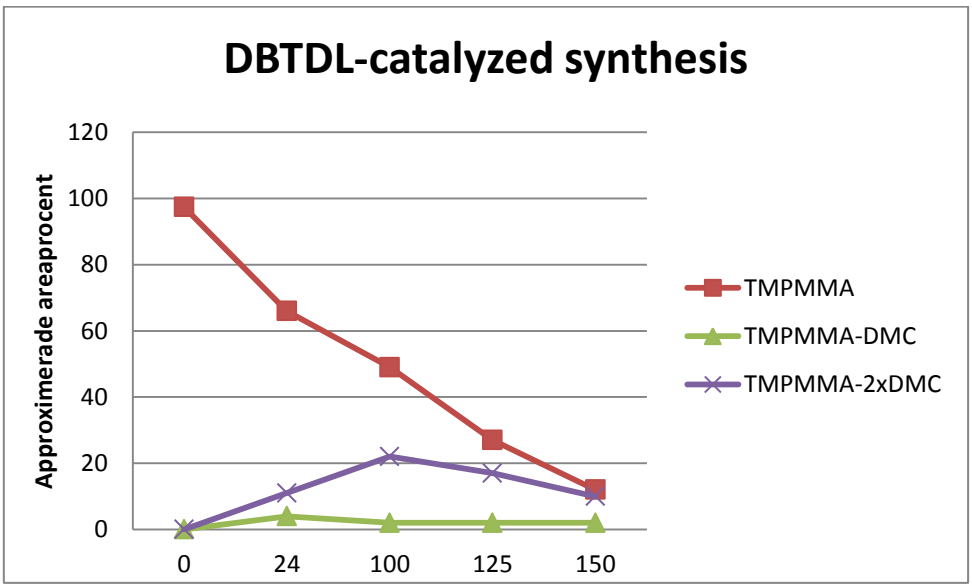


Figure 31, Weight percent of reaction mixture after evaporation

Approximate composition after 150 hours;

TMPMA 12 %, TMPMA-DMC 2 %, TMPMA-di-DMC 10% with over 35 % unidentifiable products. There was some polymerization on the molecular sieves and at the bottom of the reactor.

Crosslinking results

Larger versions of all FT-IR figures in this section can be found in the appendix under its appropriate section.

DSC

The first gradient (steadily increasing temperature) run on a blank di-TMPC sample is shown in Figure 32 with a clear peak at 101 °C and without any exothermic reactions.

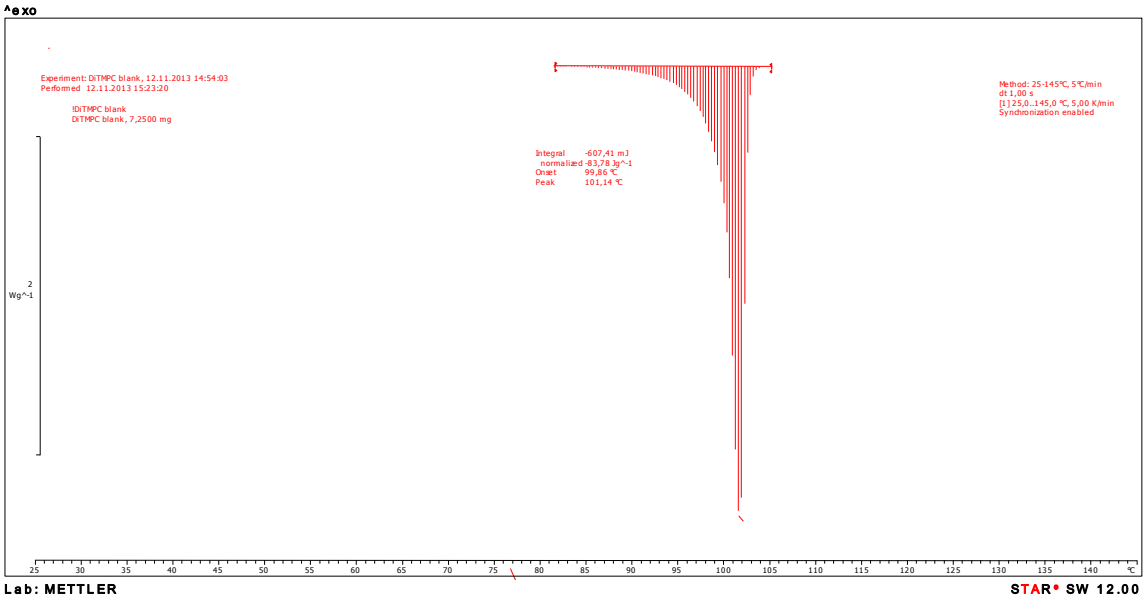


Figure 32, DSC of a pure di-TMPC sample

The Jeffamine and di-TMPC sample in black in Figure 33 is compared to the blank di-TMPC, red. A clear exothermic reaction occurs as soon as the sample is mixed with a peak at 58 °C and the reaction is supplying heat at the melting point of the di-TMPC and a small exothermic reaction is still occurring after the melting point.

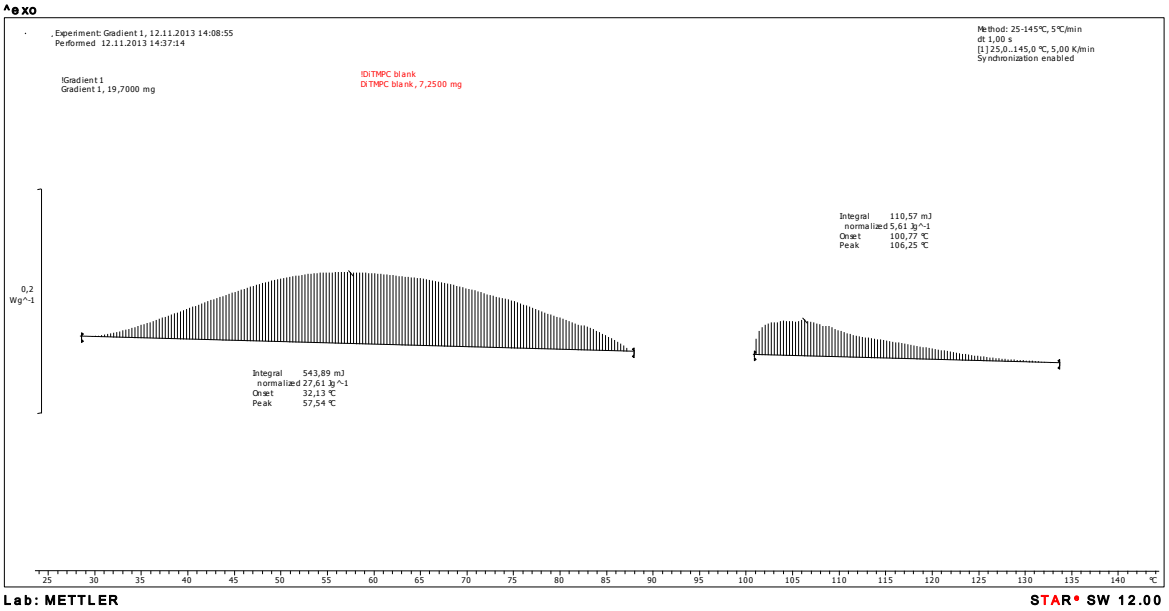


Figure 33, DSC of a Jeffamine (1.5 functionality mix) and di-TMPC mixture (black) compared to pure di-TMPC (red)

A gradient analysis of a sample mixture of Jeffamines and di-TMPC that had been stored for 10 hours at room temperature is shown below in Figure 34. No exothermic reaction is visible before the melting point. There is a small exothermic reaction occuring right after the sample has melted which is very similair to the corresponding scanning of the non-stored mixture sample.

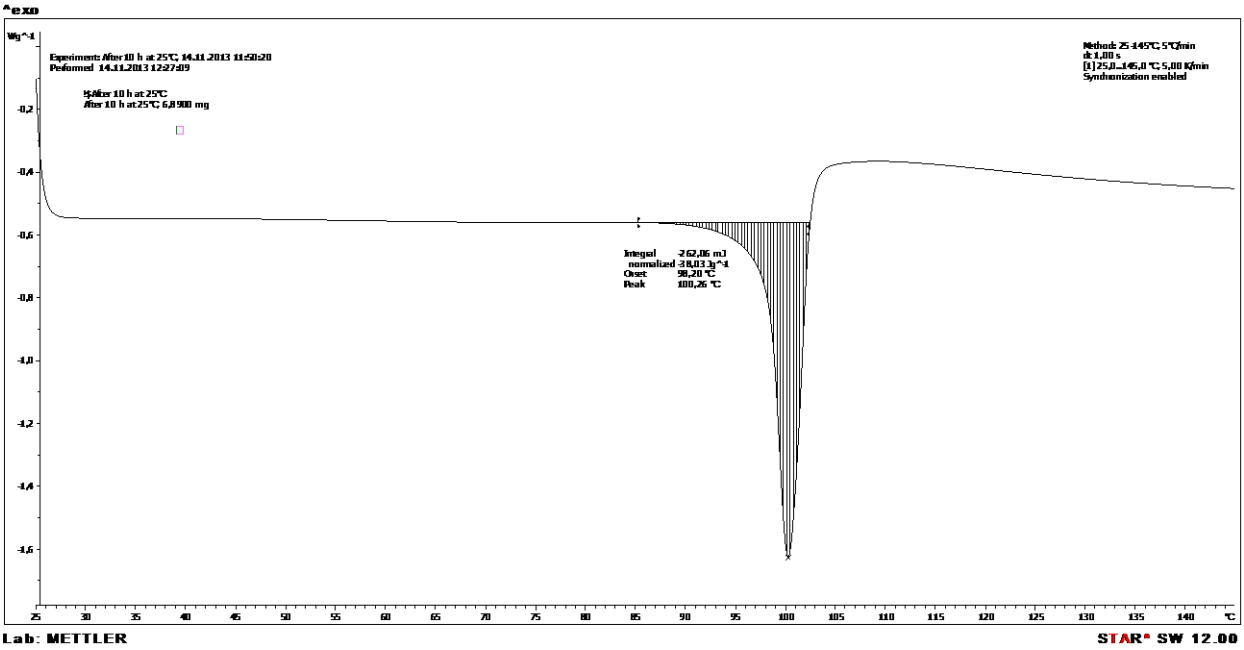


Figure 34, DSC of a reaction mixture of di-TMPC and Jeffamines (1.5 functionality mix) after being stored for 10 hours in room temperature

Reaction mixture of Jeffamines and di-TMPC monitored isothermally at 25°C for 10 hours are presented in Figure 35. A clear overall exothermic reaction is visible during the first 200 minutes of the isothermal scan. At 240 minutes a shift occurs and a very minute exothermic reaction is present afterwards for the rest of the scan.

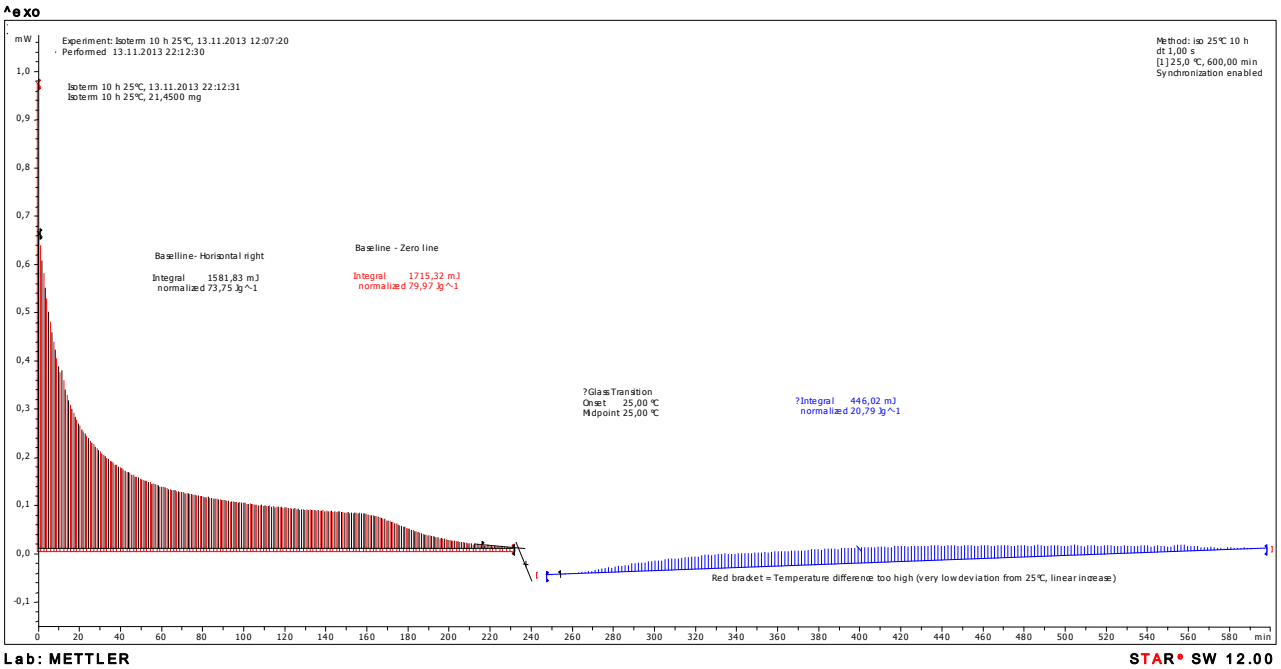


Figure 35, Isothermal DSC of a di-TMPC and Jeffamine (1.5 functionality) mixture for 10 hours

FT-IR

A full FT-IR spectrum of di-TMPC is shown in Figure 36. Prominent peaks at 1733 from cyclic –C=O [19] and many more in the fingerprint area of 1500-500 cm^{-1}.

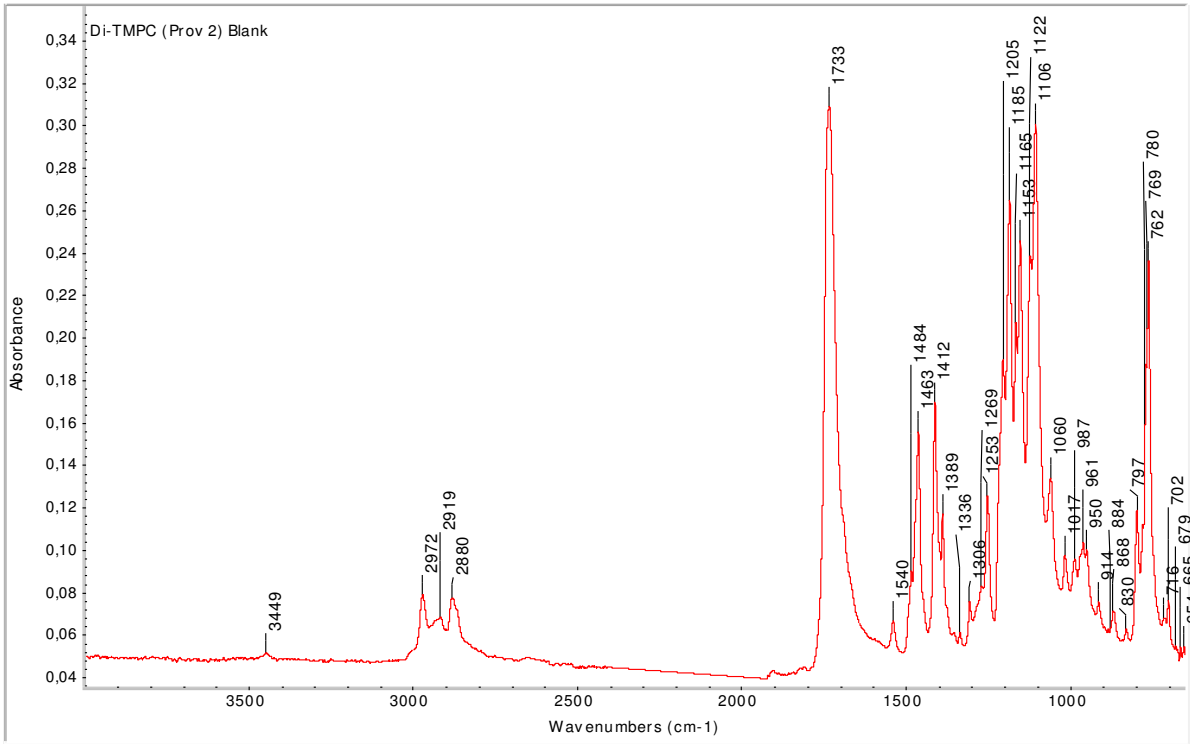


Figure 36, FT-IR spectrum of pure di-TMPC

A Jeffamine mixture (EDR-176 mixed with T-403 at 1:1 mole) spectrum is shown below in Figure 37. A strong ether peak at 1100 cm^{-1} and some other distinctive peaks are seen.

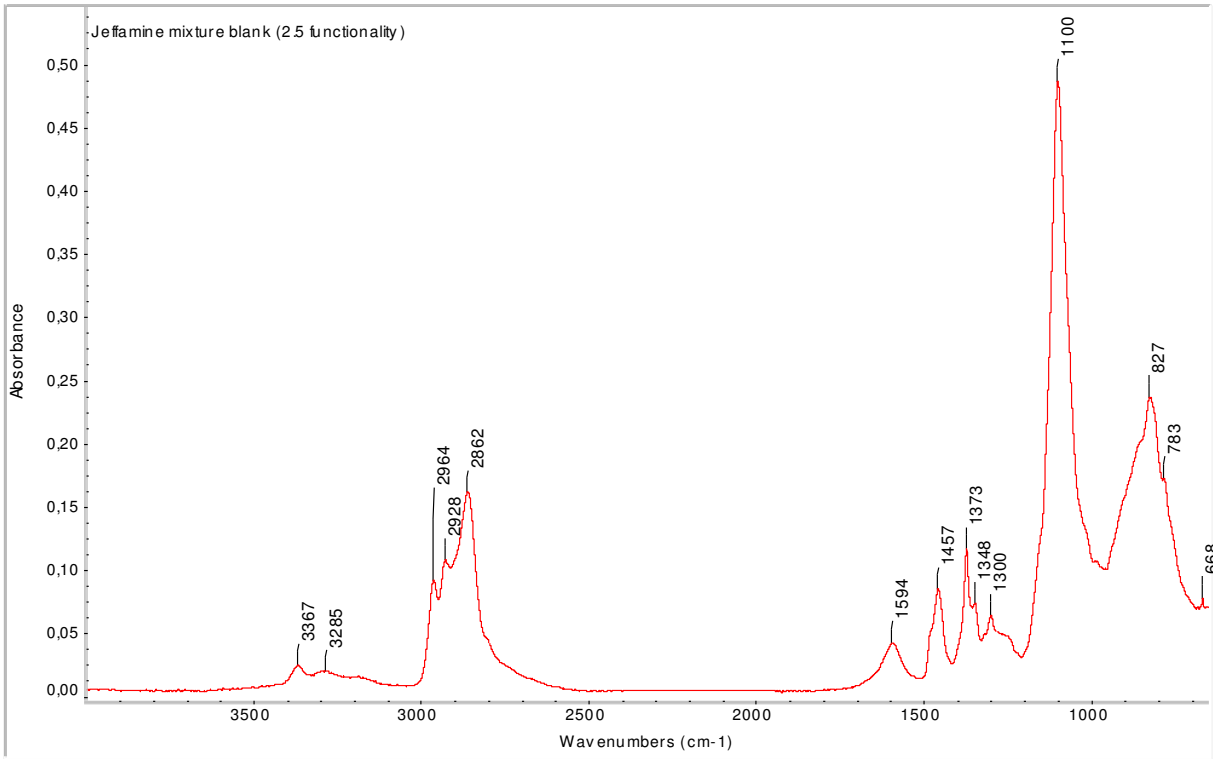


Figure 37, FT-IR spectrum of the Jeffamine mixture

The FT-IR scan of a mixture sample of Jeffamines and di-TMPC which were run through a gradient DSC are shown in Figure 38. It is clear that some reaction have taken place. The carbonate –C=O peak at 1733 cm^{-1} have shifted to a C=O urethane bond band of 1694 cm^{-1} [13][19][20][21][22][23] and a C-N stretch and N-H bend in a urethane bond is visible as the peak 1539 cm^{-1}. Another peak at 1242 cm^{-1} can be attributed to C-O in hydroxy-urethane with a very prominent OH broad band at 3350 cm^{-1}. A small peak at 1746 cm^{-1} does point towards existing unreacted di-TMPC even after the DSC run. [19]

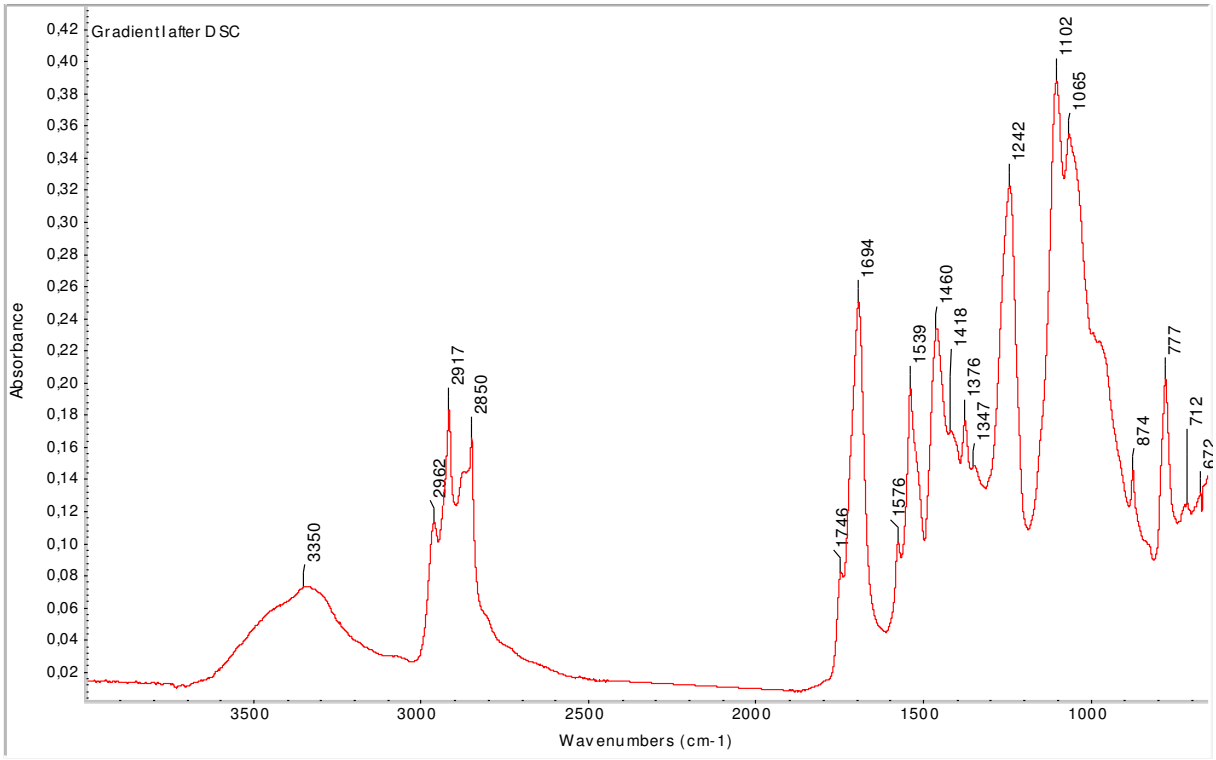


Figure 38, FT-IR scan of a reaction mixture of di-TMPC and the Jeffamines after a gradient DSC

A comparison compilation of the blanks of di-TMPC (middle, blue), the Jeffamine mixture (lower, blue) and the reaction mixture (top, red) is shown in Figure 39. Just as in previous scans, clear peaks from both reactants are still present in the reaction mixture but there is some indications of a reaction occurring at room temperature. The carbonate –C=O peak at 1733 cm^{-1} have shifted to a C=O band of 1703 cm^{-1} and a C-N stretch and N-H bend in a urethane bond is visible as the peak 1531 cm^{-1}. Another peak at 1249 cm^{-1} can be attributed to C-O in hydroxy-urethane with an OH peak at 3350 cm^{-1}. As there is still a shoulder on the 1703 cm^{-1} peak it seems like not all cyclic carbonate have reacted. [19]

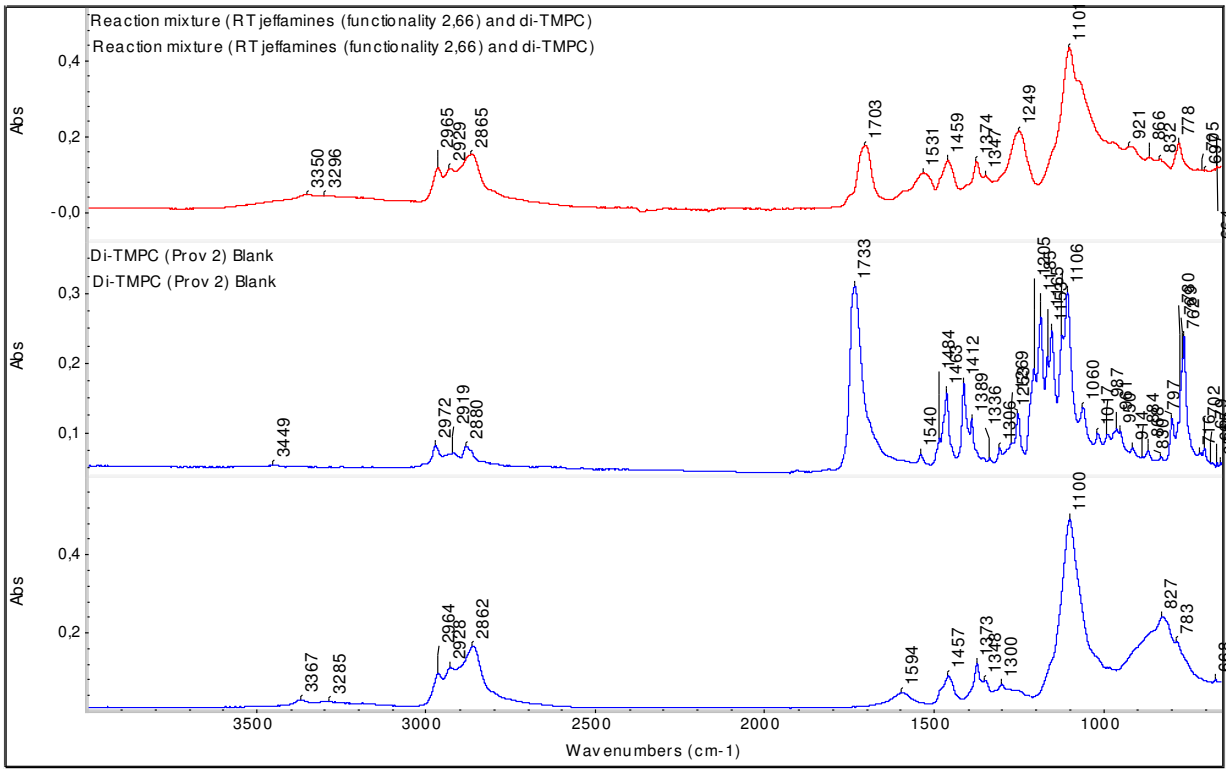


Figure 39, Comparative compilation of the polymer reaction mixture (red), pure di-TMPC (middle, blue) and the Jeffamine mixture (low, blue)

A full spectrum of a polymer sample which have been through a gradient scan in the DSC (red) and a room temperature mixture (green) is shown in Figure 40. The much greater formation of urethane bonds are evident in the 1703 cm^{-1} peak (as opposed to the twin 1751 cm^{-1} and 1714 cm^{-1} peaks of the room temperature mix), the C-N and N-H peak at 1531 cm^{-1} and the hydroxyl-urethane C-O peak at 1249 cm^{-1} coupled with the greater OH peak at 3350 cm^{-1}.

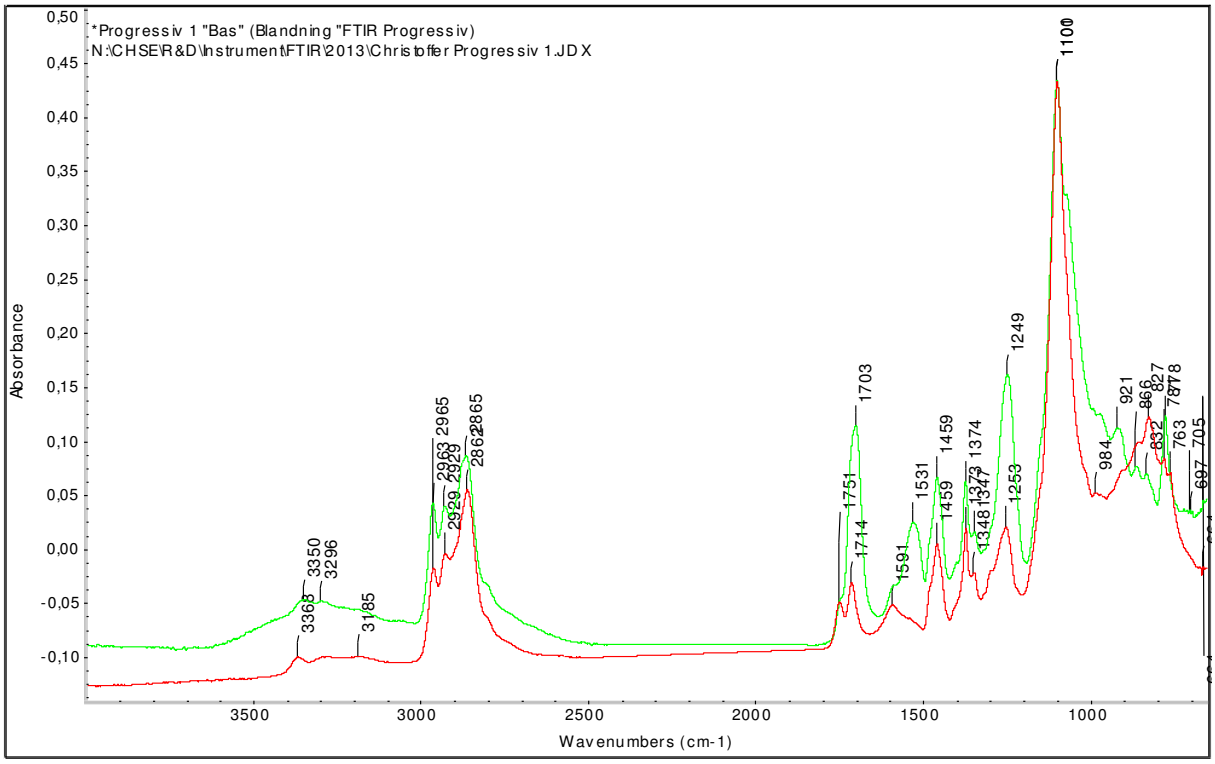


Figure 40, Stacked FT-IR spectrum of a reacted sample (green) after a gradient DSC run and a Jeffamine – di-TMPC mixture at room temperature (red)

A progressive scan was conducted in room temperature with an initial scan and an additional scanning every half hour and an additional scan after 24 hours. The fully stacked progressive spectrums can be viewed in Figure 41. As seen below the peaks are mostly changed slightly with a few exceptions such as the 1100 cm^{-1} unchanged peak. There are a lot of changes in the fingerprint area which are hard to attribute to any specific groups or bonds.

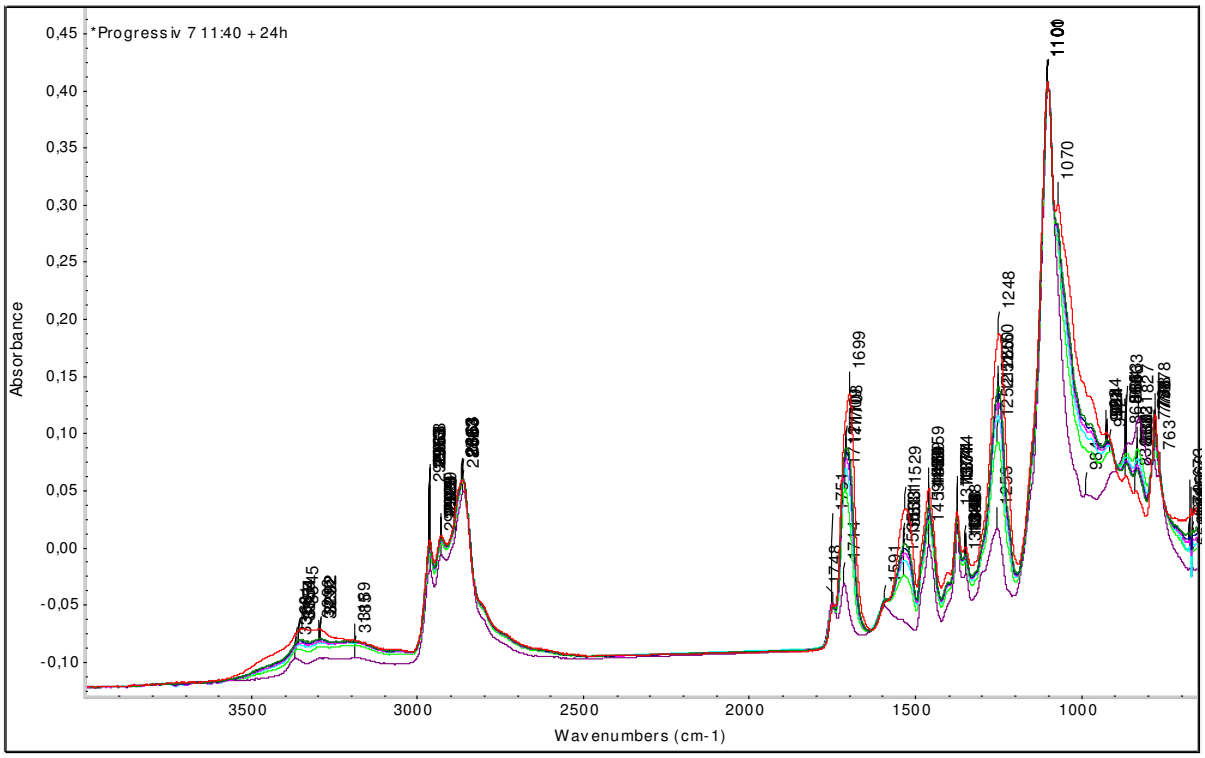


Figure 41, Progressive scans of a sample of di-TMPC and Jeffamines, scans were taken every half hour and lastly an additional scan after 24 hours (red)

The lower end (3550 - 2725 cm^{-1}) of the progressive scans is shown in Figure 42. With this magnification the notable changes are visible at the important peak 3345 cm^{-1} which is attributed to the formation of –OH in hydroxy-urethane bonds.

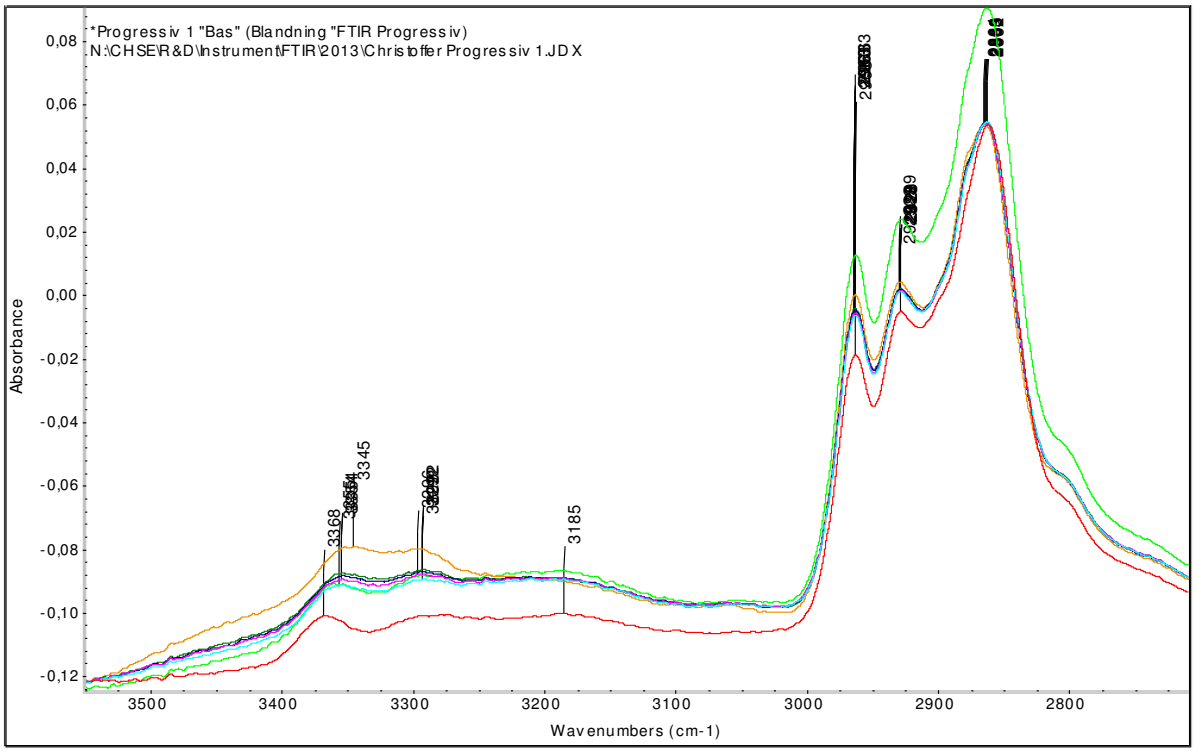


Figure 42, Lower end of the progressive scans of a sample of di-TMPC and Jeffamines, scans were taken every half hour and lastly an additional scan after 24 hours (brown)

The middle part (1840 – 1175 cm^{-1}) of the progressive scans is presented in Figure 43. The shift from 1750 cm^{-1} C=O band of the cyclic carbonate to the C=O urethane bond band at 1700 cm^{-1} is clearly visible. There is however a much defined shoulder at 1750 cm^{-1} even after 24 hours which means there are still some di-TMPC left. The formation of C-N stretch and N-H bending (from urethane bonds) at 1530 cm^{-1} is also easily spotted. Some increase in the C-O from the urethane bond peak at 1250 cm^{-1} is also visible.

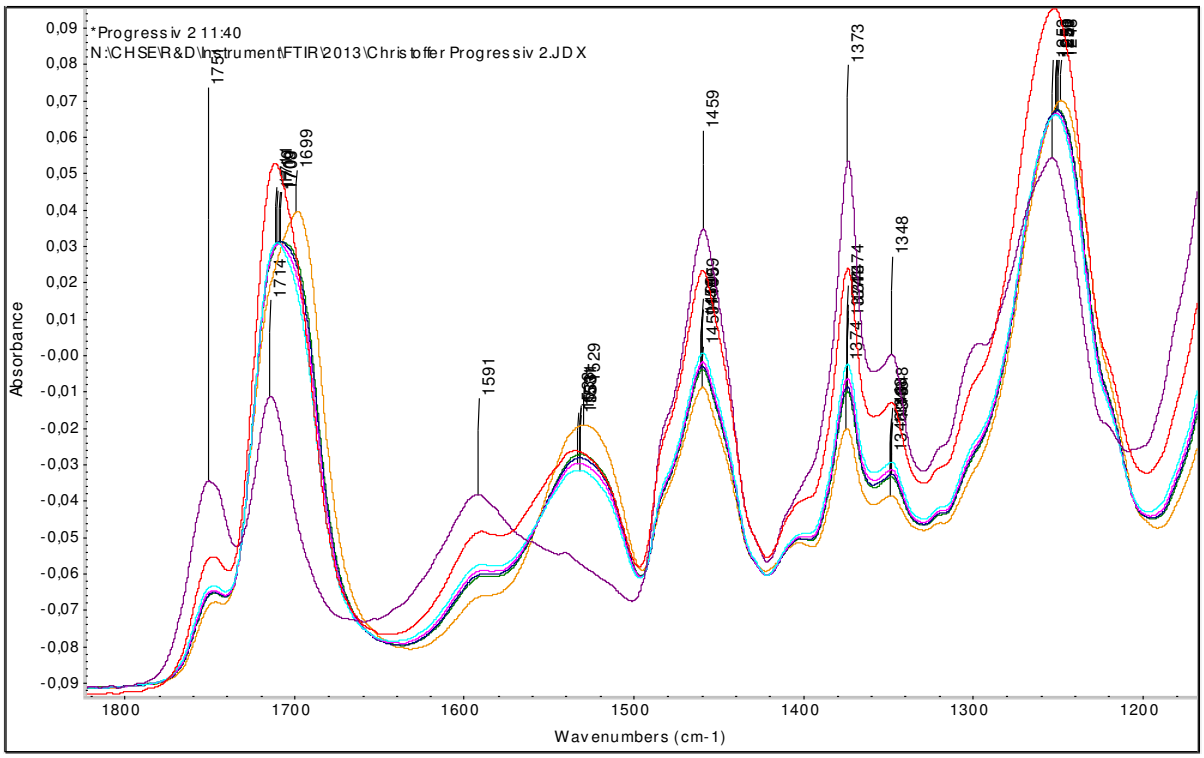


Figure 43, Middle part of the progressive scans of a sample of di-TMPC and Jeffamines, scans were taken every half hour and lastly an additional scan after 24 hours (brown)

The upper end (1180-675 cm^{-1}) of the progressive scans is found in Figure 44. Some changes are observable in this lower spectra but it is very difficult to pin any changes to any one cause.

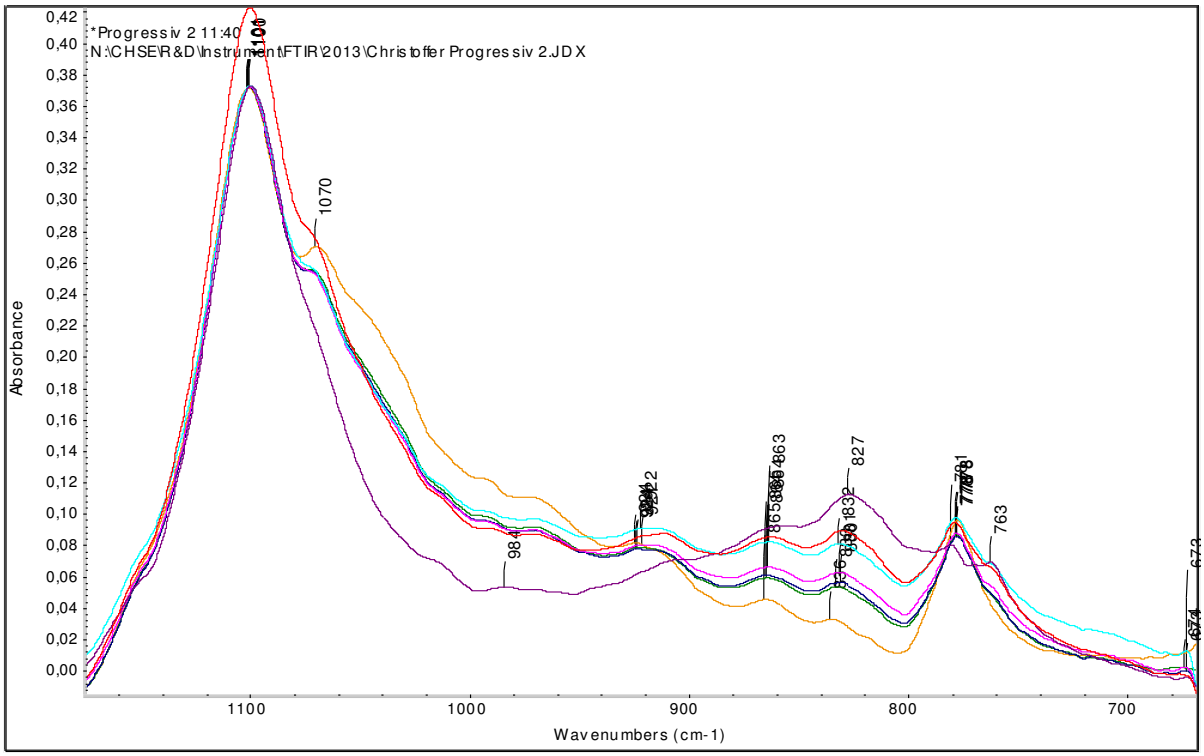


Figure 44, Upper end of the progressive scans of a sample of di-TMPC and Jeffamines, scans were taken every half hour and lastly an additional scan after 24 hours (brown)

Discussion and conclusions

Monomer synthesis

Similar monomer synthesis steps have been documented internally by Perstorp AB and the synthesis route was chosen as the purity of the produced monomer and the equipment needed were favorable and available.

Ring protection

The ring protection step of the monomer synthesis is straightforward and easily done with a moderate conversion and a good selectivity. There are almost no unreacted reactants left in the end product after refinement but the post synthesis purification requires more equipment and setup than the synthesis itself. To speed up the reaction time and to increase the conversion rate of TMP there is a surplus of acetone in the reaction mixture. The acetone is easily removed with a low pressure evaporator at a low temperature as to not damage the formed product. Further purification is necessary to separate the ring protected TMPCA from the TMP. Vacuum distillation at a higher temperature than a regular evaporated can produce a quite pure product. The product seems to be thermostable at temperatures of over 130°C.

Some of the catalyst is present despite the neutralization and precipitation of the neutralized acid. There is no need to further remove all traces of the acid as there is not enough to catalyze further reactions while being stored or in further synthesis steps. It is worth noting that water can reverse the ring protection during storage and further synthesis steps which is why it is very important to remove as much water as possible after the neutralization.

Transesterification

There are several technical challenges with the transesterification but with proper equipment the synthesis is neither tedious nor complex. There was good conversion rate and selectivity. There were initial concern of polymerization in the gas phase which was why an inhibitor was added to the reaction mixture and nitrogen gas was bubbled into the reactor. A technical fault in the reflux unit caused the automatic top column temperature control unit to fail and the reflux had to be manually controlled. This should not have had any impact on the results of the synthesis. There were remnants of the added catalyst present after evaporation but there seems to be no effect on a cooled mixture at moderate storage times of up to a week.

Ring opening

The ring opening has a simple setup and fast reaction time with good yield and few technical difficulties. There is some risk for polymerization which occurred at the initial test-runs, an estimate of 40% of the product was lost. The polymerization is believed to be initialized by the added catalyst, there was no “free” polymer particles but only some sort of gelatinous mass with a lot of catalyst granules inside.

DMC coupling and cyclization

Enzymatic DMC-Coupling

The enzymatic process showed great promise on paper but the results were not good enough when tested. The conversion rate of TMPMA was higher than on every other method tested but the enzyme did convert a lot of the desired product to further coupling and some polymerization.

The reason for the much slower reaction rates which were recorded is believed to be the addition of the methacrylate group which could act as both a steric and a group charge hindrance to the enzymes active sites. There were also concerns regarding the activity of the enzyme being lowered by the lack of water in the reaction mixture. Novozyme estimated that a few drops of water per half a liters of reaction mixture would be sufficient. There was however every possibility that the water added may have been fully absorbed by the molecular sieves that were added to absorb methanol.

The reaction rate is strongly dependent on the reaction temperature. The difference between 40 °C and 60 °C is easily spotted when comparing the different content graphs. There was however a risk of deactivating the enzyme at a too high temperature. A portion of the enzyme might be slowly deactivated over time when used in 60 °C.

The enzymes active sites might have been deactivated by blockage. The larger multi-coupled products or the methacrylate could have created a polymer layer on the enzyme, effectively blocking any active sites. There was some polymerization visible to the naked eye during the testing. There were no resources to analyze any reaction mixtures for polymer particles and their sizes.

Despite having slower reaction rate with the added methacrylate group the enzyme was the best way to create a DMC coupled monomer. The last tests confirmed that after 35-50 hours the mass content of TMPMA-DMC was over 50% with 20 % unreacted TMPMA and below 20% double coupled TMPMA-2xDMC. That suggests that if further tests were possible a “sweet spot” for terminating the synthesis could be found and used for further purification and/or cyclization.

High temperature non-Enzymatic coupling

The promising reports were unreproducible in this master thesis. Despite several tests the reaction would not occur at lower temperatures and despite having a reaction temperature of 150 °C there were not a fast enough reaction for it to be of interest. There was however some indications of there being cyclic product in very low amounts.

Hydroxide catalyzations

Hydroxide had been used on site by other engineers to enable some similar reactions and it would not initiate polymerization like an acid. The tests were very disappointing despite given very long reaction times.

There was however some complications with using hydroxide as a catalyst which may have prevented any catalyzations that would have occurred otherwise. There was firstly the concern that the hydroxide ions would be trapped inside the molecular sieves where they would not have been able to catalyze the intended reactions. There was also concerns that the hydroxide ions would be bound to acid sites on the molecular sieves and thus not being able to participate in any catalyzations. Increasing the amount of hydroxide did not seem to have any impact on the result.

The concerns mentioned above encouraged a second test with a much higher addition of hydroxide ions, but every sample from the reaction mixture had a pH of below 7 and despite the addition of five times more hydroxide and almost double in reaction time there was no improvement, on the contrary the reaction rate seemed to be slower than the previous test. It is possible that a very large amount of hydroxide could have made the solution alkaline but the effects on the molecular sieves and the reaction mixture in general would be very unpredictable. The idea was scrapped due to the time limitations.

DBTDL catalyzation

There was another wild card of a catalyst which were proposed, DBTDL which were tested in a very long experiment. The samples shows a steady decrease in reactant content but a more or less stable content of circa 15% of double coupled TMPMA, and virtually no single coupled TMPMA. After the analysis of the samples were completed it was obvious that there was some formation occurring in the reactor. Gas chromatography showed a lot of unidentifiable substances and the reactor contained a lot of polymerized product. There were no resources to analyze the polymer itself or the presence of polymer particles in the reaction mixture but it is believed that the catalyst was very efficient at coupling more than one DMC to the reactants and creating polymers of either DMC coupled TMPMA or a polyacrylate skeleton polymer.

As there was no confirmed desired product the DBTDL was eliminated from the list of usable synthesis catalysts.

High temperature post-enzymatic cyclization

Since the cyclization process is thought to be done thermically there was a chance to cyclize parts of the single coupled product produced by the enzymatic process and to thermically couple more DMC to unreacted TMPMA a sample from the first enzymatic process were inserted into the high temperature reactor and given fresh molecular sieves. The results were more in favor of coupling several DMC groups than to cyclize or create more single coupled TMPMA, the precursor to the desired cyclic product.

This means that the cyclization process would have to have a high concentration of TMPMA-DMC beforehand and that a change in solvent would be necessary as to minimize the risk of adding more DMC to the precursor TMPMA-DMC. That could eventually be achieved by finding a "sweet spot" with the enzymatic process, evaporating the unreacted DMC and adding another compatible solvent, such as acetonitrile, and running the cyclization process in a higher temperature.

Crosslinking NIPU

Over the course of the testing there were changes in plans due to compatibility issues of some of the reactants used for this experiment.

Solubility and polymerization testing

The solubility issues with the Jeffamines and the di-TMPC made any attempts on film testing obsolete. The grains of cyclic carbonate were large enough to disturb the testing the physical properties of the films entirely. There was however strong signals that there was polymerization happening.

The smaller polyetherdiamine EDR-176 is much more reactive than the tri-amine-functional T-403 which would be why there was some increase in viscosity but not a total polymer formation. It was suggested that increased temperature could increase the solubility of the carbonate in the Jeffamines. At temperatures close to 90 °C there seemed to be an increased solubility but it was soon too viscous to stir as the polymer was formed. It was later discovered in a DSC-scan of di-TMPC that the cyclic carbonate wasn't becoming dissolved into the Jeffamines as much as it was being melted and thus reacted very quickly with either of the amines to create a polymer. It was simply not possible to use this method for creating films on plates as the reaction happened too quickly. You would either get a grainy solution which would ruin the film or a polymer which would not be drawn to a thin film.

The testing did confirm other valuable data. There was very obviously some reaction happening at both a low temperature and very fast at a higher temperature.

As the intended polymer mixture did not work there were workarounds which involved different solvents for the cyclic carbonate, these included cyclohexanone and methyl-ethylketone MEK. There was however problems with both. The cyclohexanone did solve the cyclic carbonate well enough to remove the larger grains but only in a large enough concentration to render any film-making impossible. Trying to increase the temperature to create a super saturated solution failed as the solved cyclic carbonate would crystallize very fast upon cooling. There was never a clear solution with completely solved cyclic carbonate with either of the solvents tested, at any temperature tested. MEK provided similar problems and could not be used in the process of creating polymer films.

As it seemed impossible to create polymer films within the time constraints, the analysis of the polymer reaction and confirmation of the product formed was made a priority.

DSC

As mentioned earlier, the blank di-TMPC gradient DSC showed a clear melting point at 100-103 °C with some melting as low as 90 °C. This indicated that the earlier results of a polymer formation could be a polyurethane polymer formed with the Jeffamines in the test solution.

The second scan confirmed an exothermic reaction happening at temperatures as low as 35 °C. There was also a prominent exothermic reaction after the sample was fully melted suggesting immediate reaction occurring at the melting point which continued after the sample was fully melted, or that the reaction was so exothermic that there it was self-sustainable while melting the cyclic carbonate.

A sample that had been stored at room temperature for an extended period of time and was then scanned with a gradient DSC revealed that there was no reaction occurring before the melting point. This could suggest that the more reactive EDR-176 can in fact create a polymer with the cyclic carbonate at room temperature given a long time. At and after the cyclic carbonate have melted there is an exothermic reaction which also suggest polymer formation.

The isothermal DSC scan at 25 °C confirms that there is a reaction occurring at low temperatures. The intensity is gradually lowered and after 4 hours the reaction is almost at a stop.

FT-IR

It is very difficult to say exactly what is happening in the reaction mixture with only DSC data but there are strong indications of a urethane bond forming from the FT-IR data. There are problems with shifting peaks and complicated system stretching and vibrations in the lower end of the spectra which makes exact peak identification difficult. However, some comparisons with similar literature data [13][19-23] indicates the formation of some urethane bonding. Another problem with the acquired scans is the relative absorbance. The scans are dominated by some peaks which may overlap some of the smaller peaks.

When determining whether the di-TMPC have reacted with the Jeffamines to create urethane bonds there are several groups or bonds to look for. Firstly the cyclic structure of carbonate is broken and a free hydroxyl group is created. The Jeffamines primary amine groups are bound to create a urethane bond, but the Jeffamines macrostructure is unchanged which can be observed at 1100 cm^{-1} where the ether bond of the Jeffamines are.

It is difficult to say which reactions and interactions create the majority of the peaks and broad bands conclusively but it is a fair estimation that some urethane bonds are formed at room temperature.

Having a sample scanned in situ at a higher temperature would probably result in more distinctive peak differences as the reaction time would speed up and the conversion rate would increase. Due to time and equipment issues these scans were not possible. As discussed above specified wavelength scanning would be desirable as full spectrum scanning have very large peaks which makes smaller peak identification and quantification difficult.

Future work

There are several ways to continue this research of 6-membered cyclic carbonates for the use of NIPU. Unfortunately this master thesis was unable to provide any conclusive data regarding the polymers characteristics or the reactivity of the components.

Phenol-, or di-ethyl-carbonate

There could be a better way of forming the cyclic carbonate for the precursor of methacrylated or other six-membered cyclic carbonates. A suggestion for future research include the creation of a di-phenyl-carbonate or a di-ethyl-carbonate which can be decomposed thermically with a higher reactor temperature than used in the monomer synthesis in this master thesis. The reaction should take place in a reactor with reflux capabilities so that the evaporated phenol or ethanol groups can be collected from the top of the column and the bottom would contain the desired product. This would possibly enable high purity and high selectivity as the reaction may continue until the process operator have validated that all phenol or ethyl groups have been evaporated.

Solvents and molar ratios

In all instances where more than one DMC were coupled with the cyclic products there were a very large excess of DMC in the reaction mixture. Lowering the molar ratio could prevent the formation of multiple couplings and the formation of oligomers or possibly DMC-linked polymers. This would probably be feasible with either having a more viscous solution (i.e. adding less DMC) or adding another inactive solvent and having stoichiometric ratios.

Changing starting material

As there are several challenges with the tested synthesis methods chosen for this master thesis there might be other ways to easier create the same monomer by using alternate starting materials. One of the proposed monomer precursor is shown in Figure 45. This molecule has been documented to being quite easy to carbonate [24] and could thus possibly be used as an alternate route to a similar end product, a cyclic carbonate with an alyll functional group.

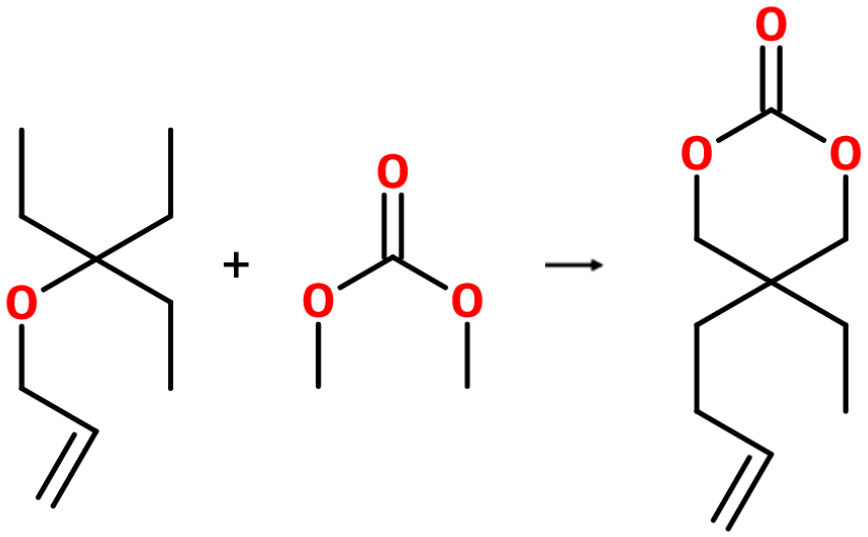


Figure 45, Alternate synthesis route for creating a suitable monomer

Polymerization with styrene to cyclic functionality

There is yet another possible way to create a polymer skeleton with cyclic carbonate functionality without having to create cyclic carbonate monomers. Figure 46 depicts the polymerization result of a monomer reactant which can be polymerized with styrene to create the end product. The cyclic carbonate content would be approximately sparse with about 3 mass-percent. But the resulting polymer could still be cross-linked with amines to create a multi-functional polyurethane polymer without the use of isocyanates.

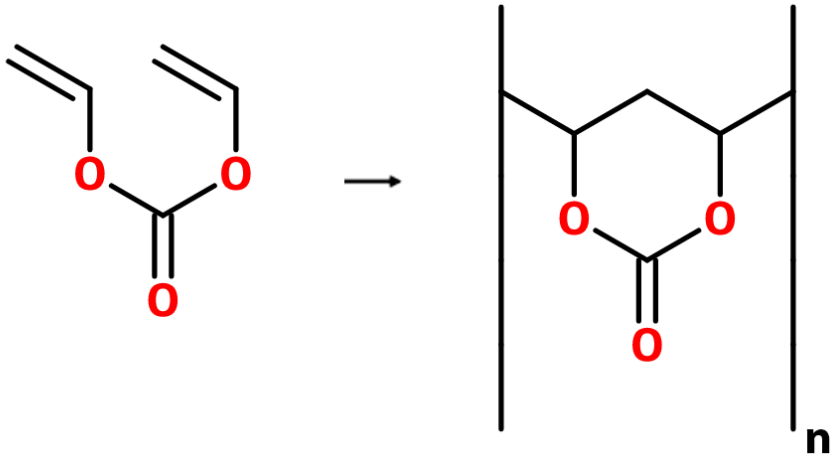


Figure 46, Styrene polymerization to create carbon skeleton polymers with carbonate functionality

Further testing with NMR and GPC

As many reactions and products were unidentified there are several other ways to help us understand, identify and verify many of the unknown aspects of the monomer synthesis. NMR could be used as both in-situ and for samples taken during the synthesis. But there is more than just the unidentified compounds which needs to be investigated, the polymers or polymer particles created in the different steps of the synthesis could be analyzed for size and occurrence which could change the approximated contents validity of the samples already taken.

Physical and chemical data for pure TMPCMMA

Lastly it would be very useful to gather physical and chemical data for pure TMPCMMA which would come to use in both the synthesis steps and moreover the purification steps taken after the synthesis. Trying to purify a product without knowing its properties can be both tedious and bound with unnecessary failures. Different purification steps would be more or less appropriate depending on the true data for the cyclic product i.e. properties discovered for the pure TMPCMMA would help stake way for the best possible way to purify the reaction mixture after synthesis.

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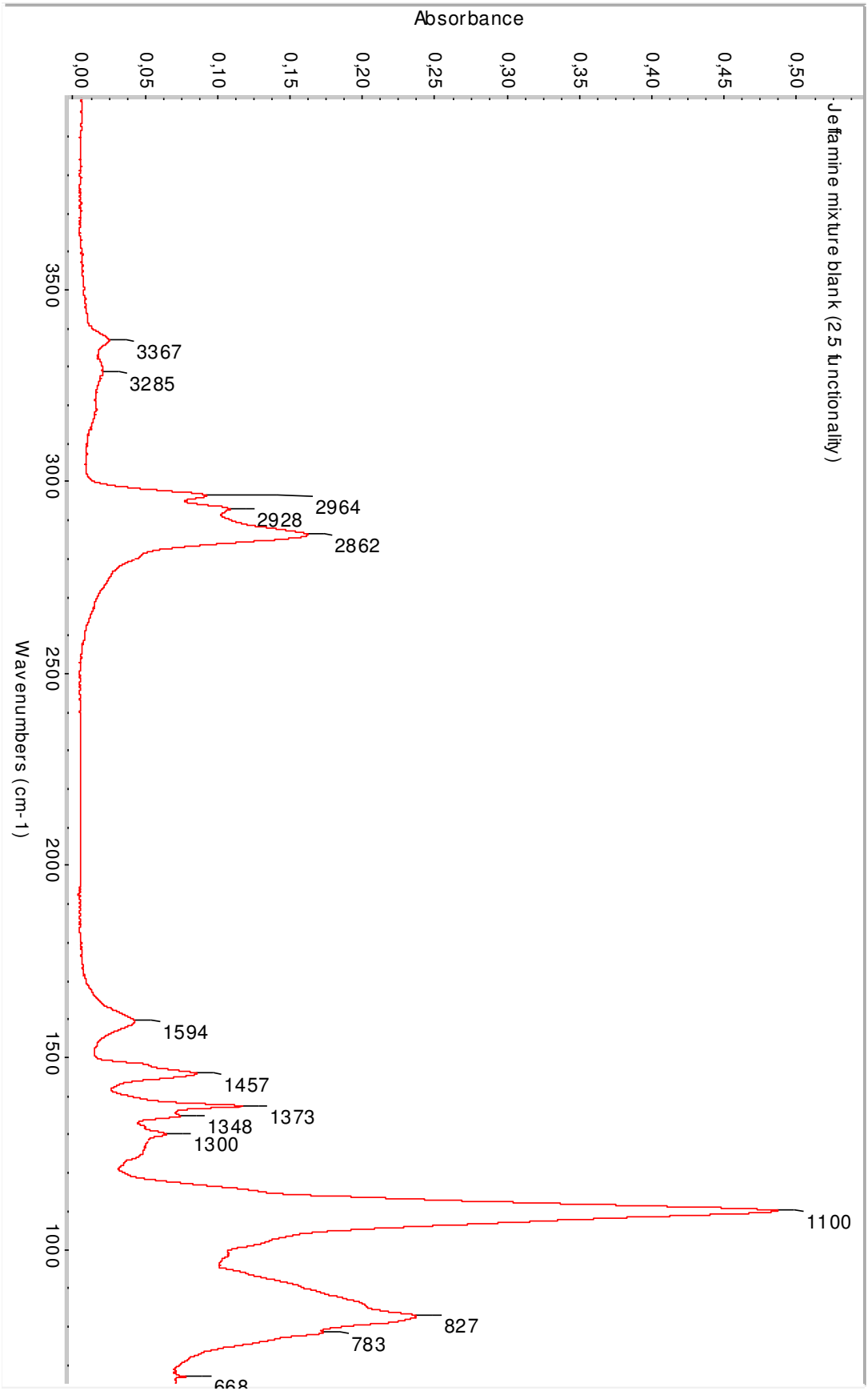
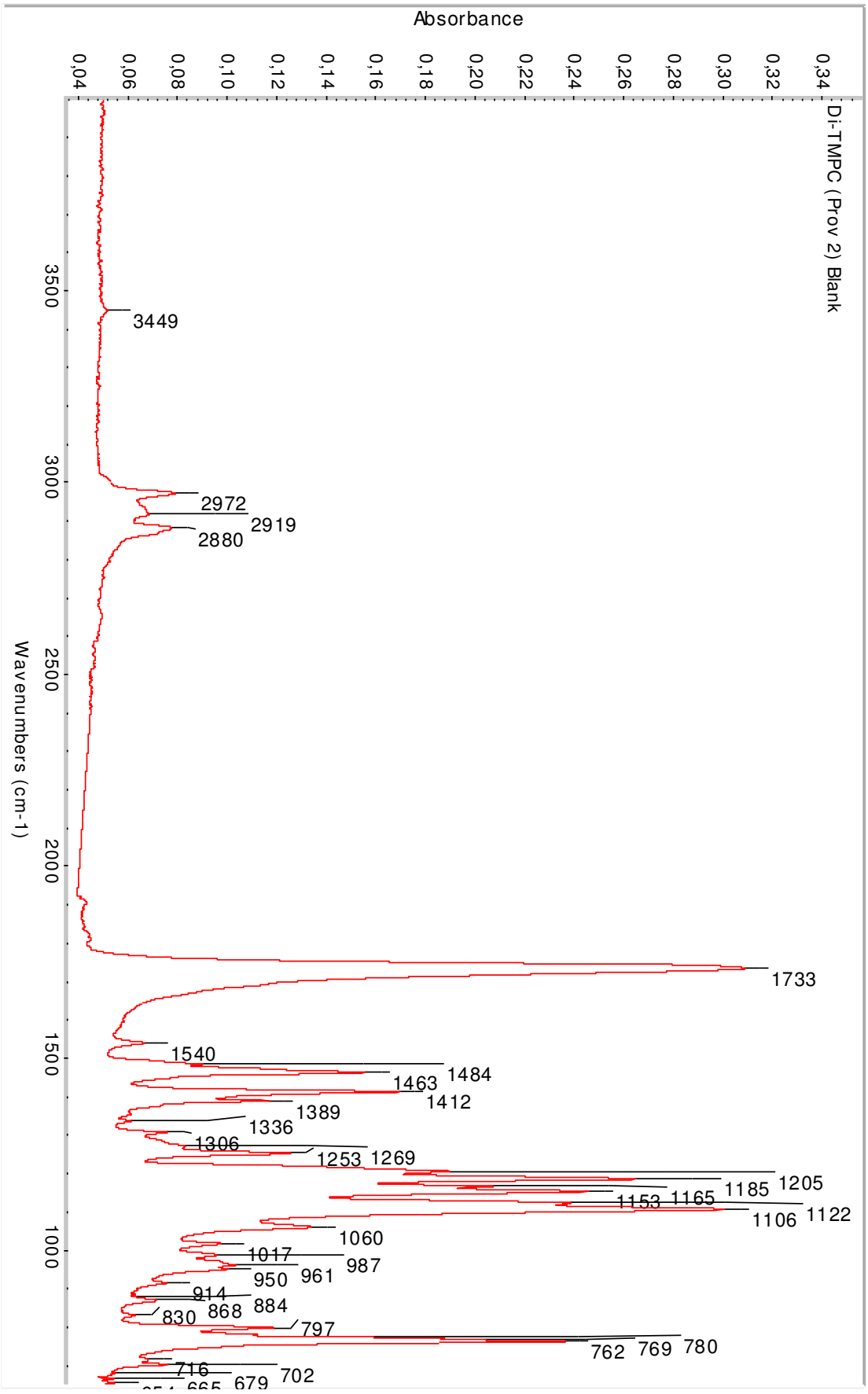
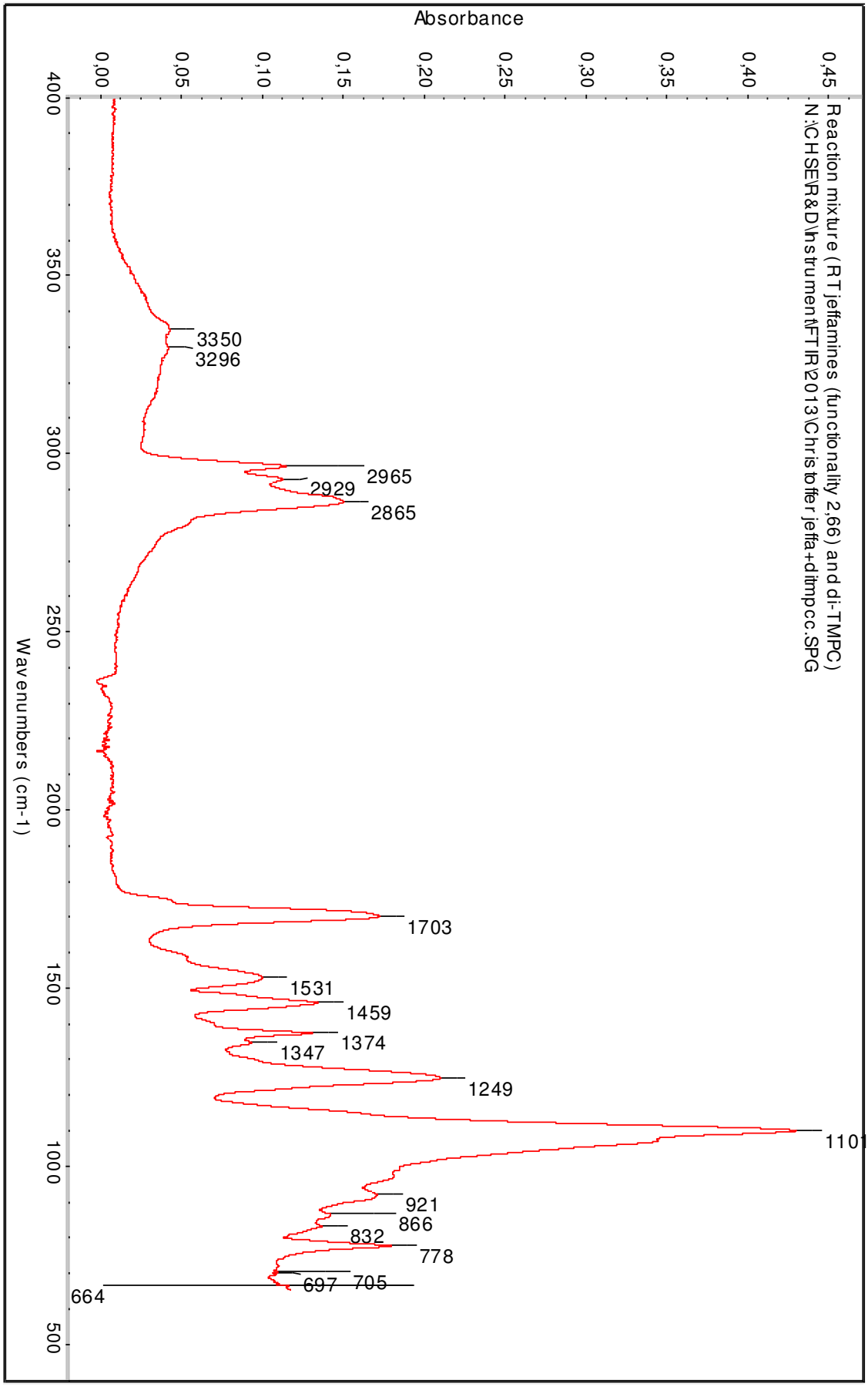
Appendix



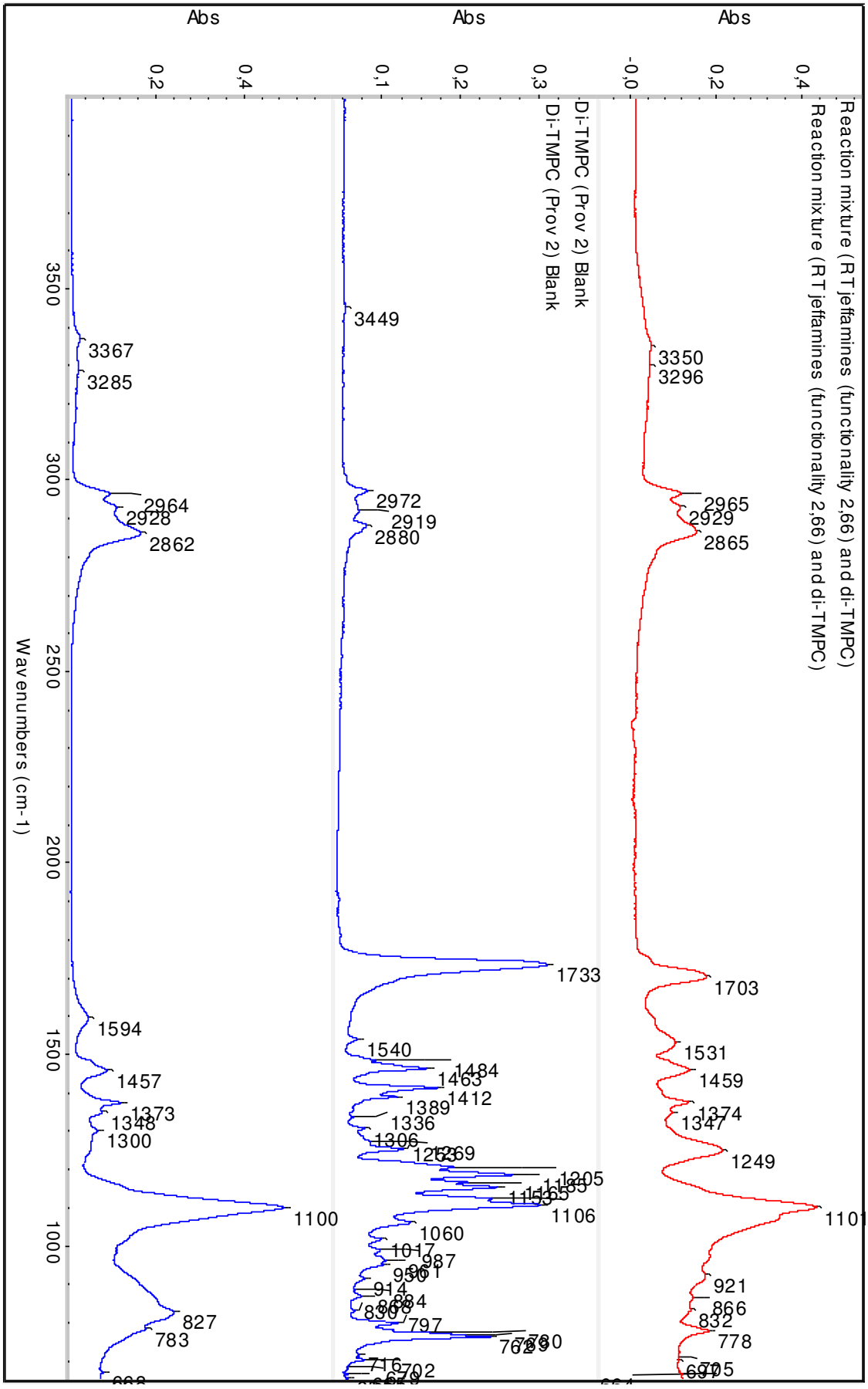
Appendix 1, Jeffamine mixture FT-IR



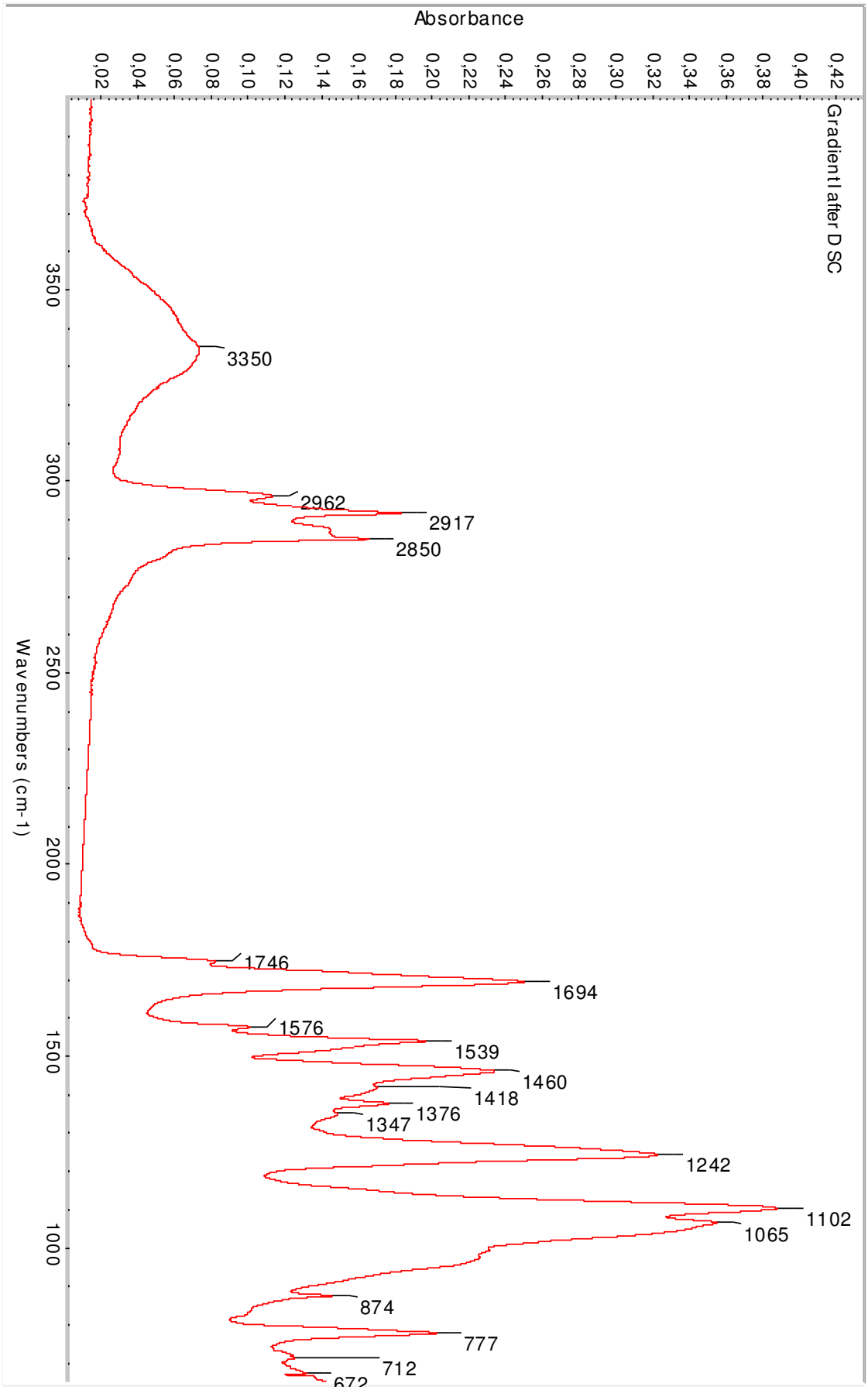
Appendix 2, Pure di-TMPC FT-IR



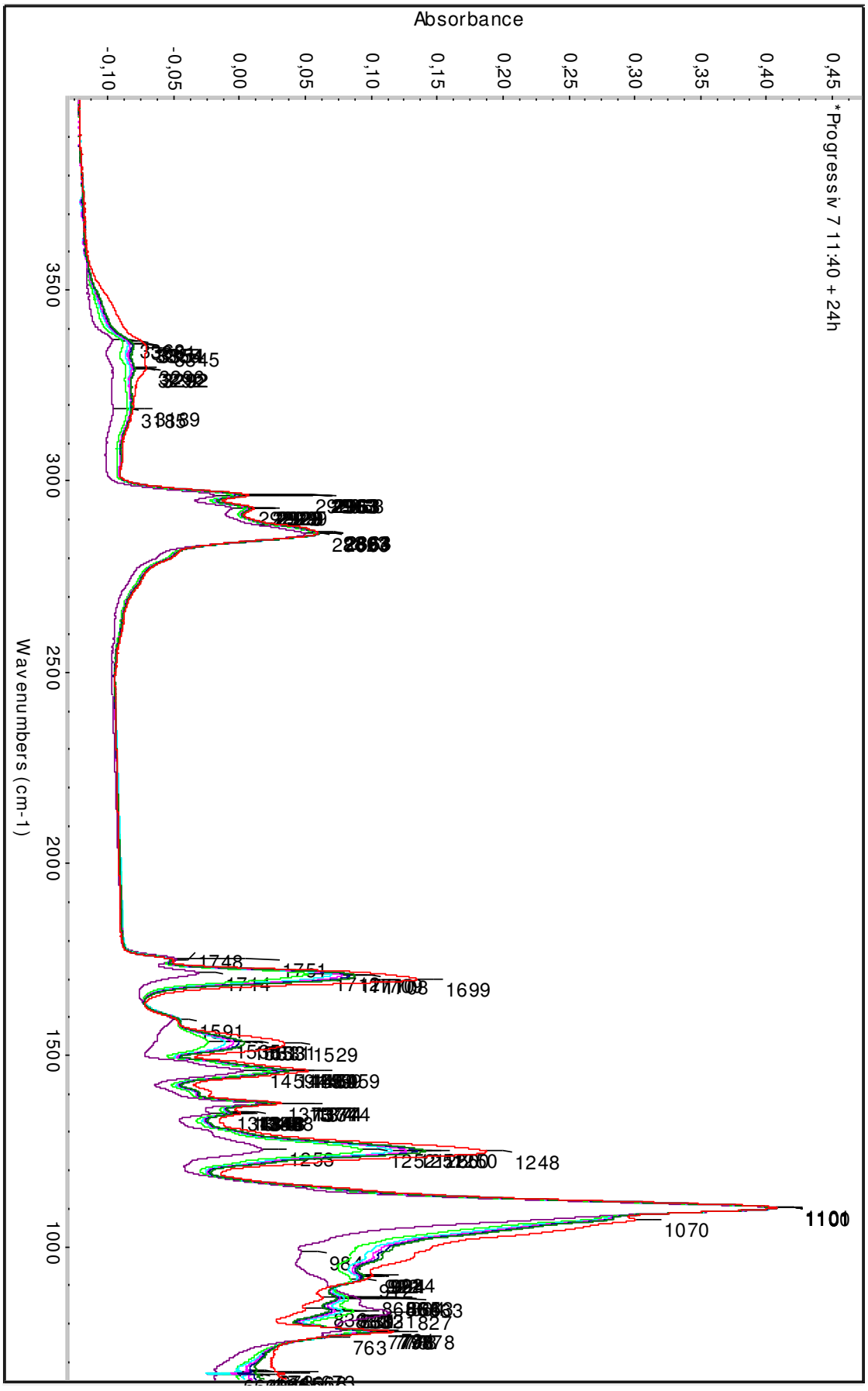
Appendix 3, Reaction mixture (di-TMPC and Jeffamines)



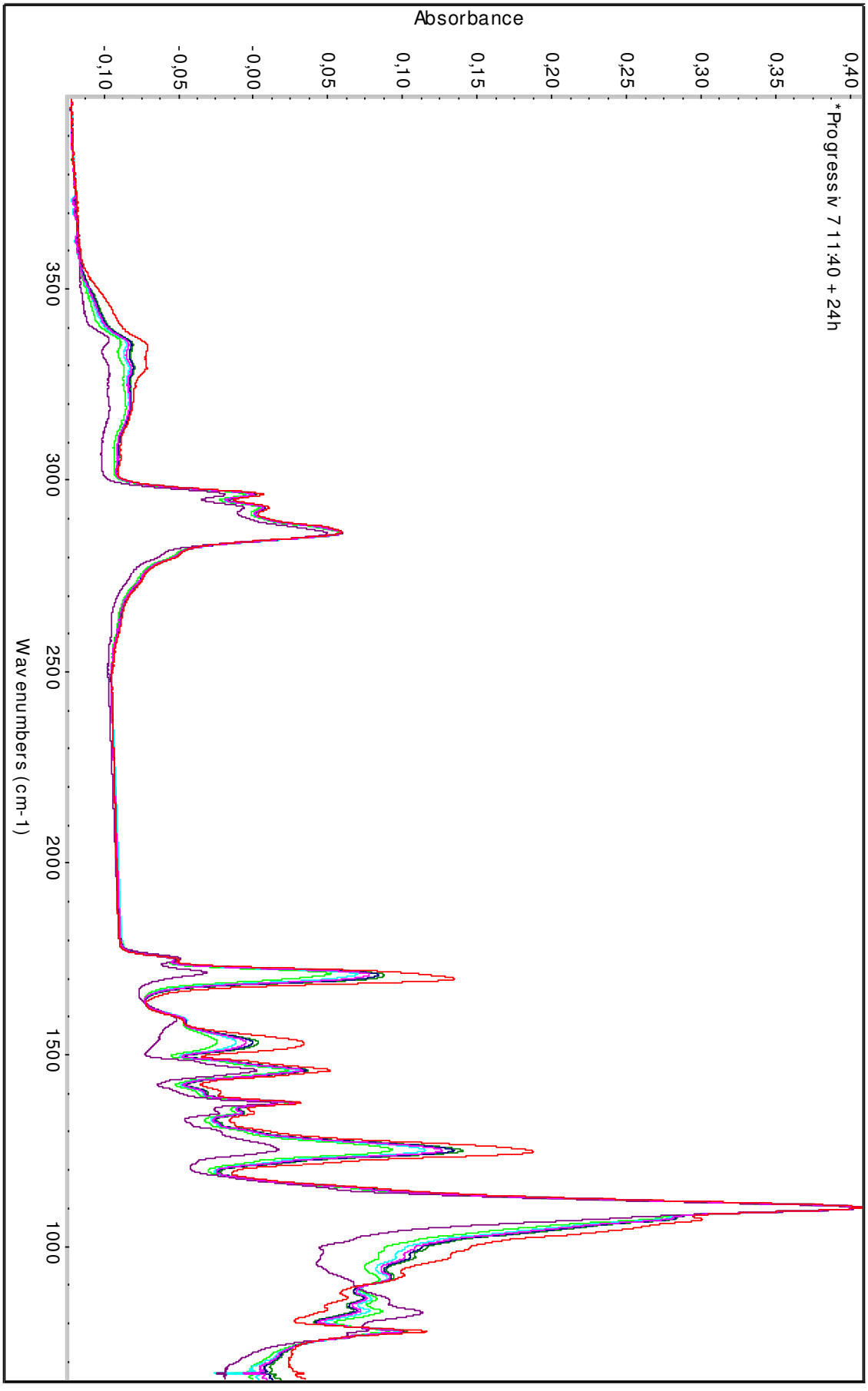
Appendix 4, Comparison of (red) reaction mixture, (blue middle) di-TMPC and (blue bottom) Jeffamines



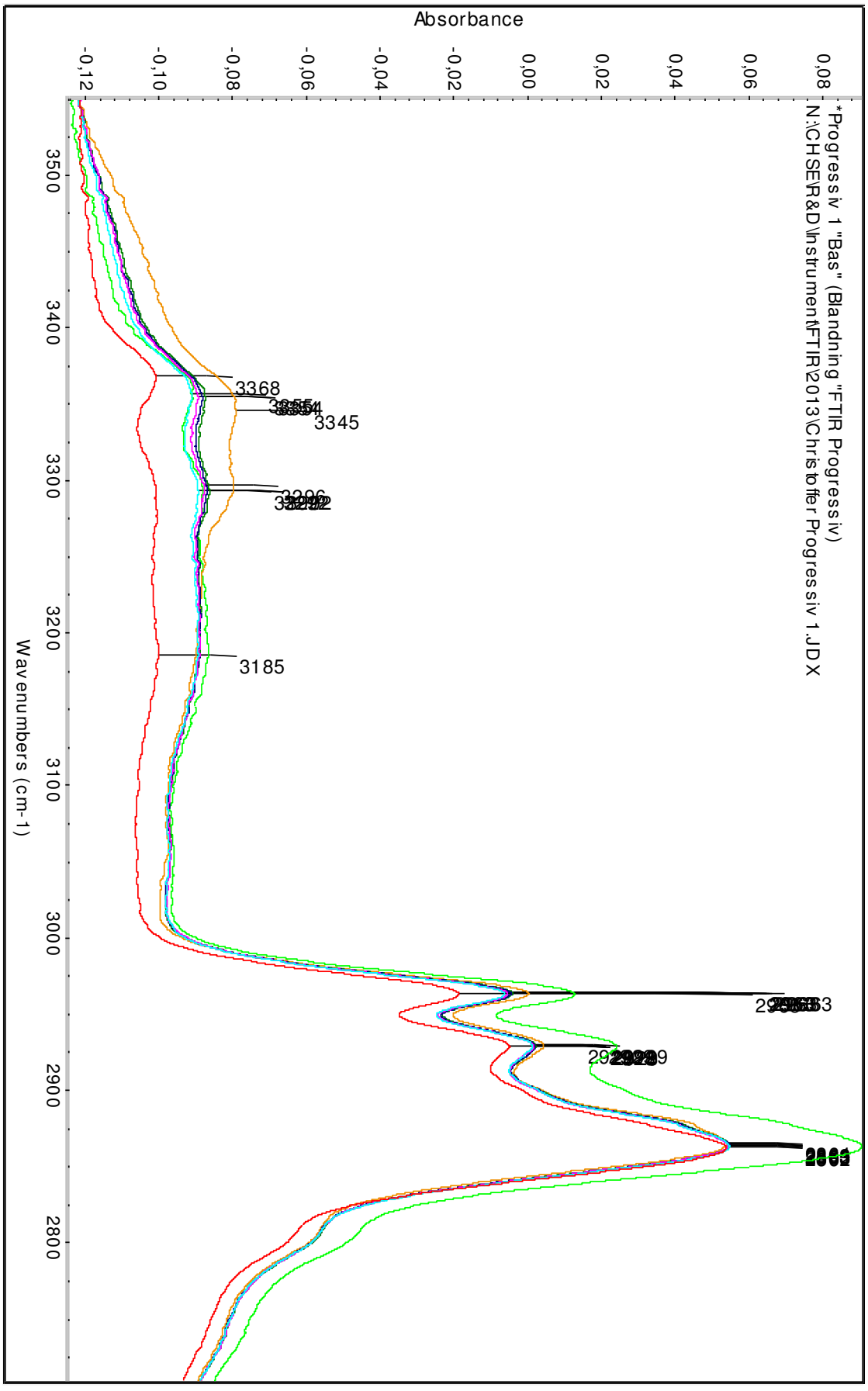
Appendix 5, FT-IR after reaction mixture been through a gradient DSC



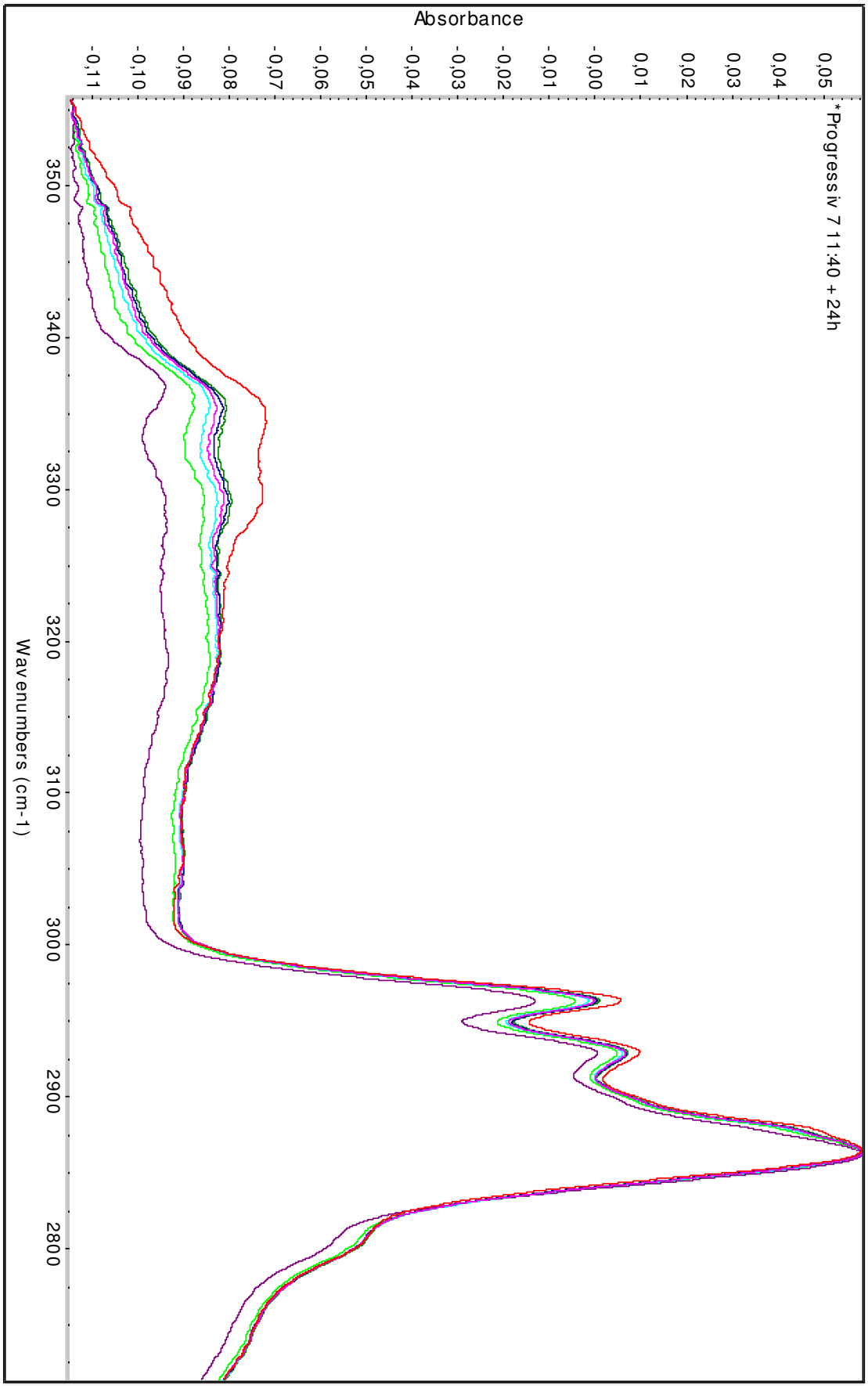
Appendix 6, Room temperature progressive scans



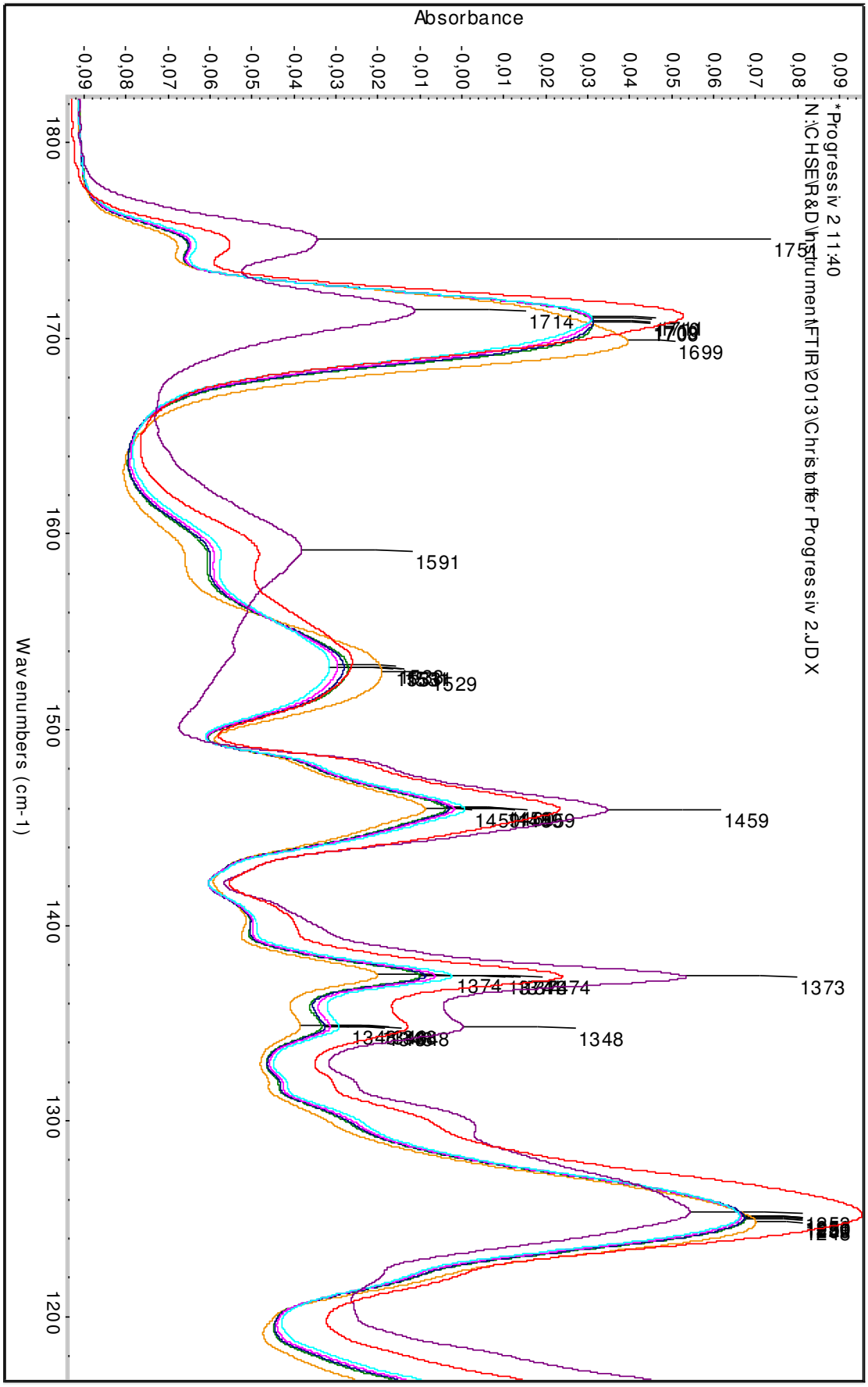
Appendix 7, Room temperature progressive scans



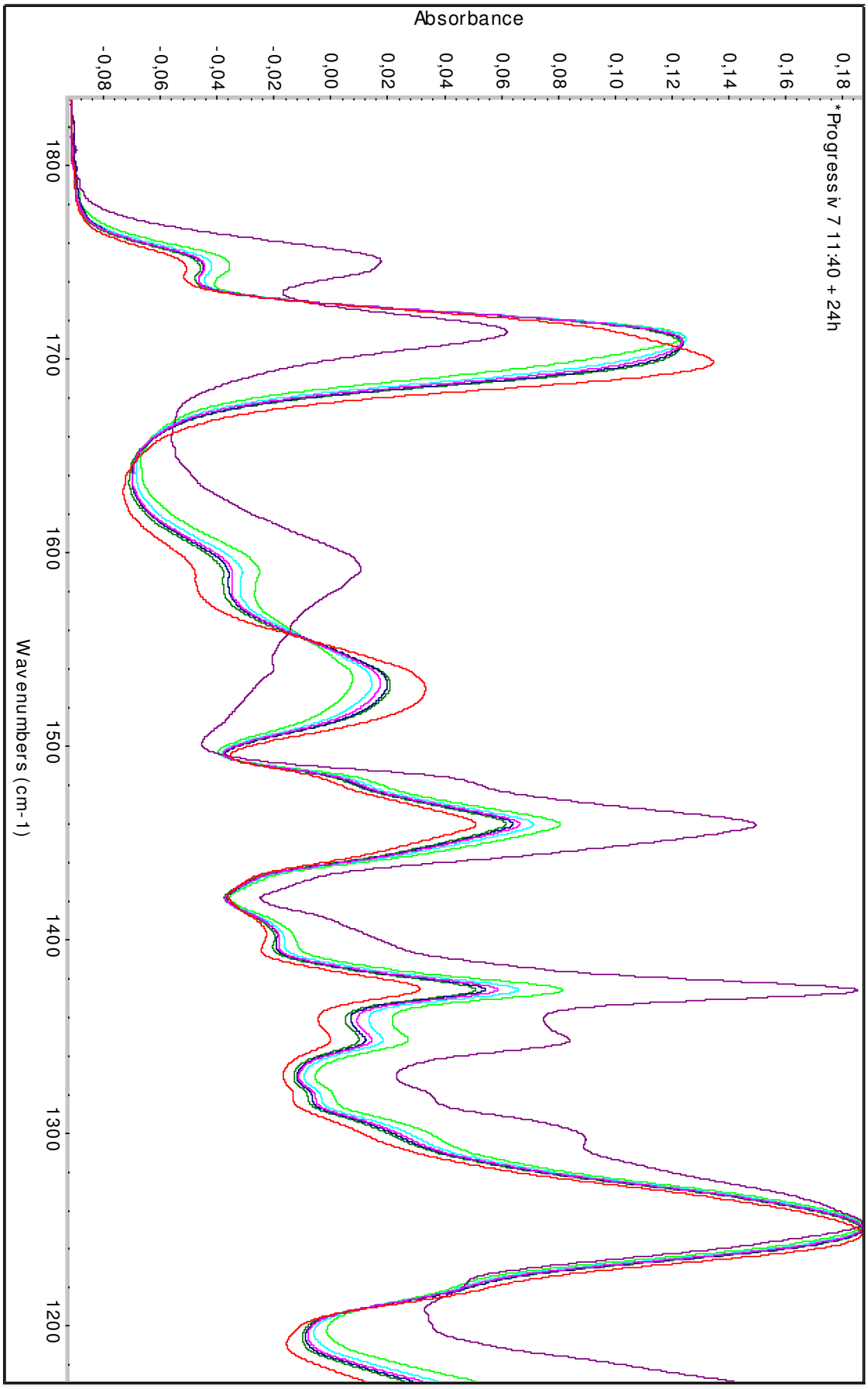
Appendix 8, Room temperature progressive scans



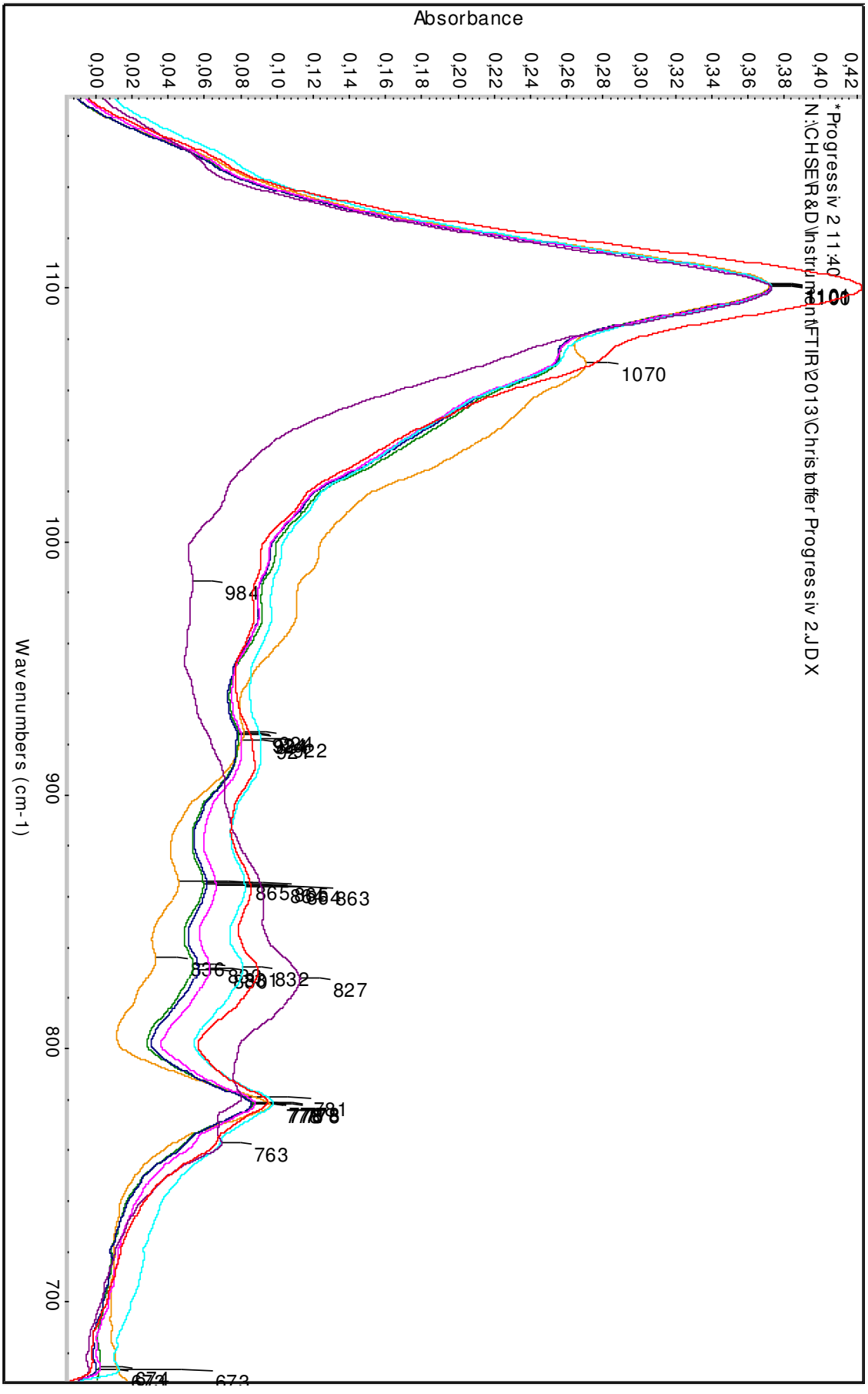
Appendix 9, Room temperature progressive scans



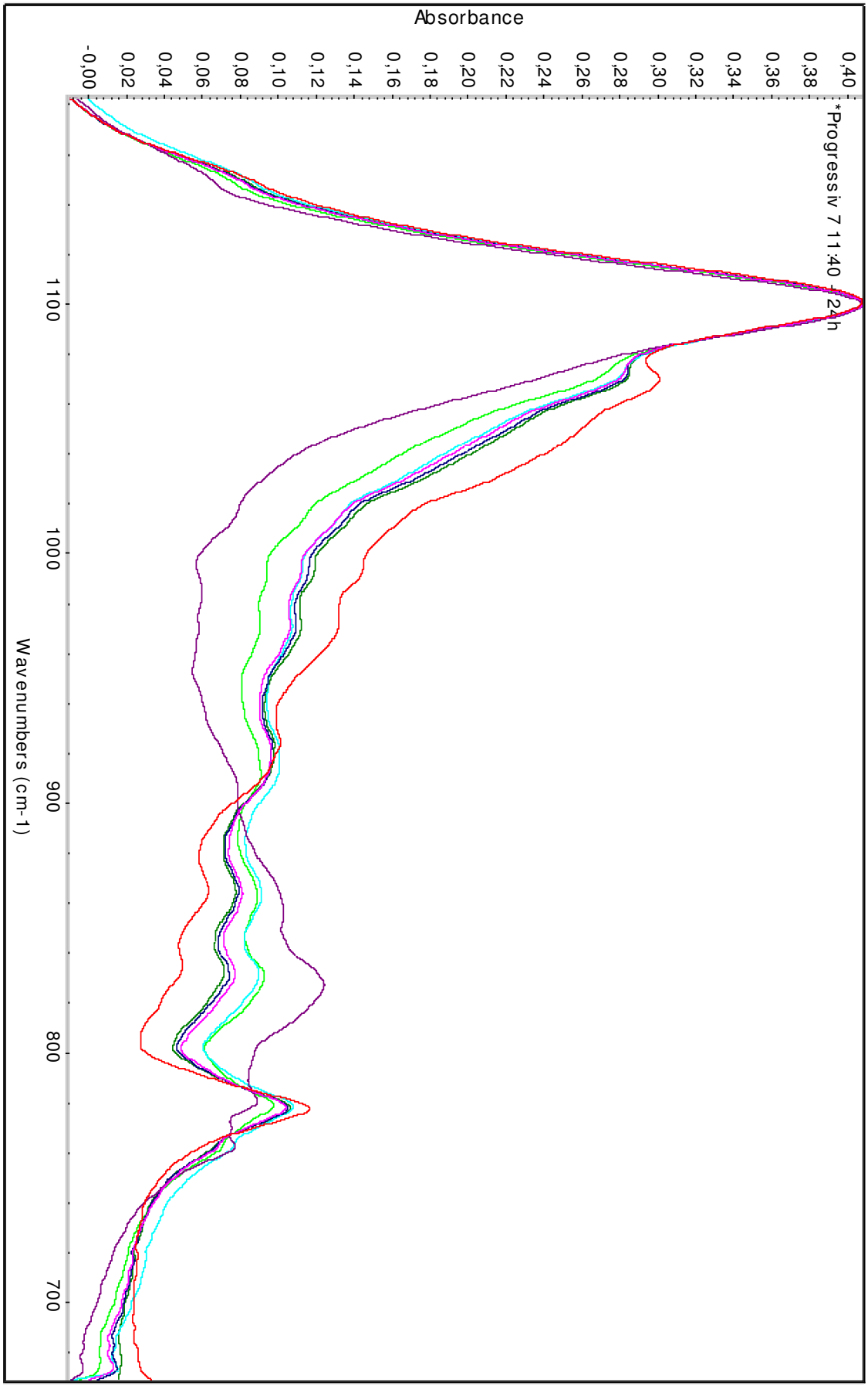
Appendix 10, Room temperature progressive scans



Appendix 11, Room temperature progressive scans



Appendix 12, Room temperature progressive scans



Appendix 13, Room temperature progressive scans