KIMIKA FAKULTATEA
FACULTAD DE QUÍMICA

Universidad del País Vasco/**Euskal Herriko Unibertsitatea/University of the Basque Country**

Faculty of Chemistry

Degree in Chemistry

GRADU AMAIERAKO LANA

Development of polythiourethane based resins for 3D printing applications using Photobase Generators

Author: Oihane Varela Manrique

Supervisor: Haritz Sardon

Donostia, March of 2022

GIPUZKOAKO CAMPUSA
CAMPUS DE GIPUZKOA
Pº. Manuel de Lardizabal, 3
20018 DONOSTIA-SAN SEBASTIAN
GIPUZKOA

INDEX

ABSTRACT

Recently additive manufacturing (AM) is gaining importance as new technologies for on demand applications are being developed. However, the variety of materials available for photopolymerization printing (VAT) is limited. Consequently, in this work photocurable resins based on polythiourethanes were studied with the aim of developing new materials for 3D printing applications by VAT photopolymerization.

Different thiol-isocyanate systems were studied to find a system that can meet the requirements for the 3D printing applications. To this effect, various photobase generators (PBG) were investigated to achieve an on demand base catalyzed thiol-isocyanate reaction.

Moreover, printing parameters were optimized to obtain high quality pieces demonstrating the use of the reported system as a competitive alternative for VAT 3D printing applications.

LABURPENA

Azkenaldian fabrikazio gehigarria garrantzia hartzen ari da teknologia berriak garatzen ari diren heinean. Hala ere, fotopolimerizazio imprimaketa (VAT) prozesurako eskura dauden materialen aniztasuna mugatua da. Ondorioz, lan honetan politiouretanoak sintetizatu dira erretxina fotopolimerizagarri gisa, VAT fotopolimerizazio prozesuaren bidez 3D imprimaketa aplikaziorako material berriak garatzeko helburuarekin.

Tiol-isozianato sistema desberdinak aztertu dira 3D imprimaketaren aplikaziorako baldintzak betzetzen dituen sistema aurkitzeko. Horretarako zenbait fotobase-sorgailu (PBG) ikertu dira base latentez katalizatutako tiol-isozianato erreakzio kontrolatua lortzeko.

Hortaz gain, imprimaketa parametro desberdinak optimizatu dira kalitate handiko piezak lortuz, politiouretano sistemaren erabilera VAT fotopolimerizazio prozesu bidezko 3D imprimaketa aplikazioetarako frogatzeko.

1 INTRODUCTION

1.1 Additive Manufacturing (AM)

Additive manufacturing (AM) is an advanced form of manufacturing that allows the construction of a three-dimensional object from a 3D digital design by adding together the material layer by layer under computer control.[1] AM is a quite recent manufacturing process used in different industries such as healthcare, aerospace and jewelry, demonstrating the versatility of these technologies.[2]

The relevance of AM has increased as new technologies have been developed, such as computer design, which enables the user to produce specific pieces in a simple way. Moreover, the recent developments on polymeric material processing made possible to create well defined 3D objects in a fast and cheap manner.[2]

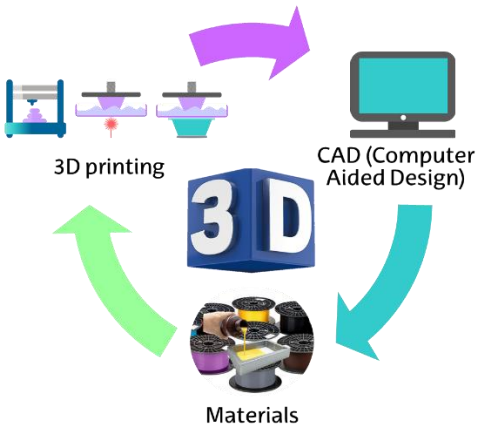


Figure 1. Scheme of the additive manufacturing process.

Additive manufacturing cover a group of techniques where a great variety of manufacturing technologies can be found. These are all based on the same concept, but their execution is different, thus are divided in seven categories: material extrusion (ME), VAT photopolymerization (VP), material jetting (MJ),

binder jetting (BJ), sheet lamination (SL), powder bed fusion (PBF) and direct energy deposition (DED).[1]

In this work material extrusion and VAT photopolymerization techniques will be addressed, as they are considered the most attractive ones for various reasons such as their popularity or their interesting technology.

1.1.1 Material extrusion (ME)

Material extrusion (ME) is an additive manufacturing technique where after the polymer is heated and melted, the material is extruded trough a nozzle and layers are build one by one. This technique is the most popular one, due to the low cost and the simplicity of the process, for that reason, a great variety of materials with different properties and colors have been developed for this AM process. However, the amount of parameters that affect in the final result, such as, diameter of the nozzle, bed temperature, printing temperature, etc. Therefore, the reproducibility and the resolution of the pieces is not as good as in other additive manufacturing techniques. For example, the resolution of the obtained piece is limited to the diameter of the nozzle which makes difficult to print high resolution objects. [3] However, due to the easy and straightforward use is the most stablished 3D printing technique.

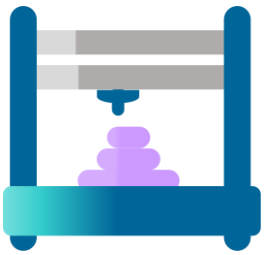


Figure 2. Scheme of material extrusion printing technique.

Polymer materials for material extrusion (ME)

Since this technique is based on the extrusion melted materials, the process is usually limited to the use of thermoplastic polymers. The most commonly used

polymers for this process are acrylonitrile-butadiene-styrene copolymers (ABS), polylactic acid (PLA), polycarbonate (PC) and polyamides (PA). In addition, material extrusion 3D printing allows the use of polymers containing different additives such as fibers, dyes and fillers.[2]

1.1.2 VAT photopolymerization (VP)

VAT photopolymerization (VP) is an additive manufacturing technique where a liquid-viscous prepolymer that is sensitive to the UV light, is selectively curated when irradiating UV light by a light activated polymerization that occurs when a catalyst or reactive species are activated by the irradiation. This technique enables the obtaining of objects with high resolution in a considerate speed. VAT photopolymerization techniques are known for their great precision and high-quality results, allowing the printing of geometrically complex pieces, but the cost is quite high. Different processes are based in this technique: digital light processing (DLP) and stereolithography (SLA).[3]

Stereolithography (SLA)

In this printing process, a tank is filled with a photosensitive liquid resin in which a build platform is submerged, and a focused laser is used to draw a pattern forming a layer that attaches to the build platform. Once the entire layer is formed, the build platform is relocated the distance equivalent to the thickness of the curated resin layer in order to form the next layer above the previous one.[4]

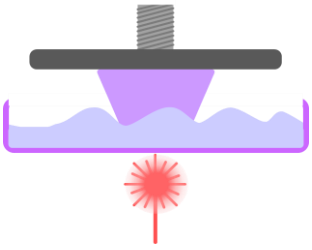


Figure 3. Scheme of SLA printing technique.

Digital Light Processing (DLP)

Similarly to SLA, in this printing process a tank is filled with a photosensitive liquid resin, and a UV light digital projector that projects the shape of the entire layer, crosslinking the resin and building a layer in one step. As in SLA, the building platform is relocated and a new pattern is projected, forming the next layer above the previous one. Since this technology builds the entire layer at a time, faster print times can be achieved with DLP compared to SLA. [5]

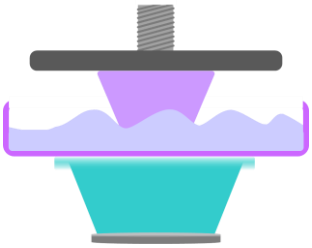


Figure 4. Scheme of DLP printing technique.

Polymer materials for VAT photopolymerization (VP)

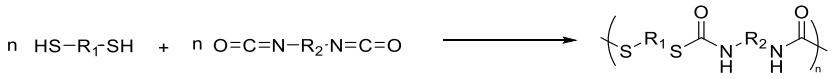
In this AM technique, generally a chain-growth polymerization takes place, which can be ionic (cationic and anionic) or radical. Radical photopolymerization is the most used mechanism, due to the high polymerization rates and more developed photopolymerization mechanism.[6] Most of the commercial resins are based on acrylate oligomers or acrylate containing resins, such as, urethane-acrylate based resins which are often used because of the enhanced mechanical properties the urethane group provides. However, these resins suffer shrinkage while polymerization, which lowers the quality of the 3D printing objects.[2] For this reason, alternate monomer systems have been developed, such as thiol-ene polymerization based formulation. Although thiol-ene based resins undergo less shrinkage, they show poor mechanical properties. Epoxides are a commonly used monomers for vat photopolymerization as well, as they suffer less shrinkage than acrylates and have good mechanical properties, but their photopolymerization occurs slower.[2,7]

Normally, after printing the obtained material is a thermoset polymer, with a three-dimensional reticulated structure, giving the material different properties.

This is what makes the great difference between VAT photopolymerization and material extrusion, considering that thermoplastic polymers are necessary for material extrusion, in order to melt the material that needs to flow from the nozzle.

1.2 Polythiourethanes

Polythiourethanes (PTUs) are macromolecules bearing thiocarbamate units (-NHCOS-) in their backbone chain. This polymer is synthesized by the polyaddition reaction between isocyanate and thiol monomers.



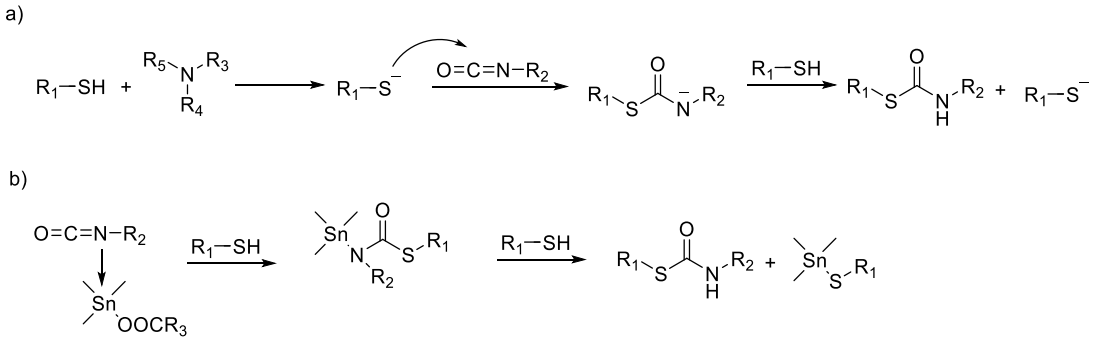
Scheme 1. General scheme of polythiourethane synthesis.

Some characteristics of polythiourethanes are their versatility, biocompatibility and excellent mechanical properties. Similar to the deeply studied polyurethanes, polythiourethanes can also be achieved with a wide range of properties by the precise choice of monomers to obtain structural lightweight materials, thermoplastic elastomers or thermosets for various applications although they have been studied to a lesser extent.[8] One advantage comparing it with traditional polyurethanes is their enhanced stability without catalyst making these mixtures more useful when long pot-life are desired. However, extremely fast reaction rates have been obtained when basic catalysts are used, since the nucleophilic addition of thiols to isocyanates in the presence of a catalyst is considered a *click reaction*.[9] On the other hand, it has to be noted that this class of polymer has been recently reported to be reprocessable expanding the interest on their study and development. [10,11]

1.2.1 Chemistry of polythiourethanes

The reaction can be catalyzed by organic bases or Lewis acids. When using base catalysts, the thiol is activated by forming the thiolate anion, which attacks

the isocyanate electrophilic carbon. At the contrary, when using Lewis acids, the acid coordinates with the isocyanate group, and it is attacked by the thiol group, however, low reaction rates have been reported for the Lewis acid catalyzed reactions due to the low nucleophilicity of the protonated thiol group.[8] Therefore, the most straightforward strategy to prepare polythiourethane materials seems to be the base catalyzed pathway.



Scheme 2. Thiol-isocyanate reaction mechanism in (a) basic and (b) Lewis acidic conditions.

The base catalyzed thiol-isocyanate reaction occurs in two steps (Scheme 2a). First, the thiol is deprotonated, producing the strong nucleophile thiolate anion. Then, the thiolate anion is coupled with the isocyanate group, forming the thiourethane and another thiolate anion at the same time on a step-growth polymerization method, thus, difunctional monomers are needed to obtain polymeric materials. The reaction continues until all functional groups are consumed to yield a high molecular weight polymer.[9] Once initiated, the reaction occurs extremely fast, making the system difficult to process as a substantial increase of the viscosity is observed. Moreover, when thermosets are desired, at least one of the reacting groups has to be trifunctional in order to obtain crosslinked materials. In this case, the problem with the low processing time is enhanced, due to the fast reaction rate which makes hard to handle these materials. In order to achieve a controlled reaction, latent type of bases have been used in order to extend the pot-life or processing time of these resins.[8]

The application of linear polythiourethanes have been implemented in 3D printing by material extrusion,[12] however, scarce studies investigate the possibility of applying VAT 3D printing technologies for this class of polymers.

1.3 Photobase generators (PBGs)

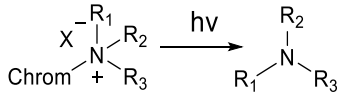
Photobase Generators (PBGs) are photolabile compounds that generate organic bases under light irradiation. Although first these compounds were utilized as crosslinkers, since they were only able to release weak primary and secondary amines; recently their use as base catalyst is gaining importance, consequently, photobases able to release strong bases as amidines, guanidines, phosphazenes or carbenes that activate anionic polymerizations have been developed. [13]

Numerous classes of PBGs have been developed, but in this work a few of them will be addressed.

1.3.1 Salts

Quaternary ammonium salts (QA)

The first bases used to generate bases were quaternary ammonium salts, where a quaternary amine is bonded to a chromophore. When irradiating a homolytic C-N bond cleavages takes place, releasing the amine. Due to the low solubility and stability of these compounds in organic solvents, new PBGs activated by deprotonation have been developed. [13]



Chrom = chromophore X = Br

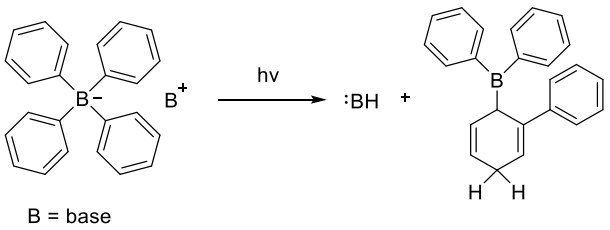
R_1, R_2, R_3 = alkyl, aryl Ph_4B

Ph_3BBu

Scheme 3. Photolysis mechanism of QAs.

Tetraphenylborate salts

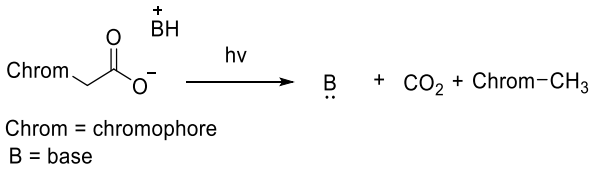
Tetraphenylborate salts (B·HBPh$_4$) are composed by a protonated base and a tetraphenyl borate anion that upon UV irradiation at 254 nm abstracts the proton from the base, releasing the free base.[14] Since BPh_4^- is only active on low wavelength, isopropylthioxanthone (ITX) has been used as a photosensitizer, increasing the activity of the photobase beyond 365 nm. These class of PBG have been used for thiol-click reactions.[15]



Scheme 4. Photolysis mechanism of tetraphenylborate salts.

Carboxylate-functional salts

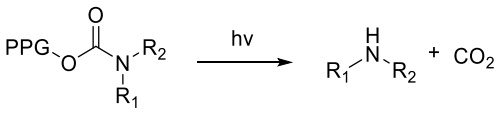
These PBGs are composed by a carboxylate-functional chromophore and a protonated base. The base is released by deprotonation via photocarboxylation. The chromophore structure can be modified in order to obtain different photochemical properties of the PBGs. It has been reported low stability of this class of photobase generators in a range of monomer mixtures due to the existing equilibrium between the protonated and non-protonated base.[13]



Scheme 5. Photolysis mechanism of carboxylate-functional salts.

1.3.2 Carbamates

Carbamates are non-ionic PBGs where a photolabile protecting group is chemically bonded to an amine by a carbamate group. When light irradiating the photodecarboxylation of the carbamate takes place, releasing primary or secondary amines.[13]



PPG = photolabile protecting group
R1, R2 = alkyl

Scheme 6. Photolysis mechanism of carbamates.

1.4 Objectives

The main objective of this work is to develop polythiourethane based photocurable resins for 3D printing application by VAT photopolymerization. Nowadays, the option of materials for this printing technology is limited, therefore, it is a major challenge apply the versatility of polythiourethanes for 3D printing applications.

To meet this aim, different polythiourethane based resins will be synthesized and their chemical, physical and rheological characterizations will be accomplished to acknowledge their behavior for VAT photopolymerization 3D printing applications. Besides, the use of photobase generators to catalyze the polythiourethane synthesis will be studied, and for that different PBGs will be synthesized and characterized. For 3D printing, various parameters will be analyzed in order to optimize the printing of the resins.

In addition, together with these objectives, it is expected to learn and develop skill in polymer characterization techniques, organic synthesis and to gain experience in lab work.

2 EXPERIMENTAL PART

2.1 Characterization methods

2.1.1 Nuclear Magnetic Resonance (NMR)

Nuclear Magnetic Resonance (NMR) is an analytical technique mainly used for determining the molecular structures and the purity of the compounds. To do this, the sample is exposed to an external magnetic field and the interaction of nuclear spins is measured, giving information of the electronic structure and functional groups of a molecule. The value of the field that each nucleus perceives is affected by electron shielding and the chemical environment.

In this work, ^{1}H-NMR data was collected on a 300 MHz in a Bruker Advance DPX Spectrometer at 20 ºC. The samples were dissolved in deuterated dimethyl sulfoxide (DMSO-d^6) or deuterated chloroform ($CDCl_3$), chemical shifts are reported in ppm and referenced to solvents peaks.

2.1.2 Fourier-Transform Infrared Spectroscopy (FTIR)

Fourier-transform infrared spectroscopy (FTIR) is an analytical technique used to identify the functional groups of a compound. This technique is based on the characteristic vibration that each type of bond shows under infrared irradiation, measuring how much infrared irradiation a sample absorbs at each wavelength. In this study, FTIR spectra were recorded using attenuated total reflection infrared spectrometry (ATR-FTIR) in a Nicolet iS20 Spectrometer, at a resolution of 2 cm^{-1} and a total of 32 interferograms.

2.1.3 Ultraviolet-Visible Spectroscopy (UV-VIS)

Ultraviolet-visible spectroscopy (UV-VIS) is an analytical technique that measures the wavelengths of UV or visible light that are absorbed by a compound compared with a reference, which depends on the composition of the sample. Molecules containing bonding and non-bonding electrons can absorb energy in the form of UV or visible light to excite these electrons to higher anti-bonding molecular orbitals.

The data was collected on a Agilent 8453 UV-Visible spectrophotometer on a range between 200 nm to 700 nm. For these measurements the samples were dissolved in acetonitrile (10^{-4} M) and placed into quartz 1 cm wide cuvettes. The effect of light irradiation on the sample was performed by irradiating the sample at 365 nm with 60 mW/cm^2 light intensity at different times.

2.1.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a technique that is used to determine the degradation temperature of the material, measuring the weight of a sample while increasing the temperature. The degradation of the polymer occurs when the material loses molecular weight.

Thermogravimetric analysis was carried out on a Q500 Thermogravimetryc Analyzer from TA instruments. The system was heated on a heating rate of 10 °C/min from room temperature to 600 °C under atmospheric conditions.

2.1.5 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a thermo-analytical technique used to determine the physical changes of the materials related to the temperature. In this technique, the sample and a reference are heated or cooled at the same time, and it measures the energy that the sample absorbs or releases when it is

heated or cooled, indicating endothermic and exothermic processes. This characterization is commonly used with polymeric material, since it allows to easily determine their thermal transitions such as, glass temperature transition (T_g), melting temperature (T_m) and crystallization temperature (T_c). In order to choose the temperature ramp, TGA analysis is done before hand to obtain the temperature range where degradation of the material will not happen.

In this case the thermal properties of the materials were analyzed on a DSC Q2000 from TA Instruments. The analysis ware performed in sealed aluminum pans, under dry N_2 atmosphere using a heating rate of 10 ºC/min a heating ramp from –80 to 160 ºC.

2.1.6 **Rheology**

The oscillatory rheometry is a technique used to determine the viscoelastic properties of the materials, where the storage modulus (G') and the loss modulus (G") change with the time and temperature. Since in this work photocurable resins are analyzed, time sweeps with and without irradiation are crucial, this way, the changes of the viscoelastic properties of the material can be determined during its cure time.

These measurements were performed on the AR-G2 rheometer from TA Instruments equipped with an UV light irradiation accessory emitting UV irradiation centered at 365 nm, of variable intensity. The used geometry was of two parallel plates of 20 mm of diameter, using an acrylic see-trough bottom plate when irradiating. The used gap value was 400 μm. The experiments were carried out at room temperature and in the linear viscoelasticity region to avoid mechanical degradation of the material.

2.1.7 3D printing

For the VAT printing, an Asiga Max-UV printer was used. This printer is a DLP type of printer which irradiates UV light centered at 385 nm. The printer has a resolution of 62 µm in the X, Y axis and 1 µm resolution in the Z axis. In order to do the slicing of the 3D objects, Asiga Composer® software was used. The printing conditions were modified in order to meet the requirements of each resin.

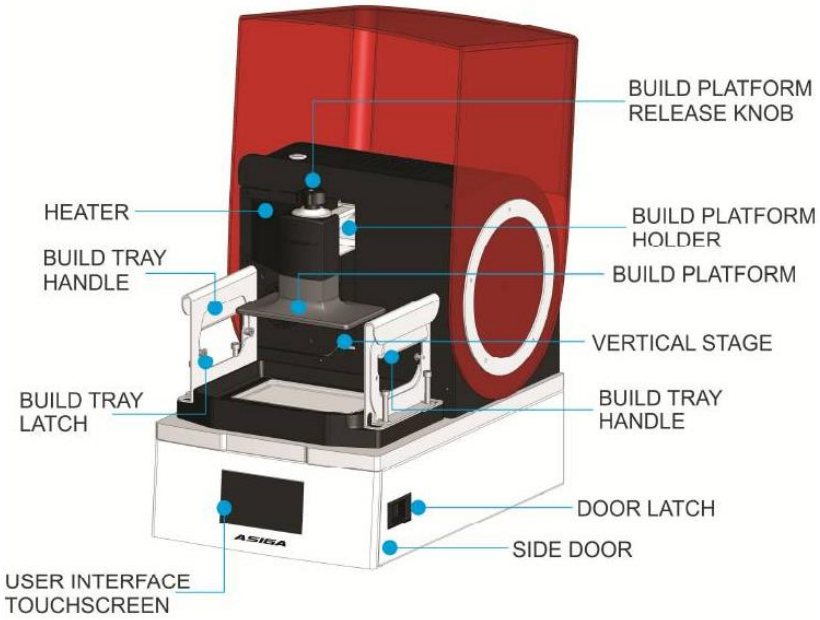


Figure 5. ASIGA MAX UV printer.

Explanation of the main parts of the printer can be found below:

- Heater: it controls the temperature of the material. It can be useful to control the viscosity of the system.
- Build platform holder: it holds the build platform and it allows the vertical movement of the platform.
- Build platform: is the base where the piece is printed, the first layer will be attached to the build platform.
- Build tray handle: is used to hold the vat to avoid it moving while printing.

- Vat: is the recipient where the material is placed. The bottom of the vat must be transparent, since the UV light has to go through it.
- Control panel: the touchscreen used to control the printer.
- LED: it has a 385 nm wavelength and a variable intensity that can go up to 20 mW/cm^2.

Before starting the printing, the calibration of the zero position of the printer was necessary, since a bad calibration can affect the printing process and the final piece. Additionally, an optimization of the material was made to select the most appropriate parameters for the printing process. The most relevant parameters when optimizing the materials:

- Exposure time: this parameter indicates how much time each layer is under irradiation. The exposure time of the burn-in layer and other layers are examined separately. The burn-in layer exposure time is quite high usually, because it is the first layer that will be attached to the printing platform and it must hold the weight of the entire piece, therefore, it is necessary for the burn-in layer to be properly attached to the platform.
- Layer thickness: this parameter indicates the thickness of each layer of the printed piece. When increasing the layer thickness, the printing time decreases, but the quality of the obtained pieces could worsen.
- Temperature: this parameter indicates the temperature of the printer. When increasing the temperature, the exposure time can be reduced.
- Irradiation intensity: this parameter indicates the intensity of the light when irradiating. The maximum irradiation intensity the printer allows is 20 mW/cm^2. In this work, all the printings were made using the maximum irradiation intensity in order to reduce the printing times.

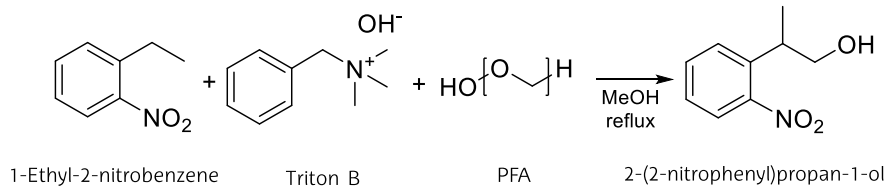
2.2 Materials and methods

2.2.1 Starting materials

Methyl lactate, 1-ethyl-2-nitrobenzene, triphosgene, isophorone diisocyanate (IPDI), isopropylthioxanthone (ITX), Sudan-1 and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased by TCI. Hexamethylene diisocyanate (HDI), polyethylene glycol (PEG) (Mn: 400 g/mol), polypropylene glycol (PPG) (Mn: 2000 g/mol), 1,5,7-triazabicyclo[4,4,0]dec-5-ene (TBD), PFA, benzyltrimethylamonium hydroxide 40 wt% in methanol (Triton B), trimethylpropane tris(3-mercaptopropionate) (TMPTMP)(triSH), pentaerythritol tetrakis(3-mercaptopropionate) (PETT) (tetraSH) and 1,1,3,3-tetramethylguanidine (TMG) were obtained from Sigma-Aldrich. Triethylamine (TEA) was acquired from Acros. Sodium tetraphenylborate ($NaBPh_4$) was purchased from abcr. Glycol di-3-mercaptopropionate (GDMP)(diSH) was received from Bruno Bock and IPDI terminated difunctional polypropylene glycol (PPG-diIPDI) (Mn: 2000 g/mol) was kindly supplied by Cidetec. All materials were used as received.

2.2.2 Synthesis of Photobase Generators

Synthesis of NPPOC-TMG



1-Ethyl-2-nitrobenzene Triton B PFA 2-(2-nitrophenyl)propan-1-ol

Scheme 7. First step of the synthesis of NPPOC-TMG.

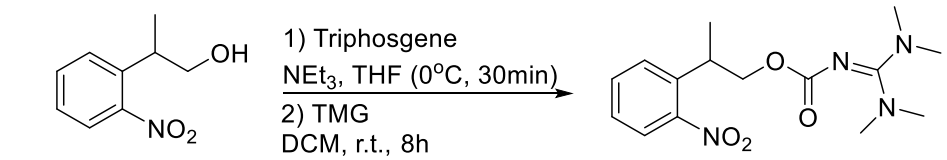
NPPOC-TMG was synthetized in two steps.

On a first step, the photobase precursor was synthesized using 5000 mg of 1-Ethyl-2-nitrobenzene (1 eq., 33.08 mmol) and 993 mg of PFA (1 eq., 33.08 mmol) together with 13300 mg of Triton B 40 wt% in methanol solution (1 eq.,

33.08 mmol) in a round-bottomed flask. The solution was stirred under reflux for 24h at 80 ºC. The mixture was acidified with a 2 M chloridric acid solution until the pH was neutral.

The solution was extracted 3 times with 30 mL of ethyl acetate, the organic phase was dried over anhydrous sodium sulfate and the solvent was removed with a rotary evaporator.

The crude product was purified by column chromatography (Hexane:Ethyl acetate, 80:20) and the solvent was removed. The obtained pure product (2.204 g, 37% yield) was used in the next step. ^{1}H-NMR (300 MHz,$CDCl_3$) δ (ppm): 7.75-7.32 (m, 4H, Ar**H**), 3.75 (d, 2H, C**H**$_2$), 3.50 (m, 1H, C**H**), 1.31 (d, 3H, C**H**$_3$).



2-(2-nitrophenyl)propan-1-ol NPPOC-TMG

Scheme 8. Second step of the synthesis of NPPOC-TMG.

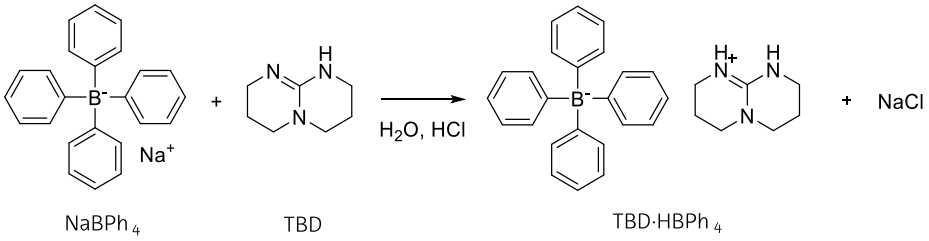
In the second reaction, 3609 mg of triphosgene (1 eq., 12.16 mmol) and 66 mL of anhydrous tetrahydrofuran were mixed under nitrogen atmosphere while heating. The mixture was cooled down and the previously synthesized 2204 mg of 2-(2-nitrophenyl)propan-1-ol (1 eq., 12.16 mmol) dissolved in 44 mL of THF and 1231 mg of triethylamine (1 eq., 12.16 mmol) were added. After 30 minutes it was filtered with Celite to remove the created salt and the solvent was removed. Then, it was dissolved in 44 mL DCM and added to a DCM (66 mL) and TMG (1541 mg, 1.1 eq., 13.38 mmol) solution at 0 ºC. When the addition was finished the mixture was kept at room temperature for 24 h.

The solution was extracted 2 times with 50 mL of $NaHCO_3$ 10% solution to neutralize the base. The aqueous phase was extracted 1 time with DCM. The organic phases were gathered and washed 3 times with 60 mL of Brire (NaCl

saturated solution) and dried over anhydrous $MgSO_4$. The solvent was removed with a rotary evaporator.

The crude was purified by column chromatography (DCM/MeOH, 95:5), yielding 1.187 g (30% yield) as a yellow oil. ^{1}H-NMR (300 MHz,$CDCl_3$) δ (ppm): 7.78-7.27 (m, 4H, Ar**H**), 4.26 (d, 2H, C**H**$_2$), 3.71 (m, 1H, C**H**), 2.80 (s, 12H, C**H**$_3$), 1.37 (d, 3H, C**H**$_3$).

Synthesis of TBD·HBPh$_4$

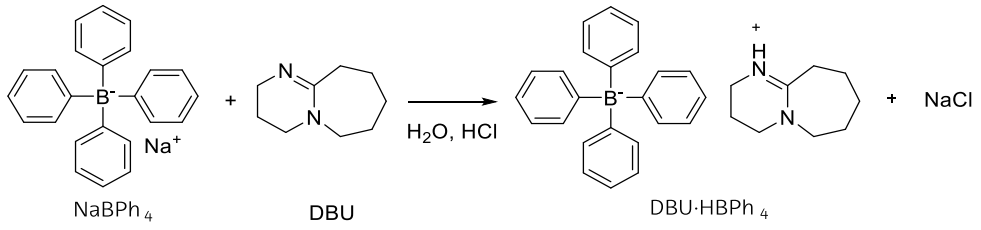


Scheme 9 . Synthesis of TBD·HBPh$_4$.

369 mg of TBD (1 eq., 2.65 mmol) were dissolved in 5 mL of 10% HCl solution. 1000 mg of $NaBPh_4$ (1.1 eq., 2.90 mmol) were dissolved in 5 mL of water and added to the previous solution.

The mixture was filtered and washed with water and finally with MeOH yielding the pure product in quantitative amounts as a white powder. ^{1}H-NMR (300 MHz, DMSO-d^6) δ (ppm): 9.95 (s, 1H, N$^+$**H**), 7.50-6.60 (m, 20H, Ar**H**), 3.27 (m, 4H, C**H**$_2$), 3.17 (m, 4H, C**H**$_2$), 1.82 (m, 4H, C**H**$_2$).

Synthesis of DBU·HBPh$_4$



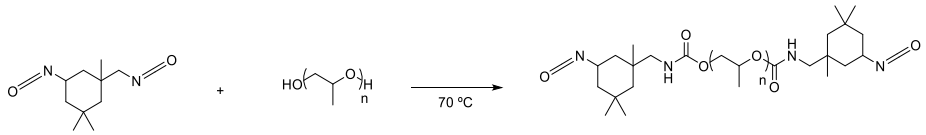
Scheme 10 . Synthesis of DBU·HBPh$_4$.

403 mg of DBU (1 eq., 2.65 mmol) were dissolved in 5 mL of 10% HCl solution. 1000 mg of $NaBPh_4$ (1.1 eq., 2.90 mmol) were dissolved in 5 mL of water and added to the previous solution.

The mixture was filtered, washed with water and finally with MeOH yielding the pure product in quantitative amounts as a white powder. ^{1}H-NMR (300 MHz, DMSO-d^6) δ (ppm): 9.50 (s, 1H, N$^+$**H**), 7.18-6.79 (m, 20H, Ar**H**), 3.54 (bs, 4H, C**H**$_2$), 3.45 (bs, 2H, C**H**$_2$), 3.24 (bs, 2H, C**H**$_2$), 2.62 (bs, 2H, C**H**$_2$), 1.90 (bs, 2H, C**H**$_2$), 1.64 (bs, 4H, C**H**$_2$).

2.2.3 Synthesis of isocyanate terminated prepolymers

Synthesis of PPG-dilPDI 1000

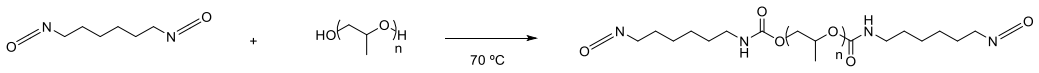


IPDI PPG-1000 PPG-dilPDI

Scheme 11. Synthesis of PPG-dilPDI 1000

In a 100 mL round, 10.00 g of PPG-1000 (Mn: 1000 g/mol) (1 eq., 10 mmol) was vacuum dried at 70 ºC over 3 h to avoid the presence of moisture that could affect in the pre-polymer formation. Once the PPG-1000 was dried, 4.68 g of IPDI (2.1 eq., 21 mmol) were added and the mixture stirred at 70 ºC under vacuum. The reaction was monitored by FTIR spectroscopy until the presence of isocyanate decreased 50 %. The resulting PPG-dilPDI 1000 was achieved as a colorless viscous liquid which was stored in the fridge.

Synthesis of PPG-diHDI 1000

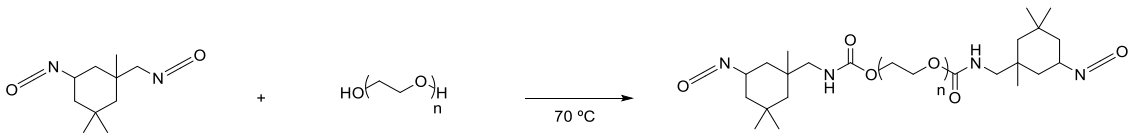


HDI PPG-1000 PPG-diHDI

Scheme 12. Synthesis of PPG-diHDI 1000

In a 100 mL round bottom flask, 10.00 g of PPG-1000 (Mn: 1000 g/mol) (1 eq.,10 mmol) was vacuum dried at 70 ºC over 3 h to avoid the presence of moisture that could affect in the pre-polymer formation. Once the PPG-1000 was dried, 3.53 g of HDI (2.1 eq., 21 mmol) were added and the mixture stirred at 70 ºC under vacuum. The reaction was monitored by FTIR spectroscopy until the presence of isocyanate decreased 50 %. The resulting PPG-diHDI 1000 was achieved as a colorless viscous liquid which was stored in the fridge.

Synthesis of PEG-dilPDI 400



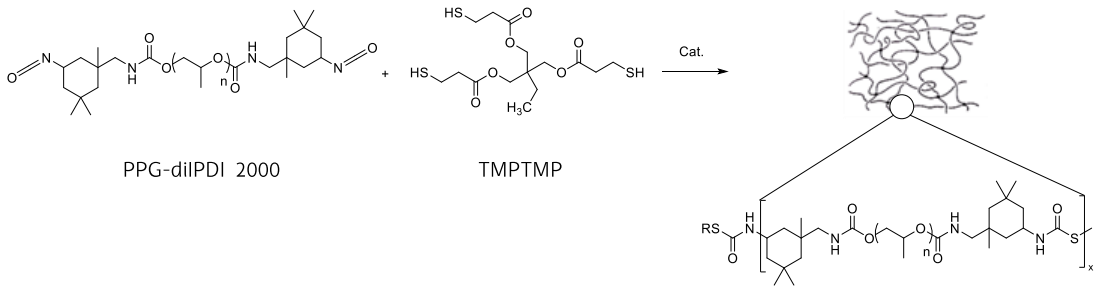
IPDI PEG-400 PEG-dilPDI

Scheme 13. Synthesis of PEG-dilPDI 400

In a 100 mL round bottom flask, 15.00 g of PEG-400 (Mn: 400 g/mol) (1 eq., 37.5 mmol) were dried by azeotropic distillation using toluene. This procedure was repeated three times. Once the PEG-400 was dried, 17.50 g of IPDI (2.1 eq., 78.7 mmol) were added and the mixture stirred at 70 ºC under vacuum. The reaction conversion was monitored by FTIR spectroscopy and the reaction stopped when 50 % of the isocyanate groups were converted. The resulting PEG-dilPDI 400 was obtained as a colorless viscous liquid which was stored in the fridge.

2.2.4 General synthesis of polythiourethane networks using PBGs

To investigate the polymerization rate of a thiol-isocyanate containing mixture, stoichiometric amounts of isocyanate and thiol groups were mixed with different PBGs. It must be noted that at least tri functional thiols were used in order to obtain crosslinked polythiourethane networks.



Scheme 14: Example of the synthesis of the PPG-dilPDI 2000 and TMPTMP containing polythiourethane thermoset.

1000.00 mg of PPG-dilPDI 2000 and 109.00 mg of TMPTMP were mixed in a 26 mL glass vial. On the other hand, 5.50 mg of catalyst and 2.75 mg of sensitizer (ITX), if needed, were mixed and dissolved in the appropriate solvent. Ethyl acetate (34.00 mg) was used as solvent with NPPOC-TMG, and acetone (300.00 mg) with TBD·$HBPh_4$ and DBU·$HBPh_4$.

The solution with the catalyst system was added to the mixture containing the isocyanate and the thiol and it was stirred until a homogeneous mixture was obtained. This mixture was placed on circular 1 cm diameter silicon molds and irradiated with an UV-light centered at 365 nm with 60 mW/cm^2 light intensity for 15 minutes. In order to know if the formation of the polythiourethane occurred after irradiation, FTIR spectra were performed before and after irradiating the material to confirm the disappearance of the isocyanate band.

In the Figure 6, it can be seen the difference between the irradiated and non-irradiated formulation.

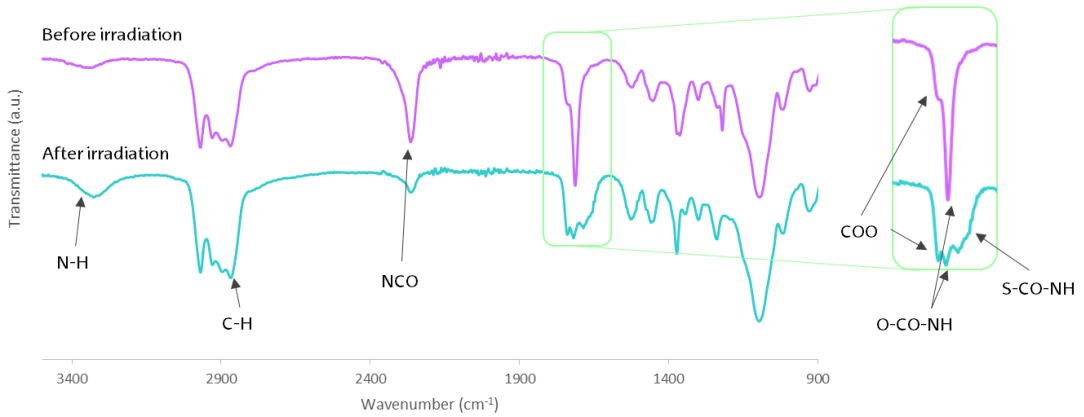


Figure 6. FTIR spectra of PTU-TBD·HBPh4 before (purple) and after irradiation (blue).

In the spectrum that corresponds to the irradiated sample, it is visible the thiourethane signal (1750 cm-1) that cannot be seen in the spectrum of the material before irradiation, meaning that the reaction occurs and the thiourethane is formed. The position of this band is in agreement with the reported one for the thiourethane bond. Besides, the signal of the isocyanate substantially decreases, leading to the formation of thiourethane band. It should be noted that the NCO band it does not disappear completely. This fact can be related with the effect of the crosslinking of the material which makes difficult for all the end-groups to react. It is remarkable that in both spectra the urethane signal (1720 cm^{-1}) is visible, since this material contains an isocyanate terminated prepolymer that contains urethane bonds. The signal that corresponds to the ester group of TMPTMP can be observed in both spectra.

To fully consume the unreacted NCO groups, a post treatment was performed in an oven at 50 ºC for 24 h.

Table 1. Formulations of the polythiourethanes

Entry	Isocyanate	Thiol	Catalyst	Cat. (wt%)	ITX (wt%)	Cat:ITX
PTU-NPPOC-TMG	PPG-dilPDI (2000)	TMPTMP	NPPOC-TMG	0.5	-	-
PTU-TBD·HBPh4	PPG-dilPDI (2000)	TMPTMP	TBD·HBPh4	0.5	0.25	2:1
PTU-DBU·HBPh4	PPG-dilPDI (2000)	TMPTMP	DBU·HBPh4	0.5	0.25	2:1

Other formulations were prepared in order to obtain different crosslinked materials, and the structure of all the polythiourethanes was confirmed by FTIR.

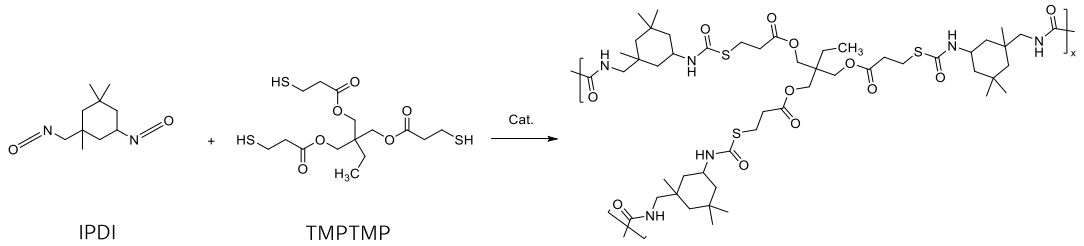
3 RESULTS AND DISCUSSION

As mentioned above, the objective of this work is to develop a polythiourethane photoprintable resin which is able to be printed by VAT 3D printing technique. To do so, resins containing isocyanate and thiol functionality are going to be investigated, their stability over time and ability of organic bases to catalyze this polymerization is going to be tested. Moreover, the effect of the implementation of photobase generators (PBGs) in this system is going to be investigated together with efficiency of them to trigger the base catalyzed photopolymerization reaction. The most interesting formulations are going to be used in a VAT type of 3D printer and printing conditions are going to be optimized.

To meet this aim, first an organic base catalyst able to reach fast polymerization rate is needed. Then, a resin formulation system that is reasonably stable over time in the absence of light has to be found. On the other hand, a PBG able to meet the previously explained expectations is required.

3.1 Investigation of the base catalyzed polythiourethane network formation

In order to understand the effect of different organic bases on the polymerization rate of an isocyanate-thiol system, a formulation containing an equimolar amount of isocyanate and thiol was tested (See Scheme 15). In this case, the difunctional isophorone diisocyanate (IPDI) was mixed with trimethylpropane tris(3-mercaptopropionate) (TMPTMP). To this formulation, three organic bases, 1,1,3,3-tetramethylguanidine (TMG), 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) and triethylamine (TEA) (0.125 wt%) were added. These bases were chosen as they are liquid and have different pKa values which could help to elucidate the effect of the basicity in the polymerization rate.

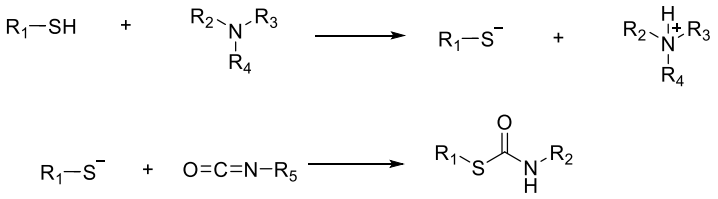


Scheme 15. Synthesis of IPDI and TMPTMP based polythiourethane networks using different catalysts.

Table 2. Details about the reactants used in the base catalyzed polythiourethane reaction.

	Isocyanate	Thiol	Base	pK_a	Base wt%
PTU-TMG	IPDI	TMPTMP	TMG	13.5	0.125
PTU-DBU	IPDI	TMPTMP	DBU	13.0	0.125
PTU-TEA	IPDI	TMPTMP	TEA	10.8	0.125

When using strong bases such as TMG or DBU (pK_a, 13.5 and 13.0 resepctively[16]), the material was instantly solidified when adding the base, suggesting an extremely fast polymerization rate. On the contrary, when a weaker base such as TEA (pK_a 10.8) was added, no change on the reaction mixture was observed after adding the base. These results suggest that the efficiency of the bases in catalyzing the thiol-isocyanate reaction depend on the acid dissociation constant (pK_a). These findings agree with the base catalyzed polythiourethane reaction reported in literature.[17] According to them the polymerization rate of a base catalyzed thiol-isocyanate reaction depends both on the basicity of the basic catalyst and the thiol. When the pK_a value of the organic base slightly overcomes the one from the thiol the reaction rates are low. However, when this pK_a difference increases substantially, an acceleration of the reaction was observed. Furthermore, the basicity of the base must be higher that the basicity of the thiol for the reaction to take place, since a strong base that has a higher pK_a value than the one of the thiol is able to abstract the proton form the thiol group and form a very strong nucleophilic thiolate anion that will attack the isocyanate group.



Scheme 16. Amine catalyzed thiol-isocyanate nucleophilic reaction mechanism.

It was tried to follow reaction conversion by analytical techniques, such as FTIR. However, due to the fast polymerization rate observed in the DBU and TMG catalyzed systems, it was not possible to obtain information in this aspect.

3.2 Synthesis and characterization of PBGs

Considering the obtained results, it was thought that it was necessary to use a PBG able to release a strong base such as TMG, DBU or TBD in order to obtain fast polymerization rates to meet the demands of 3D printing technique.

According to a literature review, the following catalysts were found promising for the synthesis of polythiourethane networks as these catalyst can release strong organic bases and have been effectively used for other kind of polymerizations such as ring-opening polymerization of cyclic esters,[18,19] or base catalyzed thiol-michael addition.[20] The chosen catalysts were NPPOC-TMG, TBD·HBPh$_4$ and DBU·HBPh$_4$ (See Figure 7).

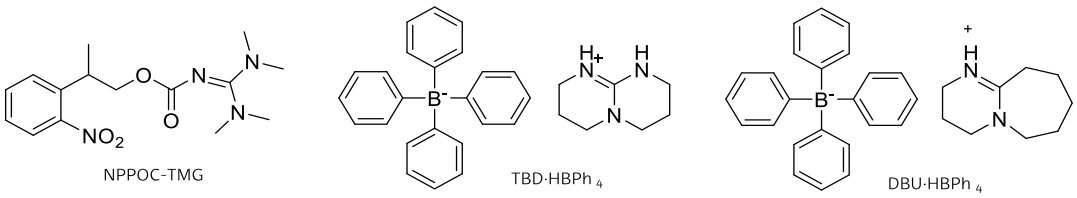
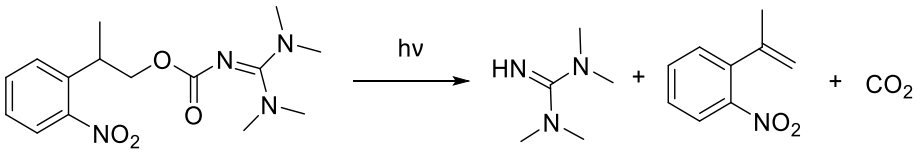


Figure 7. Molecular structures of the PBGs used in this work.

3.2.1 NPPOC-TMG

This photobase generator belongs to the carbamates class of irreversible PBGs, in which the carbamate group goes through a photodecarboxylation process upon UV light irradiation, in order to release primary or secondary bases (See Scheme 17). This class of PBG can be coupled to different bases, in this case TMG was the selected catalyst, due to the high pK_a value and effective photorelease of this photocatalyst that has been reported.[19,20] Besides that, this non-ionic photocatalyst appears as an attractive option as non-ionic PBGs have shown enhanced stability comparing to PBGs based on carboxylic acid salts.[13]



Scheme 17. Photodecomposition pathway of NPPOC-TMG upon light irradiation.

This PBG was synthetized from 1-Ethyl-2-nitrobenzene in two steps to yield the final product in medium yields. The correct formation of the PBG was further confirmed by ^{1}H NMR spectroscopy.

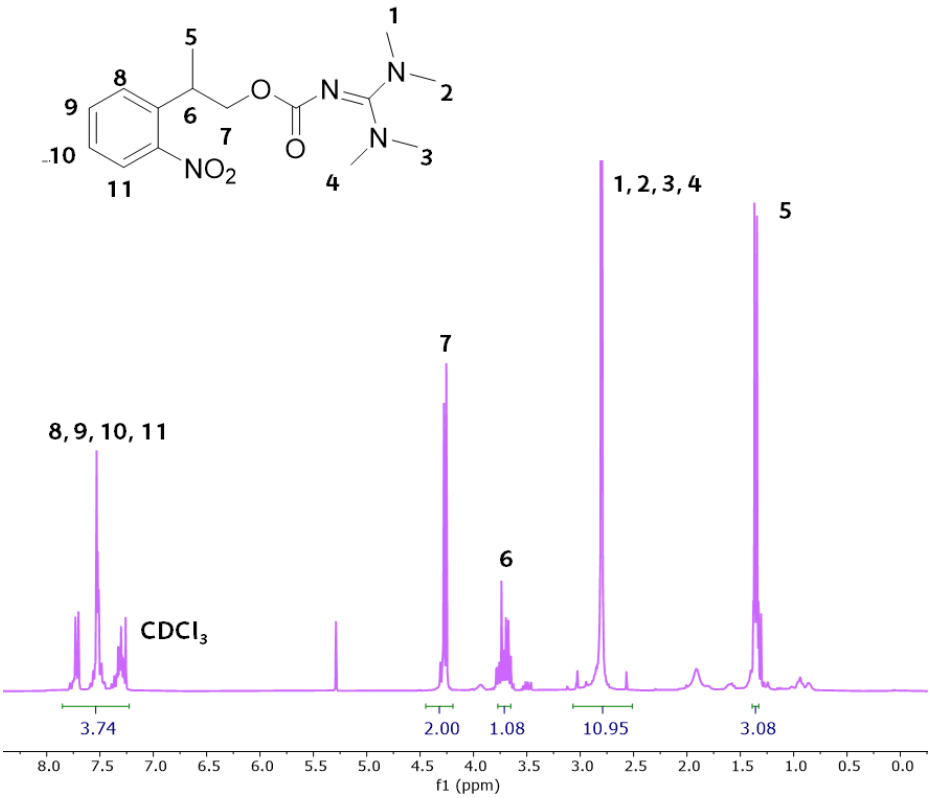


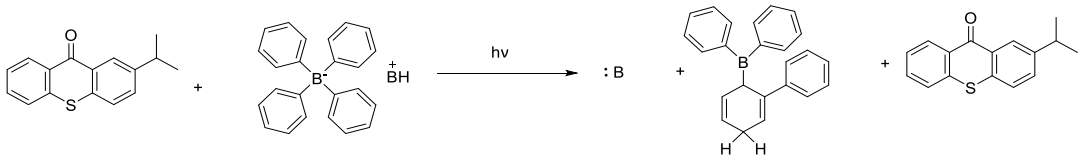
Figure 8. ^{1}H-NMR of NPPOC-TMG.

The ^{1}H-NMR spectrum of NPPOC-TMG is presented above. In there, the typical bands related with aromatic protons are observed at 7.78-7.27 ppm. At 2.80 ppm the methyl groups of the TMG are present. The integral of these band agree with the expected ones and are also in agreement with the reported spectrum for NPPOC-TMG[21] so we can conclude the proper formation of the PBG.

3.2.2 Tetraphenylborate Salts

Tetraphenylborate salts are ionic photocatalysts where the base appears protonated and is released after a rearrangement that occurs on the tetraphenylborate moiety. This kind of PBGs have been studied for polymerization reactions including thiol-isocyanate reactions with good results.[8] It must be noted that the release of the base can be performed either by light irradiation or thermally. Both activation pathways have been recently used for the synthesis of polythiourethane networks.[8,22] In this case, we were interested in the photoactivation of the PBG for its application in VAT type 3D printing. One

drawback of these catalysts is that they only present activity at short wavelength UV light (around 250 nm) which is in the UV-A region and thus it has low penetration depth, and it is harmful for living organisms which is not appropriate for our aims.[23] To avoid the use of such an energetic UV-light, 2-isopropylthioxanthone, ITX, have been used as photosensitizer. It has been reported that the use of this chromophore effectively activates many photoreactions, including the activation of tetraphenylborate salts.[24] In this way, the catalytic system can be activated using a 365 nm UV-light which is less harmful and moreover meets the requirements of our 3D printer.[15]



Scheme 18. Photodecomposition pathway of tetraphenylborate salts upon light irradiation in the presence of ITX.

These tetraphenylborate photocatalyst were considerate appropriate for this work, considering on the one hand, that the synthesis is quite simple and thus these PBGs can be prepared in large scale with no synthetic challenges.[18] On the other hand, this class of photocatalyst have been shown to be versatile, since a great variation of bases can be used.[18] In this case, the selected bases were TBD and DBU, as strong bases were needed.

These PBGs were synthesized by mixing the corresponding base and $NaBPh_4$ in an acidic aqueous environment and filtering the obtained solid to yield the final product in quantitative amounts. The formation of the PBGs was confirmed by ^{1}H-NMR spectroscopy (Figures A2 and A3).

Photolysis studies

The photolyisis of the catalyst was performed for TBD·$HBPh_4$ in order to confirm the release of the base upon UV-light irradiation. To do so, ^{1}HNMR spectra were performed to a solution containing TBD·$HBPh_4$ and ITX (2:1 in wt%)

before and after irradiating the sample with a UV light source centered at 365 nm with 60 mW/cm^2 light intensity at different times (See Figure 9).

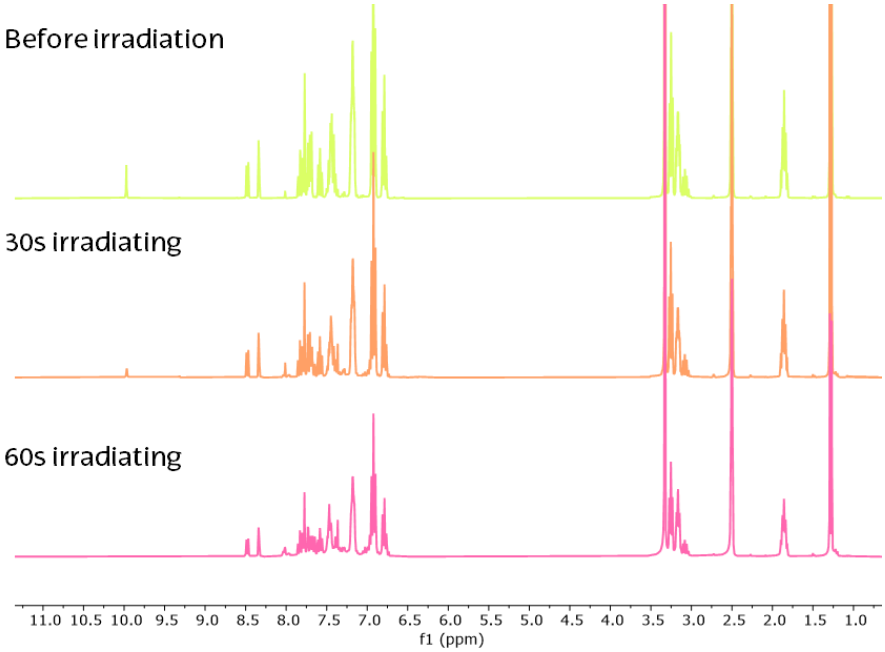


Figure 9. ^{1}H-NMR of TBD·HBPh$_4$ photolysis at different irradiation times.

From the obtained spectra it was observed the disappearance of the signal that belongs to the protonated guanidine (N$^+$**H**) after irradiation of 60 s. This observation suggests the release of the free base. In the rest of the spectra, no substantial change was observed over irradiation time, probably due to the very similar chemical structures of the secondary products.

On the other hand, light absorbance properties of the catalytic systems were investigated using UV-VIS spectroscopy. TBD·HBPh$_4$ or DBU·HBPh$_4$ were mixed together with ITX (2:1 in wt%) and dissolved in acetonitrile (10^{-4} M). Both catalysts showed two medium absorbance bands at 300 nm and 385 nm. The molar extinction coefficients at 385 nm (ε_{385}) were between 4900-6200 $M^{-1}\cdot cm^{-1}$. These optical properties are in agreement with the ones reported for ITX containing tetraphenylborate salts.[17]

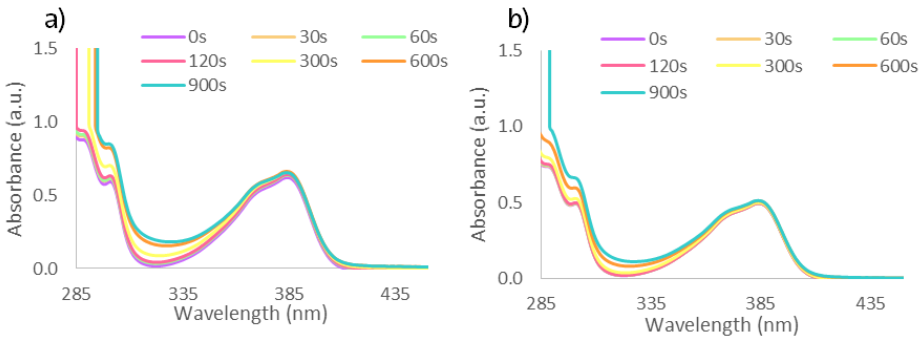
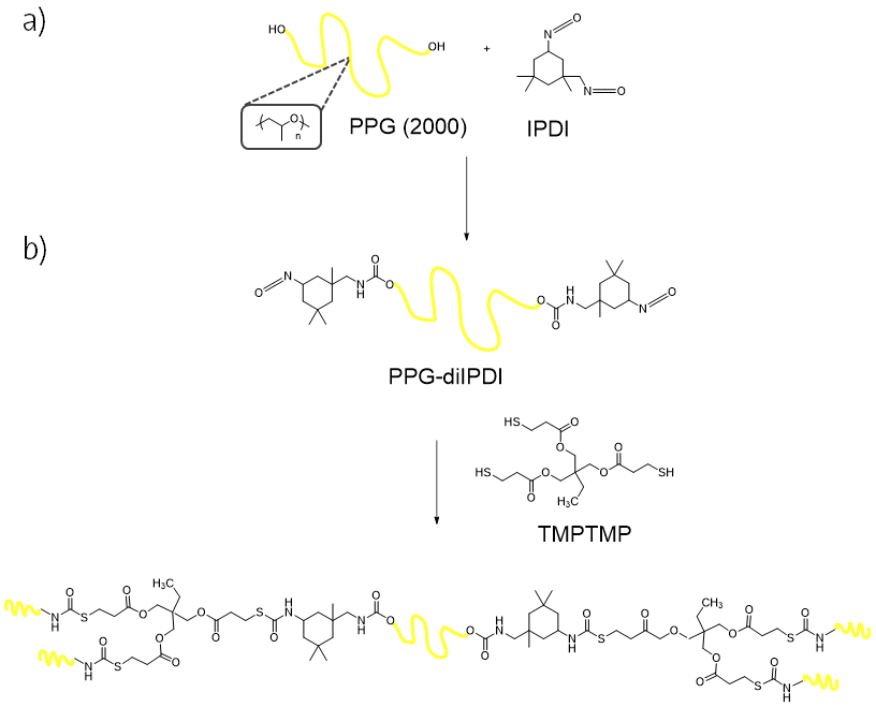


Figure 10. UV-VIS spectra of (a) TBD·$HBPh_4$ and (b) DBU·$HBPh_4$ in acetonitrile 10^{-4} M.

The evolution of the absorbance properties was checked upon UV light irradiation to see if the release of the base produces any change in the absorbance of the PBGs. To do so the samples dissolved in acetonitrile (10^{-4} M) were irradiated for different times using a UV light centered at 365 nm with 60 mW/cm^2 light intensity. No substantial change was observed in any of the tested PBGs. A slight increment of the absorbance at the 385 nm centered band was observed when increasing the irradiation time together with an increase of the shoulder at around 300 nm. However, these slight changes are not significant and can be related to solvent evaporation over time which will increase the final concentration of the PBG.

3.3 Synthesis of polythiourethane networks using PBGs

Once the PBGs were selected, the efficiency of them to promote the polymerization of polythiourethane networks was investigated. To do so, first the stability of a thiol-isocyanate containing resin was tested before the implementation of PBGs.



Scheme 19. (a) Synthesis of PPG-dilPDI (2000), (b) synthesis of the PPG-dilPDI (2000) and TMPTMP conatining polythiourethane.

The synthesized materials were characterized using rheological, thermal and spectroscopical methods in order to acknowledge their composition and behavior.

3.3.1 Stability of the thiol-isocyanate system

Since the main aim of this work is to propose new materials for VAT printing, it is required to find a system that is stable, as it might be necessary to keep the material for hours before or while the printing process.

First, it was necessary to find a system that is stable over time without the photobase generator, demonstrating that no reaction occurs in the absence of PBG. Various experiments were performed, such as FTIR and rheological studies. In these experiments, PPGdilPDI 2000 was used as the isocyanate source whereas TMPTMP was chosen as a trifunctional primary thiol (Scheme 19b).

FTIR

With the aim of proving the stability of the thiol-isocyanate system in the darkness, the conversion of the reaction was followed by FTIR spectroscopy. To do so, the area of the isocyanate band was used, referenced to the area of a band that does not change over time, in this case, to the band corresponding to the vibration of C-H placed around 2900 cm^{-1}.

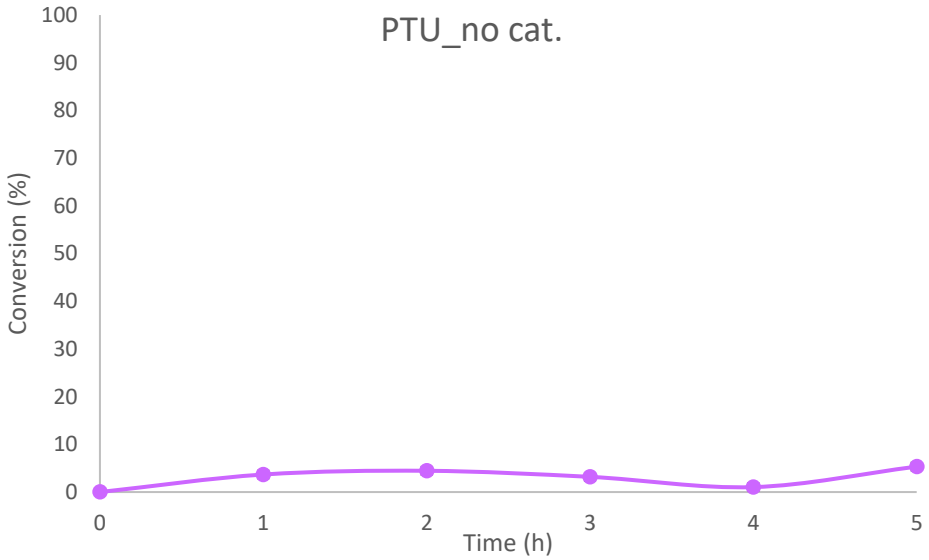


Figure 11. Conversion of the thiol-isocyanate system with no PBG followed by FTIR.

The sample was analyzed every 1 h for 5 hours, within that time barely any conversion was observed, showing the stability of the thiol-isocyanate system without catalyst.

Rheological studies

In an effort to confirm the stability of the thiol-isocyanate system, different rheological studies were performed, as these experiments allow the measurement of different rheological parameters, such as storage and loss moduli, that show the stability of the system over time. All the experiments were executed using PPGdiIPDI 2000 as the isocyanate source and TMPTMP as a trifunctional primary thiol (Scheme 19b).

All the experiments must be performed in the linear viscoelasticity region, and in order to find this region an amplitude sweep of the reticulated material was carried out. The crosslinked material was obtained by irradiating the material containing TBD·$HBPh_4$:ITX (2:1) 0.5 wt% over 0.5 hours with a UV light centered at 365 nm and 60 mW/cm^2 light intensity in order to obtain full monomer conversion. From the results obtained in this experiment for the crosslinked material, it was observed that the lineal region was between 10 and 10000 Pa (See Figure A11). In the following experiments, time sweeps with or without irradiation were performed at which the rheological properties of the material change substantially between liquid to crosslinked. Therefore, oscillatory stress of 20 Pa was selected to follow the measurements as it will lead to better results in the "liquid" region without losing a lot of resolution in the "solid" region.

First the evolution of the moduli of the materials over time was measured with no irradiation to understand the stability of the systems in the darkness without catalyst. For that, a time sweep experiment without irradiation was performed. As it can be seen in the Figure 12, the value of the moduli stays the same, around 27 Pa over 20000 s suggesting that no reaction is happening since the moduli stayed stable over that time.

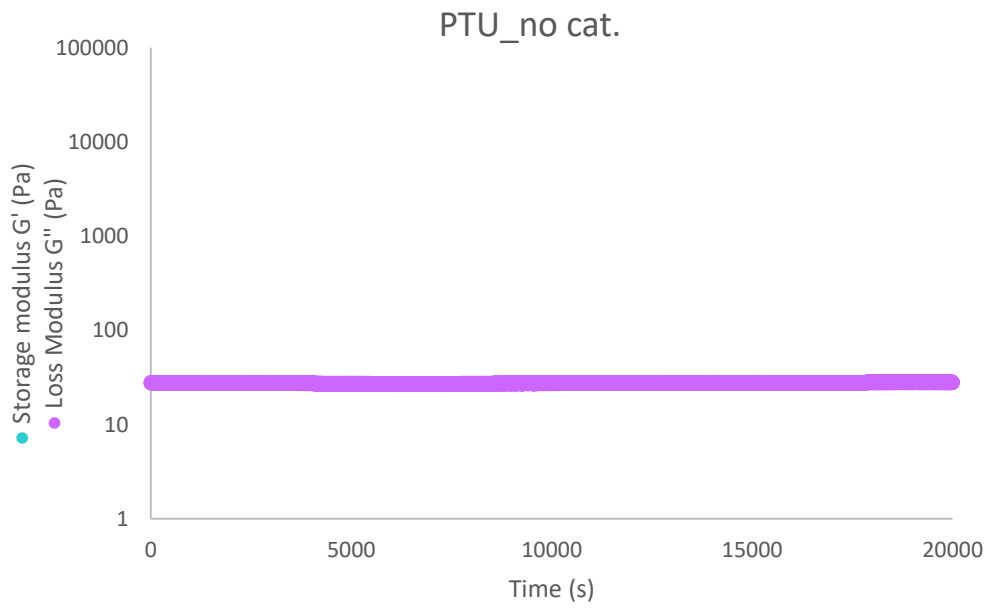


Figure 12. Dark time sweep of PPG-dilPDI (2000) and TMPTMP system with no catalyst.

When performing the time sweep experiment in the darkness, no rise of the moduli was observed over time. The same behavior was observed when FTIR spectra were recorded (See Figure 11). These results suggest that no polymerization is taking place when the mixture is kept without irradiation and that the thiol-isocyanate based resin appears as an interesting candidate for VAT 3D printing applications since particularly stable resins could be obtained. In comparison with traditionally more studied hydroxy-isocyanate formulations, thiol based resins appear to be more stable over time, lengthening its pot-life.[25]

3.3.2 Effect of the incorporation of PBGs into the thiol-isocyanate system

Once the stability of the system was confirmed without catalyst, the effect of the incorporation of various photobase generators was investigated. To do so, 0.5 wt% of photocatalyst was added to a formulation containing equimolar amounts of isocyanate and thiol functional groups, and an oscillatory time sweep experiment was performed in the darkness.

The first tested PBG was NPPOC-TMG as in principle it was the most stable candidate since it is a non-ionic PBG. The whole preparation was done by mixing all the components together with 3.5 wt% of ethyl acetate which acted as a solvent to dissolve the NPPOC-TMG.

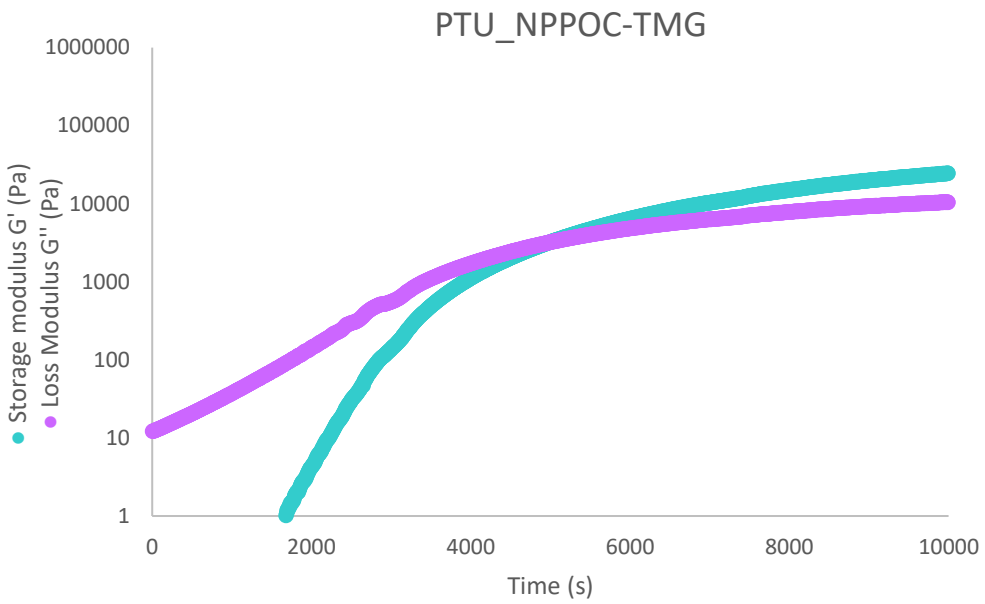
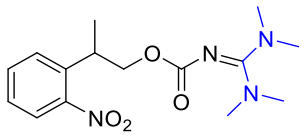


Figure 13. Dark time sweep experiment of NPPOC-TMG catalyzed system.

At first the material shows a viscous behavior (G''›G'), but as time passes by, the moduli start to increase and at 5000 s (G'›G'') the material is crosslinked, meaning this catalyst induces polymerization even in the darkness and thus it is not suitable for this system. We hypotezize that the lack of stability could be related to intrinsic basicity of this PBG as it contains 2 tertiary amines in the guanidine moiety that could be basic enough to catalyze the polymerization reaction.



NPPOC-TMG

Figure 14. Molecular structure of NPPOC-TMG.

Dissencouraged from the previous result we explored the use of tetraphenylborate salts as an alternative PBG for the aforementioned system. To do so, 0.5 wt% of photocatalyst and 0.25 wt% of ITX was added to a formulation containing equimolar amounts of isocyanate and thiol functional groups, and an oscillatory time sweep experiment was performed in the darkness.

The whole preparation was done by mixing all the components together the catalyst and ITX dissolved in acetone. In order to completely dissolve the catalyst system, acetone 30 wt% was used, that not only acted as a solvent but also avoided the high viscosity of the material.

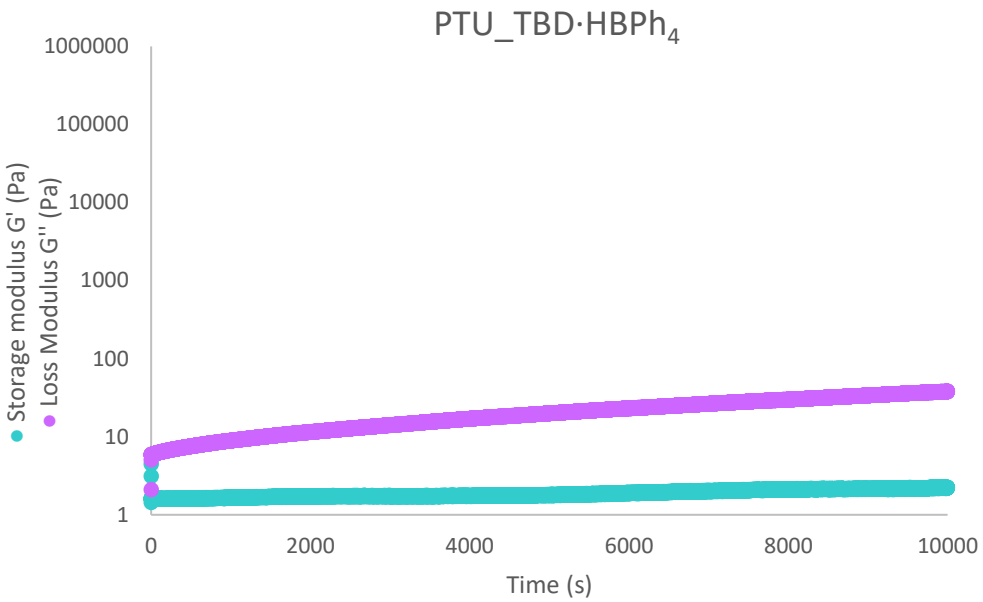


Figure 15. Dark time sweep experiment of TBD·HBPh$_4$ catalyzed system.

The system using TBDH·BPh$_4$/ITX as the catalyst also shows a viscous behavior at first (G''>G'), however, it does not show a increment of the moduli and a crossover point along the experiments (10000 s) on the contrary to the material using NPPOC-TMG, suggesting a higher stability of the catalyst in this system. It must be noted that a slight increase of the modulus was observed over time, this fact can be related with the evaporation of the diluent used in the formulation.

Encouraged by these results, we went forward on investigating the system containing tetraphenylborate salts together with ITX as latent catalyst system. To further investigate the latent behavior of this system, oscillatory time sweep experiments were performed with UV light irradiation.

3.3.3 Photorheological investigation of PBG containing thiol-isocyanate systems

Prior to printing the materials, photorheological studies were made to observe the behavior of these materials under irradiation with UV light. All the experiments in this section were performed using a stress value of 20 Pa and a frequency value of 1 Hz. First, the samples were kept 60 s in the darkness, and then it was proceeded with the irradiation of the sample at 20 mW/cm^2 over time with a UV light source centered at 365 nm.

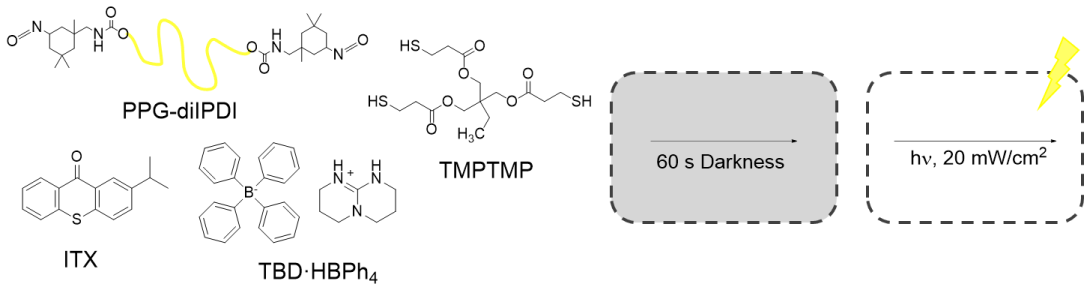


Figure 16. General scheme of the photorheological study for PBG containing thiol-isocyanate resins.

In general, time sweep experiment with irradiation were made using a formulation containing equimolar amounts of isocyanate and thiol groups these being PPG-dilPDI 2000 as diisocyanate and TMPTMP as a trifunctional primary thiol source, together with 0.5 wt% of TBD·HBPh$_4$ and 0.25 wt% of ITX dissolved in a 30 wt% acetone according to the total mass unless otherwise specified. (Figure 16)

First, an experiment to understand the photorheologycal behavior of the resin was performed with the aforementioned conditions.

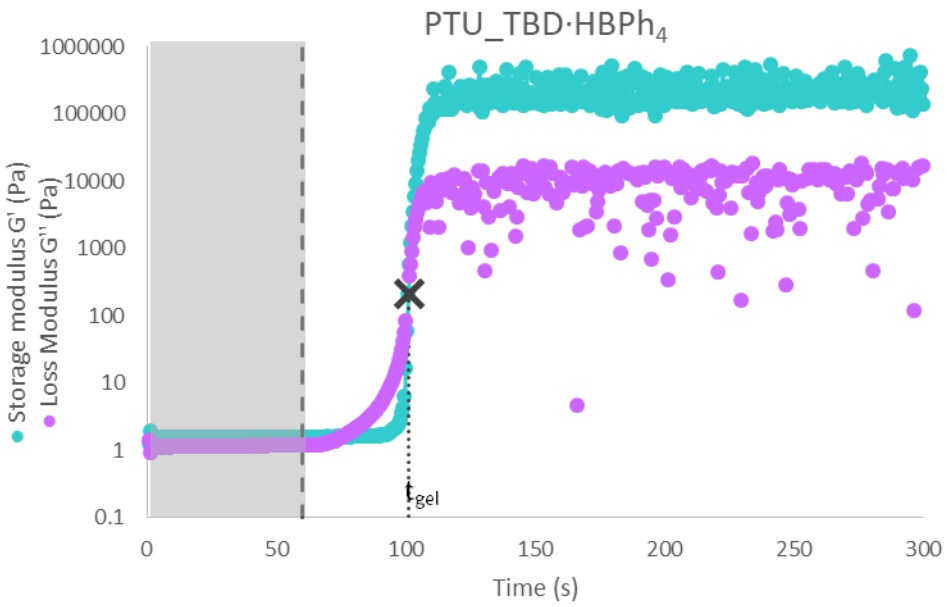


Figure 17. Irradiated time sweep experiment of TBD·$HBPh_4$ catalyzed system.

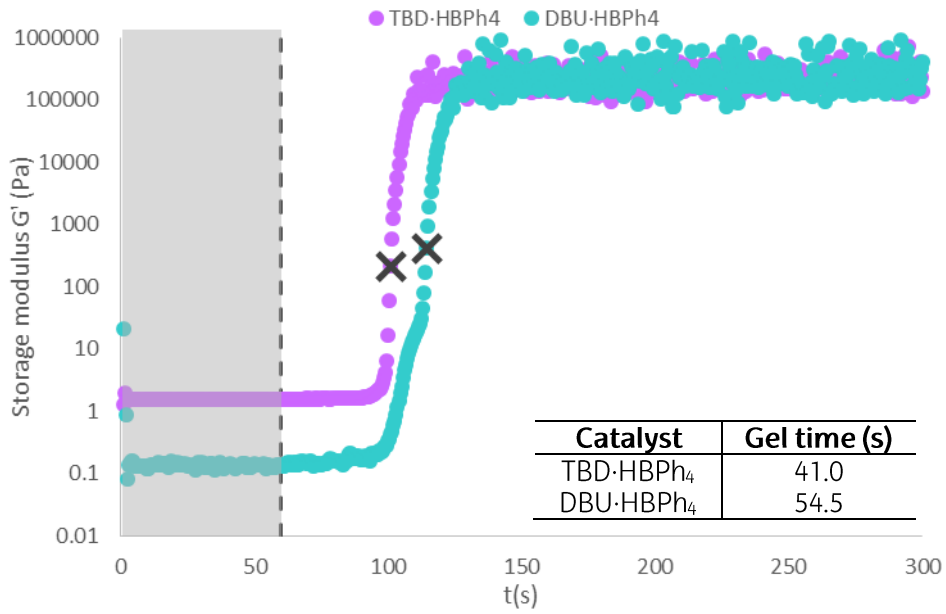
As shown in the Figure 17, the tested formualtion shows an stable moduli over the time while kept in the darkness, although a sudden increase of the moduly was observed once the sample was irradiated. The crossover point was achieved after 41 s of irradiation and the final storage modulus of the material was around $1 \cdot 10^5$ Pa.

From now on, the gel time of the materials is going to be considered as the time for the crossover point between the loss and the storage moduli after beginning the irradiation of the sample and is going to be shown with a black cross on the curves (See Figure 17).

In order to deeply study this system various measurements were made, changing different parameters such as; the catalyst, the catalyst quantity, the catalyst and sensitizer ratio, the intensity of the irradiation and the resin formulation.

Catalyst screening

With the aim of selecting the most efficient catalyst for this system, a time sweep experiment with irradiation was performed to formulation using TBD·HBPh$_4$ or DBU·HBPh$_4$ as tetraphenylborates together with ITX as sensitizer.



Catalyst	Gel time (s)
TBD·HBPh$_4$	41.0
DBU·HBPh$_4$	54.5

Figure 18. Irradiated sweep experiment using TBD·HBPh$_4$ (purple) or DBU·HBPh$_4$ (blue) as catalysts.

Both systems, using TBD·HBPh$_4$ and DBU·HBPh$_4$, present a very similar curve; before irradiation the materials have a liquid behavior, but after irradiation they both crosslink at similar times. The formulation catalyzed by the TBD containing photocatalyst, reaches the gel time within 41 s, while the one bearing DBU needs around 55 s. Even the time difference is small, it can be related with the higher pK_a value of the TBD in comparison with DBU which might also increase the polymerization rate. Nevertheless, both catalysts are appropriate for preparing crosslinked polythiourethane networks.

The effect of the catalyst percentage was also tested by an oscillatory time sweep with irradiation of a formulation containing TBD·HBPh$_4$/ITX (2:1 in weight) in different quantities.

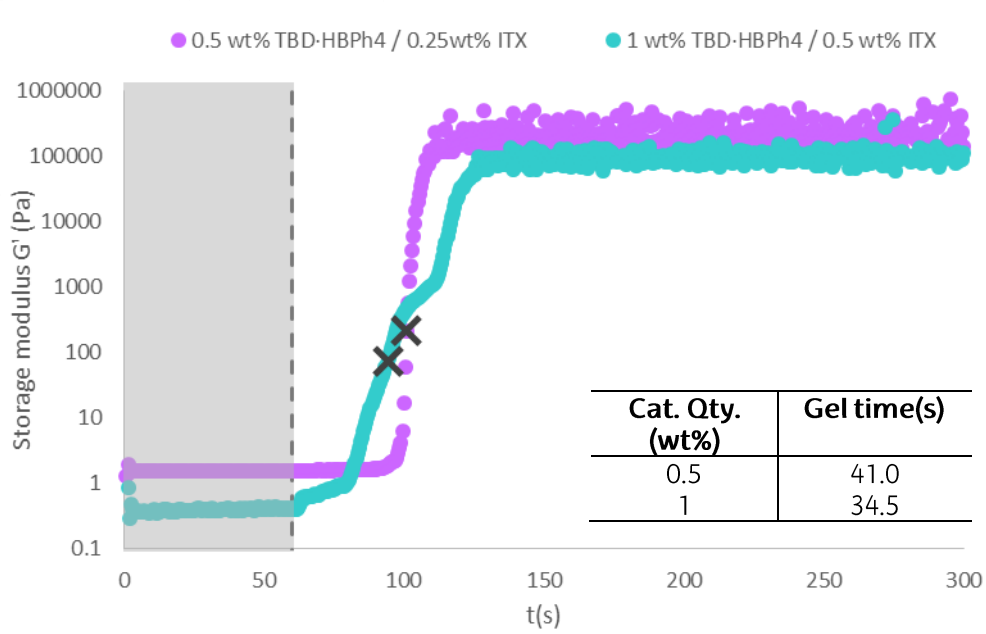


Figure 19. Irradiated sweep experiment using 0.5 wt% TBD·$HBPh_4$ (purple) or 1 wt% TBD·$HBPh_4$ (blue) catalyst quantities.

Both systems present the same behavior before and after irradiation; prior to being irradiated, the samples show a liquid behavior, and a solid behavior after. When using more catalyst loading, the crosslinking occurs a bit faster with a difference of 6 s in reaching the gel time. However, we observed that the system using 1 wt% of PBG loses stability in the darkness as an increment of the viscosity was observed after 1 h.

In order to understand the effect of the catalyst/sensitizer ratio, an oscillatory time sweep with irradiation was performed using different TBDH·BPh_4/ITX ratio in weight. The chosen ratios were 1:1 (1:1.8 in mol), 2:1 (1:0.9 in mol), 1:2 (1:3.6 in mol), 5:1 (1:0.4 in mol), 1:0 (1:0 in mol) and 0:1 (0:1 in mol).

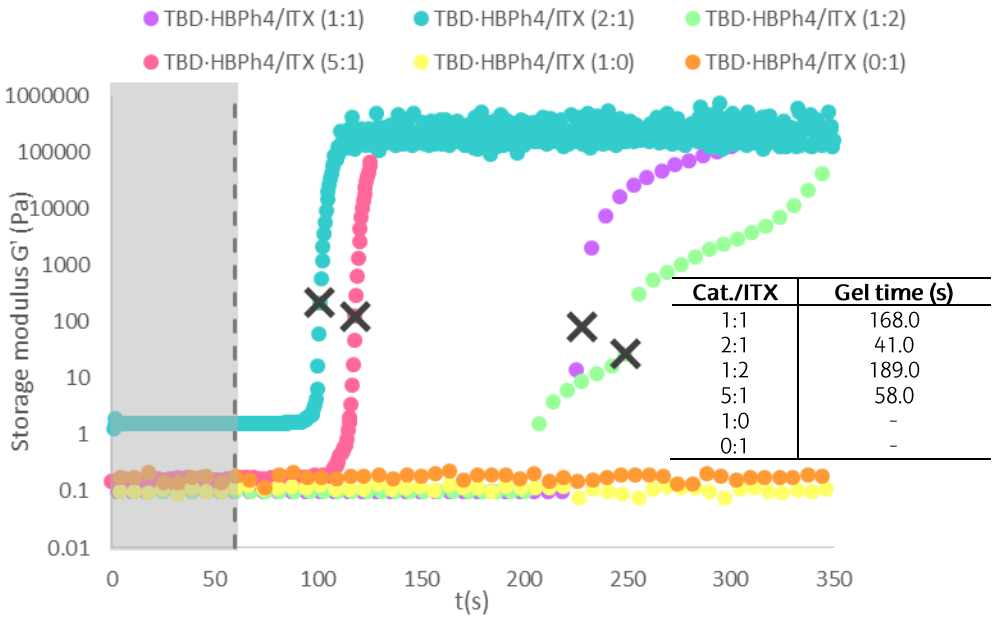


Figure 20. Irradiated sweep experiment using 1:1 (purple), 2:1 (blue), 1:2 (green), 5:1 (pink), 1:0 (yellow) or 0:1 (orange) TBD·HBPh$_4$/ITX ratios.

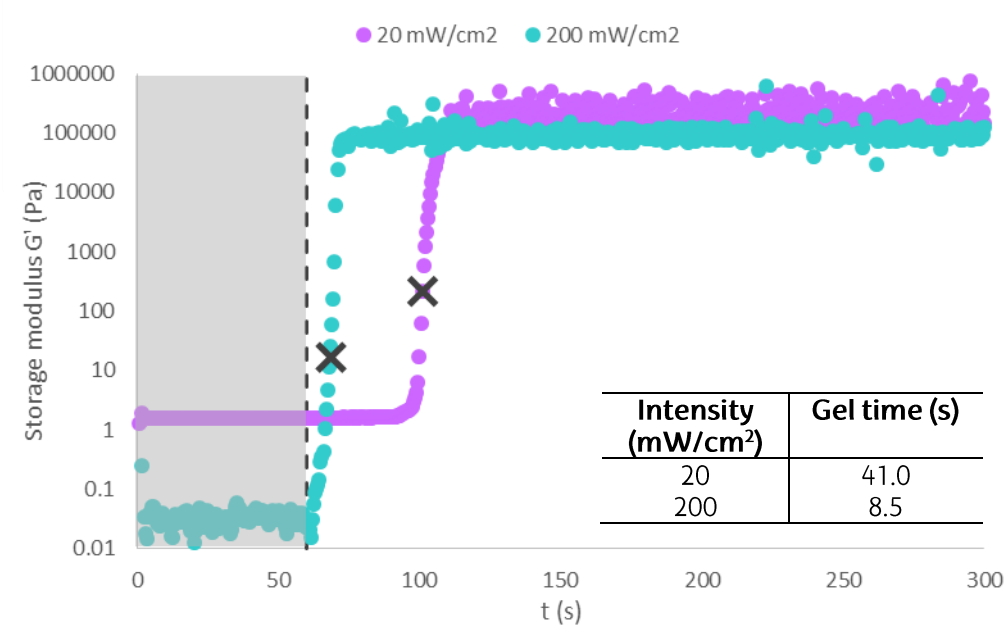
When using just the catalyst (TBD·HBPh$_4$) or just the sensitizer (ITX), the moduli do not change with irradiation and no crossover point can be observed, meaning no reaction is occurring and, therefore, both the catalyst and the sensitizer are necessary for the reaction to take place.

Using the catalyst sensitizer system, the reaction occurs slower when the quantity of the ITX in weight is the same as (t_{gel}=168 s) or higher than (t_{gel}=189 s) the quantity of TBDH·BPh$_4$. Meanwhile, when the percentage in weight of the catalyst is higher than the sensitizer one, the crosslinking happens faster. Nevertheless, when using 5:1 ratio (t_{gel}=58 s) the gel time is slightly higher than when using 2:1 ratio. It must be noted that the 2:1 ratio corresponds with almost the stoichiometric amount of TBDH·BPh$_4$ towards ITX.

In the curve corresponding to the 1:2 ratio, a double increment of the modulus can be observed. This can be a consequence of the radical excitation behavior of ITX when irradiated,[24] which could influence on the kinetics of the reaction, although this was no further explored.

Irradiation intensity

In order to understand the effect of the intensity of the light used for irradiating the sample, a time sweep with irradiation using different intensity of irradiation was carried out.



Intensity (mW/cm²)	Gel time (s)
20	41.0
200	8.5

Figure 21. Irradiated sweep experiment using 20 mW/cm² (purple) or 200 mW/cm² (blue) light intensities.

When the intensity of irradiation is higher the crosslinking of the material occurs faster, showing the dependency of the catalyst on the intensity of the light. In this case, when an irradiation value of 200 mW/cm² was applied, the gel time was achieved within 8.5 s. This result is in agreement with a higher activation of the PBG with an increased irradiation light intensity. This variable can be introduced to modify the polymerization rate of the sample, thus tuning the printing conditions.

Diluent

Due to the high viscosity of the raw resin a diluent was needed to make the resin applicable for 3D printing. In order to select the most appropiate diluent, a time sweep experiment with irradiation using different diluents was carried out.

In this case two different diluents were used. On the one hand, acetone was used as it is a volatile solvent easily available. Moreover, it perfectly dissolves the catalyst/sensitizer system. On the other hand, methyl lactate was selected as diluent as this has been used as a non-reactive diluent in various research works.[26]

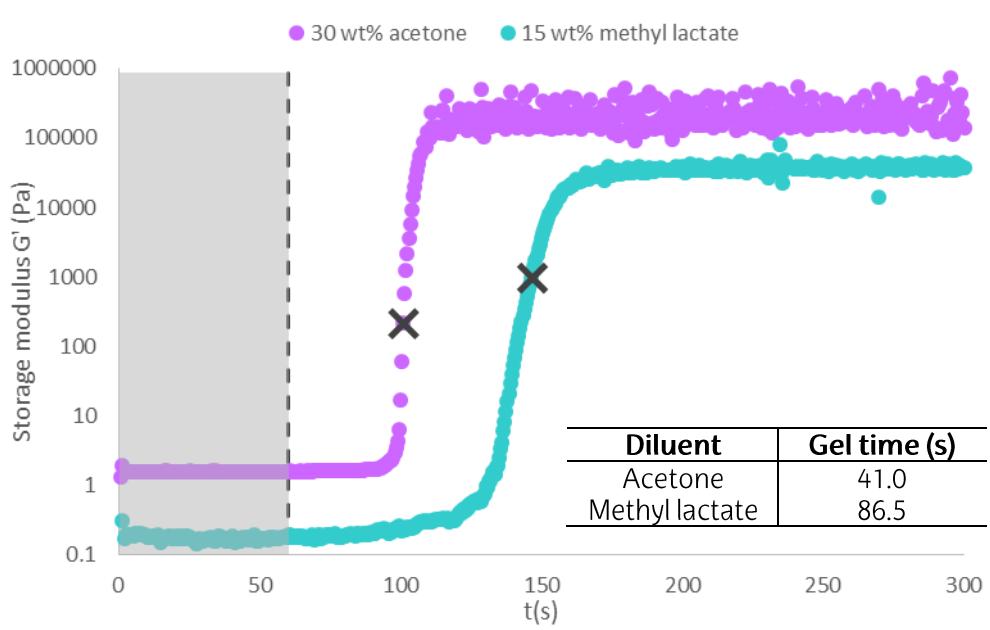


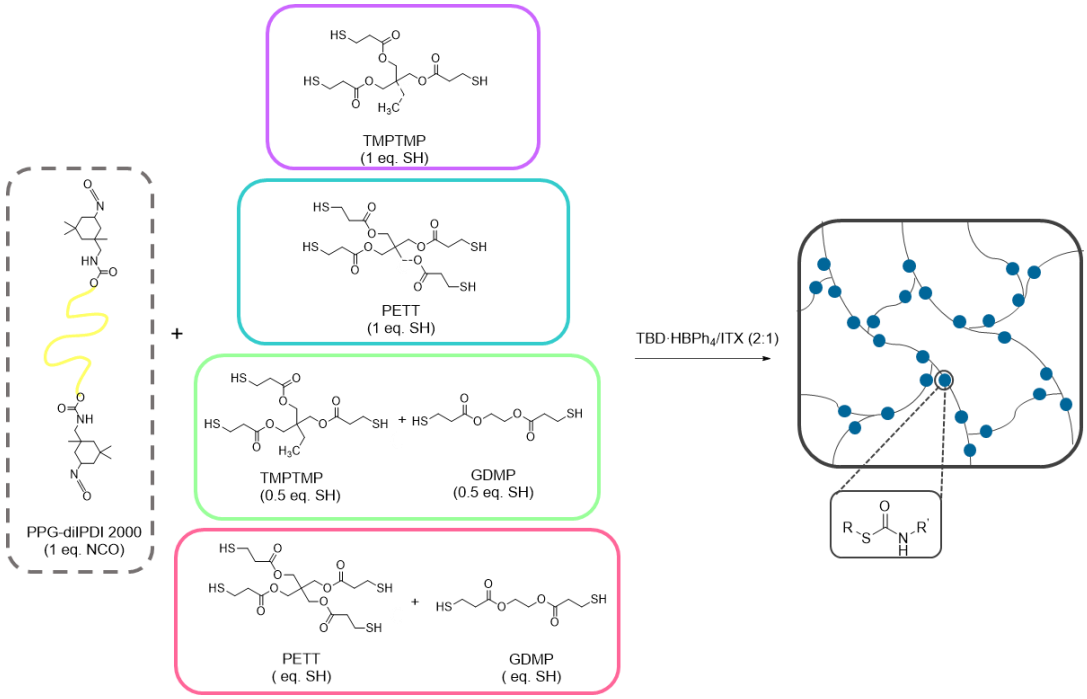
Figure 22. Irradiated sweep experiment using acetone (purple) or methyl lactate (blue) as diluents.

The selected quantity of acetone was 30 wt%, since it was necessary in order to completely dissolve the catalyst and ITX. It needs to be considered that the amount of acetone decreases over time due to the high volatility of the solvent, lowering the wt% of it in the resin. Regarding the methyl lactate, it was observed that 15 wt% was enough to adjust the viscosity for 3D printing. To obtain this resin, the crude mixture containing acetone was completely dried under vacuum and then the amount of methyl lactate was added.

When using methyl lactate as the diluent (t_{gel}=87 s) the crosslinking of the material is slower even 15 wt% was used. It has to be noted that the starting modulus seems to be also lower probably meaning that the viscosity of the system is lower and thus more time to crosslink.

Formulation

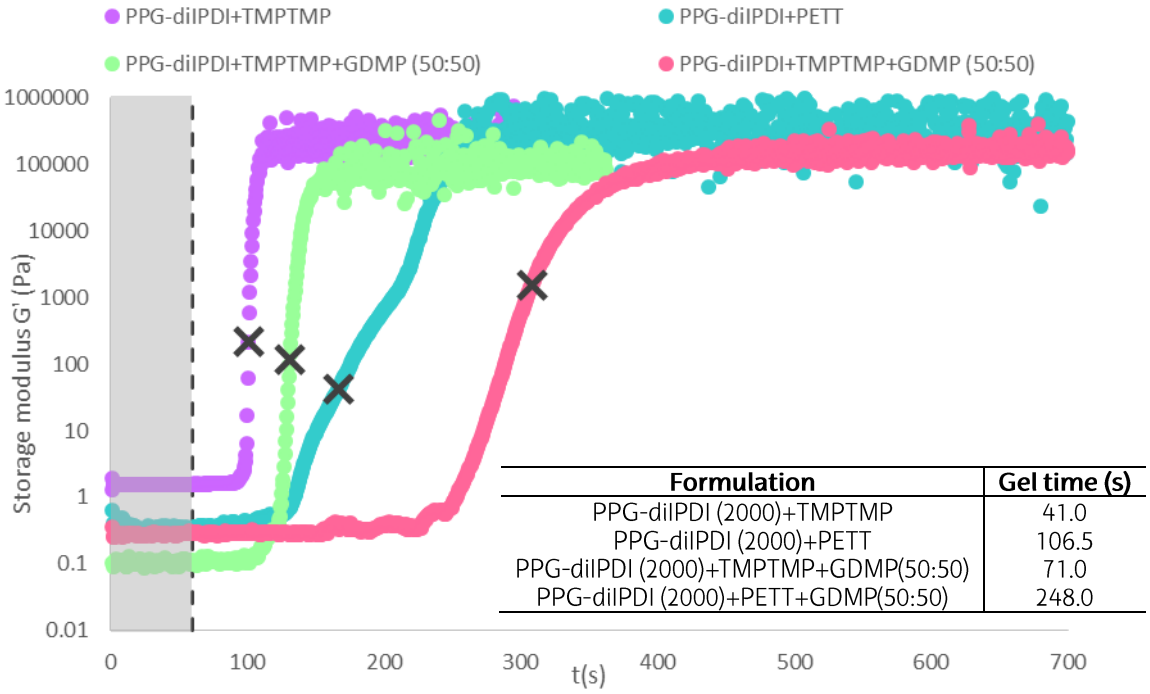
In order to understand the effect of the polymerization reaction using different isocyanates and thiols, various time sweeps were performed using diverse formulations with TBD·$HBPh_4$ 0.5 wt% and ITX (2:1) as catalyst (Scheme 20).



Scheme 20. Synthesis of polythiourethane using PPG-dilPDI (2000) and TMPTMP (purple), PETT (blue), TMPTMP/GDMP (green) or TMPTMP/GDMP (pink) as thiols.

On the one hand, the effect of the use of different thiols was tested. Surprisingly, the formulation using a tetrafunctional thiols (Pentaerythritol tetrakis(3-mercaptopropionate) (PETT)) needs a longer time for the crosslinking to happen (t_{gel}=107 s) than the formulation with trifuntional thiol (TMPTMP) (t_{gel}=41 s). At first it was expected that the tetrafunctional thiol reaches higher crosslinking density, so a faster rise of the moduli was anticipated. It is also noticeable that when adding a difunctional thiol (Glycol di-3-mercaptopropionate (GDMP)) on a 50:50 thiol-mol ratio with the tetra- or trifunctional-thiol, maintaining the equimolarity between the diisocyanate and thiol compounds; the gel time is lower, tetraSH (t_{gel}=248 s), triSH (t_{gel}=71.0 s)

than when using only tetra or trifunctional thiols. When using the dithiol, there are fewer crosslinking points, making the material crosslink slower.



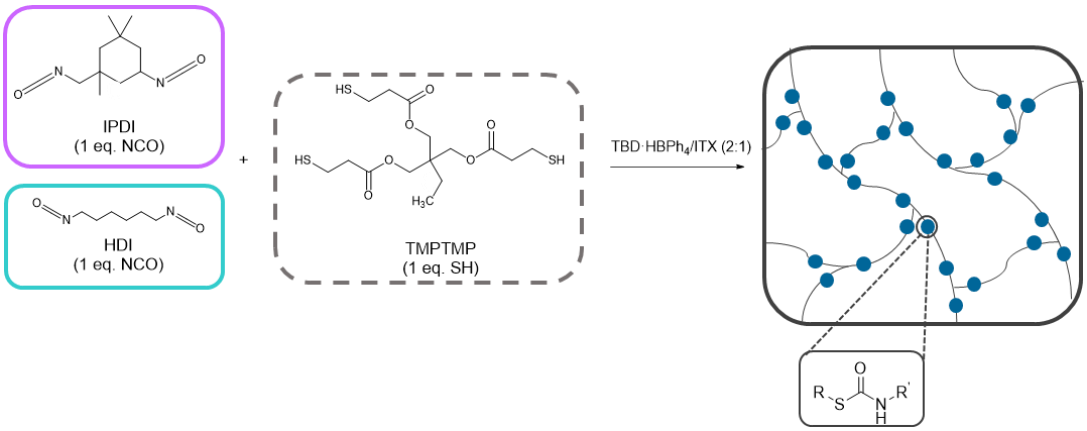
Formulation	Gel time (s)
PPG-diIPDI (2000)+TMPTMP	41.0
PPG-diIPDI (2000)+PETT	106.5
PPG-diIPDI (2000)+TMPTMP+GDMP(50:50)	71.0
PPG-diIPDI (2000)+PETT+GDMP(50:50)	248.0

Figure 23. Irradiated sweep experiment using TMPTMP (purple), PETT (blue), TMPTMP/GDMP (green) or PETT/GDMP (pink) as thiols.

Crosslinked materials were obtained with all the formulations, demonstrating that different reticulated materials, with different properties, can be achieved when using a variety of thiols.

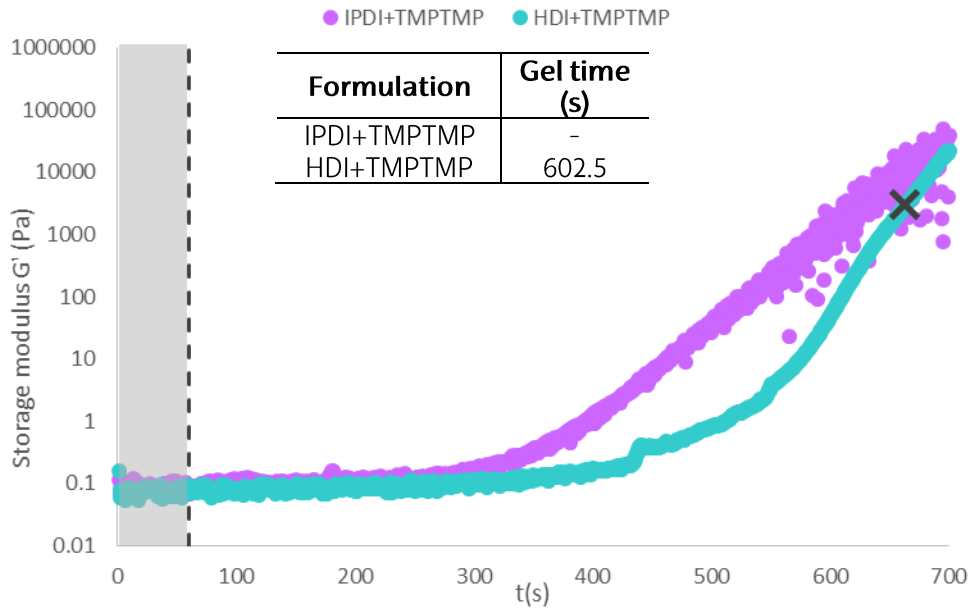
On the other hand, different isocyanate sources were tested and mixed together with TMPTMP as tri-functional thiol monomer. To do so, either isocyanate-terminated prepolymers or simple diisocyanates were used.

First, the use of simple diisocyanates is going to be discussed.



Scheme 21. Synthesis of polythiourethane using TMPTMP and IPDI (purple) or HDI (blue) as diisocyanates.

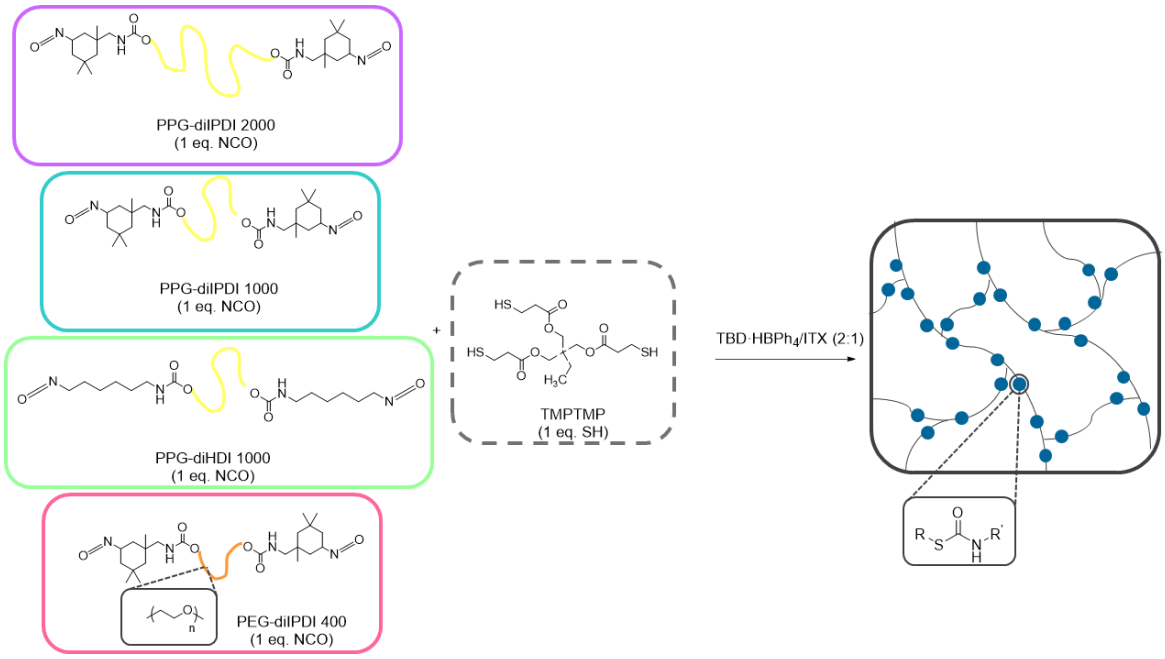
When using HDI and IPDI the moduli increase very slowly (Figure 24). While the system with HDI as the isocyanate shows the gel time (t_{gel}=603 s), in the system with IPDI, a crossover point cannot be clearly observed. HDI is a more reactive diisocyanate than IPDI, as it has both primary isocyanates. On the other hand, IPDI has a primary and a secondary isocyanate which limits the reactivity mainly the one of the secondary isocyanate as it is substantially less electrophilic due to steric hindrance.[27]



Formulation	Gel time (s)
IPDI+TMPTMP	-
HDI+TMPTMP	602.5

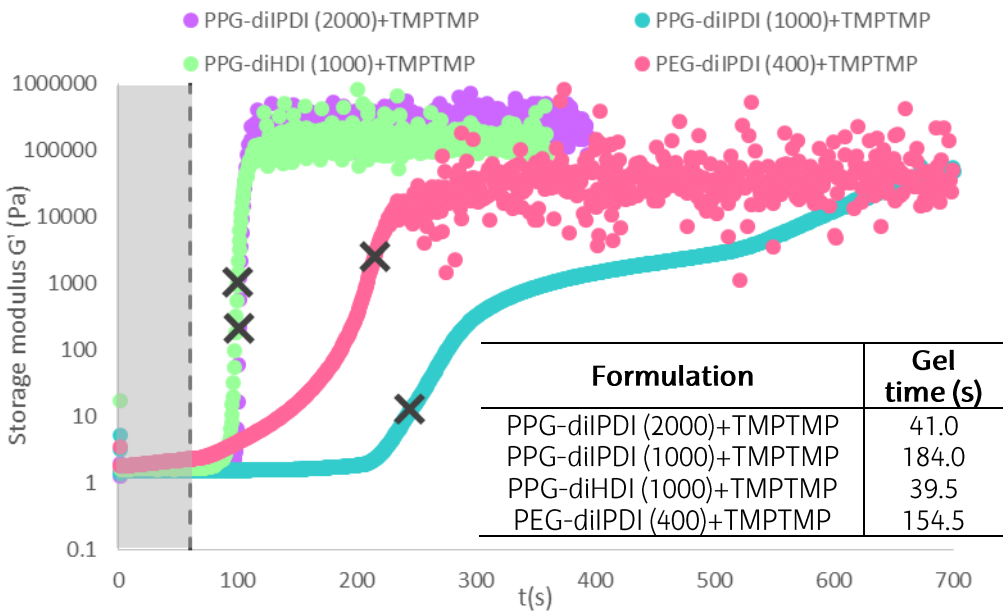
Figure 24. Irradiated sweep experiment using IPDI (purple) or HDI (blue) as diisocyanates.

On the other hand, isocyanate-terminated prepolymers were tested in order to investigate the effect of the prepolymer in the polymerization reaction.



Scheme 22. Synthesis of polythiourethane using TMPTMP and PPG-dilPDI (2000) (purple), PPG-dilPDI (1000) (blue), PPG-diHDI (1000) (green) or PEG-dilPDI (400) (pink) as diisocyanate terminated prepolymers.

When using a 1000 g/mol molecular weight PPG-dilPDI (t_{gel}=184 s) the crosslinking occurs slower than when using a 2000 g/mol molecular weight PPG-dilPDI (t_{gel}=41.0 s) as shown in Figure 25. This result is related to the viscosity of the prepolymer, since the viscosity of the PPG-dilPDI (Mn=2000 g/mol) is higher, the moduli increase faster, reducing the time to achieve crossover point.



Formulation	Gel time (s)
PPG-diIPDI (2000)+TMPTMP	41.0
PPG-diIPDI (1000)+TMPTMP	184.0
PPG-diHDI (1000)+TMPTMP	39.5
PEG-diIPDI (400)+TMPTMP	154.5

Figure 25. Irradiated sweep experiment using PPG-diIPDI (2000) (purple), PPG-diIPDI (1000) (blue), PPG-diHDI (1000) (green) or PEG-diIPDI (400) (pink) as diisocyanate terminated prepolymers.

Using a prepolymer with terminal HDI (PPG-diHDI (1000)) (t_{gel}=40 s), the obtained gel time of the material is lower than when using IPDI terminated prepolymer (PPG-IPDI (1000)) due to difference in reactivity between primary and secondary isocyanates explained above. It has to be noted that both isocyanate groups from PPG-diIPDI (1000) are mainly secondary, as this prepolymer is synthesized by using double equivalents of isocyanate towards hydroxy groups. Therefore, only the primary isocyanate groups react when full conversion of hydroxy groups is achieved.

Polyethylene glycol (PEG) based isocyanate terminated prepolymer was also used (PEG-diIPDI (400)), in this case the crossover point was achieved within 155 s. It must be noted that the molecular weight is different comparing to the PPG prepolymers. In this case a PEG prepolymer with a molecular weight of 400 g/mol was used as it is liquid at room temperature, since PEG is a semicrystalline polymer that starts to be solid at room temperature from a molecular weight of 600 g/mol. This case is not convenient for room temperature 3D printing applications and thus was not investigated.

To sum this section up, by performing photorheological experiments it is concluded that the use of tetraphenylborate salts as catalysts is appropriate for this system, always considering the importance of catalyst/ITX ratio. It is also noticeable the capacity of obtaining different crosslinked materials by using different formulations. In this sense, the resins comprised by isocyanate terminated prepolymers and trifuntional thiols appear to be the most promising ones for 3D printing applications.

3.3.4 Characterization of the synthesized polythiourethane networks

DSC

In order to learn the transition temperatures and the effect of the formulation on the thermal properties of the material calorimetric experiments were performed using a DSC equipment. To select the temperature ramp a TGA was performed under atmospheric conditions and using a 10 ºC heating rate. A weight loss of 95% was observed at 238 ºC, therefore, the experiment was carried out under this temperature to avoid the thermal decomposition of the material that could damage the equipment (Figure A12).

To prepare the samples for DSC, the isocyanate and the thiol were mixed and the catalyst and ITX dissolved in acetone were added to the mixture and were stirred until homogeneity was achieved. From this mixture aliquots of 300 µL were transferred into silicone discs with a diameter of 1 cm and irradiated over 0.5 hours with a UV light centered at 365 nm (Hamamatsu, 60 mW/cm^2). Afterwards, the plates were cured for 24 h at 50 ºC.

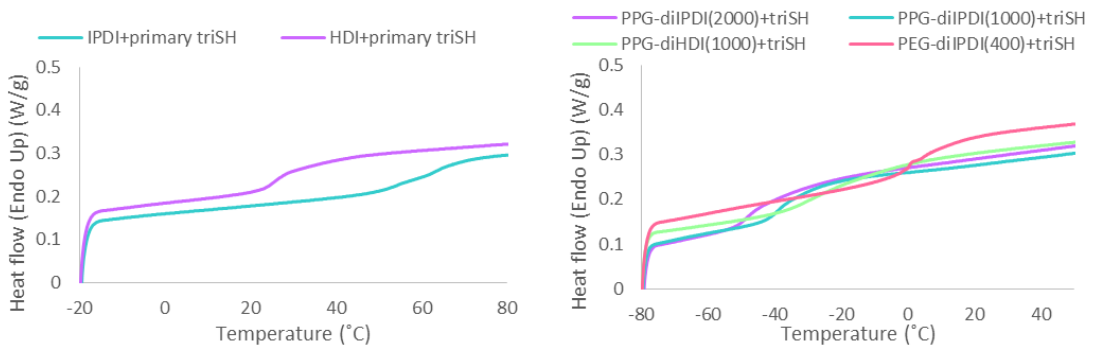


Figure 26. DSC experiment of different crosslinked polythiourethanes.

The obtained results reveal that the studied materials are amorphous, as only the glass-transition (T_g) can be observed in all the cases. It can also be highlighted that different thermal properties can be obtained depending on the starting formulation; when using isocyanate terminated prepolymers, the obtained materials are more flexible, as the T_g is under room temperature, at the contrary, when using low molecular weight diisocyanates the material becomes more rigid due to the higher amount of thiourethane bonds in the system having H bonding, increasing chain interaction.

On the one hand, comparing the T_g values of the materials obtained when using IPDI (T_g=56.69 ºC) or HDI (T_g=25.57 ºC) containing formulations, it is noticeable that the value increases when using IPDI, as the ring of its structure provides rigidity to the material comparing to the aliphatic chain offered from the HDI isocyanate.

On the other hand, when observing the T_g values of the formulations that contain different isocyanate terminated prepolymers, it can be noted that the T_g value is lower when using PPG-diIPDI 2000 (T_g=-49.40 ºC) than when using PPG-diIPDI 1000 (T_g=-39.30 ºC). These results show that when increasing the molecular weight of the prepolymer, the T_g value of the material decreases, since the percentage of segments of the polymer chain that provide rigidity (thiourethane groups) is reduced and therefore, the effect of these segments decreases while the effect of the soft segments (PPG) increases.

The obtained T_g values for the formulations with PPG-diIPDI (1000) (T_g=-39.30 ºC) and PPG-diHDI (1000) (T_g=-34.10 ºC). As previously explained, when using high molecular weight prepolymers the effect of the isocyanates decreases, and the value of the T_g relies on the PPG. However, it has to be noted that the T_g value for the system with PPG-diHDI is slightly higher, this might happen due to the flexibility of the aliphatic chain of HDI to promote H bonding between (thio)urethane bond and providing a slight rigidity to the material.

In the case of the material with PEG-diIPDI (400) (T_g=0.51 ºC), the T_g value is quite higher when comparing it to the other obtained values. It needs to be considered that PEG, as it is a semicrystalline polymer, that starts to be solid at room temperature from 600 g/mol. Although in this case 400 g/mol PEG was used, the rigidity of the material is considerably higher than the one for the materials containing PPG as prepolymer and it has an effect on the T_g value. Besides, the higher T_g value might be also due to the lower molecular weight of the prepolymer, increasing the effect of the rigid thiourethane groups.

FTIR

The crosslinked polymers were also characterized using FTIR spectroscopy. In the Figure 27, it can be seen the difference between the materials obtained using different diisocyanates mixed with TMPTMP, 0.5 wt% of TBD·HBPh$_4$ and 0.25 wt% of ITX dissolved in acetone 30 wt%. All the sample were post curated in an oven at 50 ºC for 24 h in order to remove the remaining isocyanate groups.

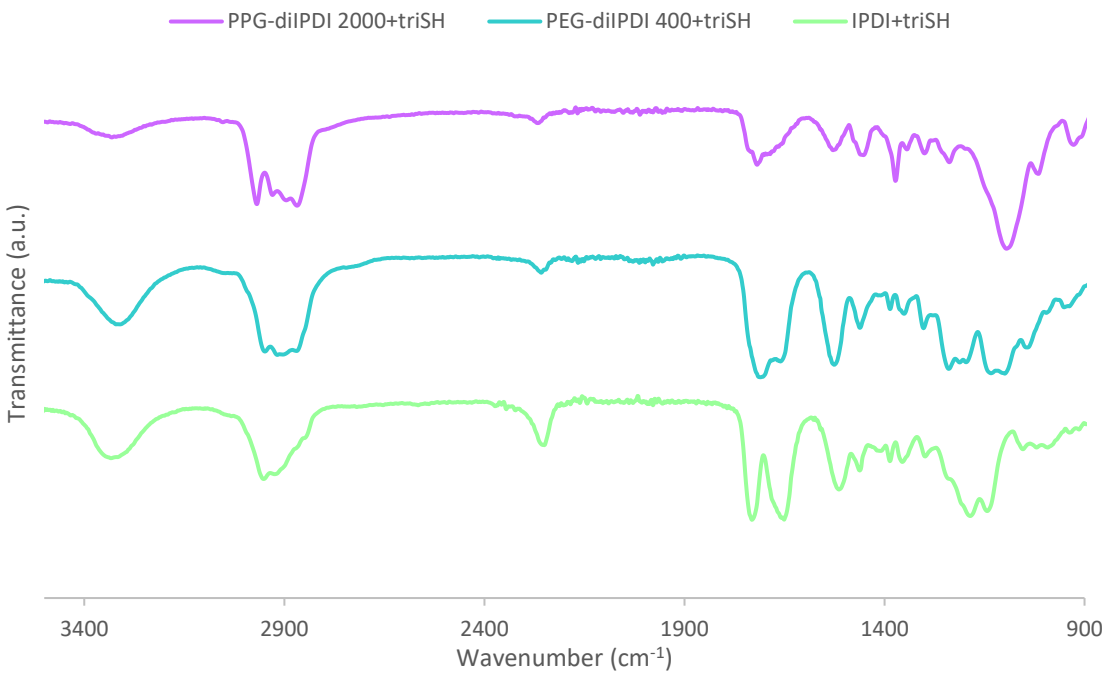


Figure 27. FTIR spectra of polythiourethanes with different isocyanates.

In the spectrum that corresponds to the IPDI containing material, it is visible the isocyanate signal (2250 cm^{-1}) that should not be seen in the spectrum of the post curated material. However, due to the rigidity of the material, the remaining isocyanates have limited mobility and are not able to react.

It has to be noted that both spectra of the formulations containing isocyanate terminated prepolymers, show the urethane (1720 cm^{-1}) signal as this prepolymers are synthesized by using double equivalents of isocyanate towards hydroxy groups, forming urethane bonds. In all the spectra are visible the signal corresponding to the thiourethane bond (1750 cm^{-1}), confirming the formation of the polythiourethanes. The FTIR spectra of the rest polythiourethane materials are shown in the Appendix (Figure A8-A10).

3.4 Printing process of polythiourethanes

3.4.1 Printing optimization and results

After performing the previously explained characterization experiments, the selected formulation for 3D printing was the one containing a PPG-dilPDI 2000 and TMPTMP as a trifunctional primary thiol source, together with 0.5 wt% of TBD·$HBPh_4$ and 0.25 wt% of ITX. This formulation shows a reasonable stability in the darkness and the crosslinking of the material happens quite fast when irradiating as confirmed by photorheological experiments. Besides, the obtained material with this system is flexible and the reagents are liquid, what makes this system easier to work with.

The printing conditions were optimized using different diluents and dyes, and the optimization was made for each of the formulations. The following parameters were considered when optimizing the printing: burn-in and other layers irradiation exposure time, layer thickness and temperature.

The optimization of the material and the exposure times for the layers are related to the relation between the energy of the light and the thickness of the reticulated material, and in order to find this relation an experiment was performed as it follows: a drop of the material was placed in a cover glass and it was irradiated using 20 mW/cm^2 intensity for different times, and the thickness of the obtained layer was measured using a micrometer. The energy was calculated for each exposure time and plotted against the layer thickness.

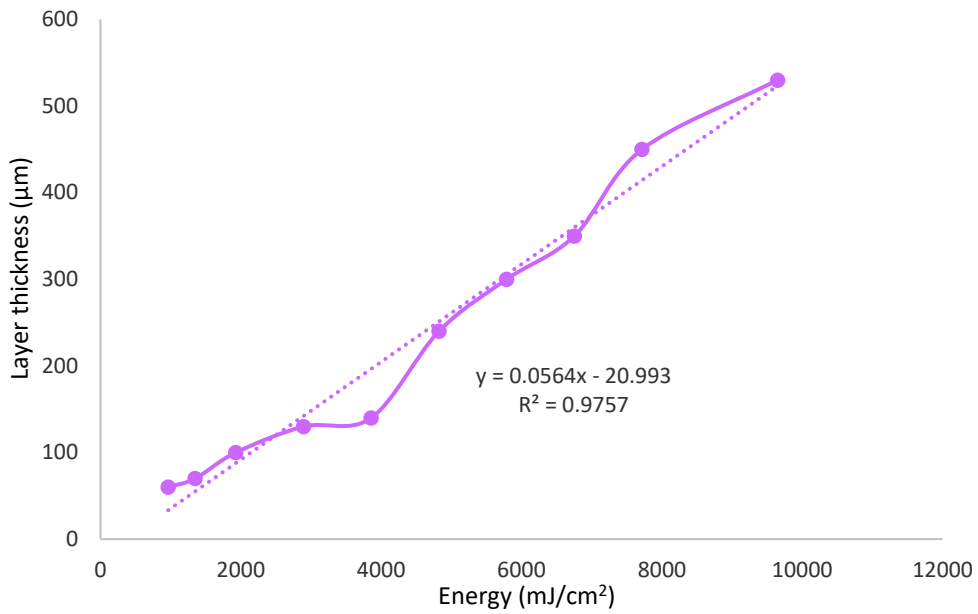


Figure 28. Layer thickness vs energy plot for the selected polythiourethane resin.

Based on the relation between the energy and the layer thickness, it was concluded that the ideal exposure time was 65 s for a 50 µm layer thickness. It must be noted that experimentally we have observed that this optimization works for the burn-in layer exposition time but not ideally for the rest of the printed layers exposure time.

For the optimization of the material the detailed piece shown in Figure 29 was printed. In this piece there is a hole and an out-coming cylinder. These shapes make the piece challenging to print. The hole is designed to determine if the selected exposure times for the layers are excessive, since when an excess of irradiation happens this shape cannot be achieved. On the contrary, the cylinder is design to find out if the selected exposure times are insufficient, as when this occurs the adhesion between layers is poor and outgoing shape with more height are not able to obtain properly. The dimension of the base are 1 mm x 15 mm x 5 mm, and the diameter of the hole and cylinder is 2 mm. The height of the cylinder is 1.5 mm.

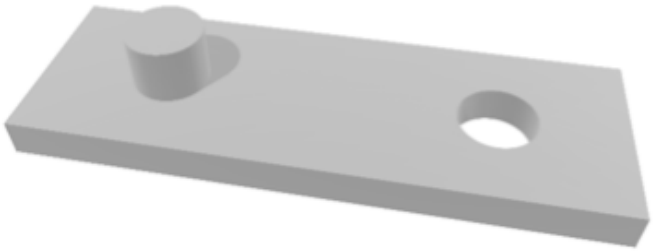


Figure 29. 3D design of the detailed piece for optimization of the material.

All the printings were made using a 20 mW/cm^2 (maximum irradiation intensity of the 3D printer) irradiation and the printed pieces were cleaned with ethyl acetate and thermally post-treated for 24 h in an oven at 50 ^{o}C.

Table 3. Optimization conditions and results for the polythiourethane using acetone as the diluent (30 wt%).

Temperature (ºC)	Burn-in layer exposure time (s)	Other layers exposure time (s)	Layer thickness (µm)	Results
25	70	10	50	
	30	10	50	
		15	50	
		20	50	
			100	
			150	
30	30	10	50	
		5	50	

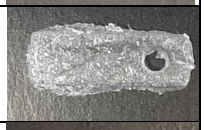
First it was attempted to print the material at room temperature, using a 70 s exposure time for the burn-in layer and 10 s for the other layers while using a 50 µm layer thickness. These printing times were selected according to the previously performed material characterization experiment. The piece was attached to the build platform, although it was observed that the hole of the shape was not achieved provably due to an excess of irradiation. Then, a shorter exposure time was tried for the burn-in layer, and it was decided that 30 s was an appropriate exposure time for the burn-in layer. A slight improvement on the resolution was observed however the cylinder was not obtained suggesting low layer irradiation times.

The exposure time of the other layers was increased in order to obtain a better quality, choosing 20 s as the more preferable. Higher layer thicknesses were used with the aim of reducing the printing time, and 100 μm layer thickness was found promising. On the contrary, when 150 μm layer thickness was used, the cylinder was not observed suggesting an excessive layer weight for the selected exposure time.

Besides, the printing was performed at 30 ºC in order to reduce the exposure times, but the obtained pieces showed a reduced resolution, probably due to a faster evaporation of acetone in the printing time.

Furthermore, the option of avoiding the use of acetone as diluent was studied, as it is a volatile diluent that can change the behavior of the material and therefore, varies the printing condition over time. In order to avoid the acetone as non-reactive diluent, the methyl lactate was chosen.

Table 4. Optimization conditions and results for the polythiourethane using methyl lactate as the diluent.

Methyl lactate wt%	Burn-in layer exposure time (s)	Other layers exposure time (s)	Results
7.5	30	20	
		25	
		30	
10	30	20	
15	30	20	

The optimization of the methyl lactate quantity that was needed for the 3D printing of this material, different percentages were used, using the ideal exposure times for the previously optimized material (30 s for the burn-in layer and 20 s for other layers) and 50 μm layer thickness. When using a higher percentage of methyl lactate, the obtained quality decreased, therefore, it was decided to use 7.5 wt%. The exposure time of the layers was increased with the purpose of obtaining better results, but it lowered the resolution of the pieces. So we finally concluded that methyl lactate does not help on diluting the system for printing as low resolution pieces were obtained and thus we think that another strategy must be found in the future.

In order to achieve results with higher resolution, the use of a dye was considered. When using a dye, the scattering of the light in the printable resin can be avoided, and therefore, polymerization in the parts where no irradiation is happening can be reduced enhancing the final resolution of the printed object.[28] Various studies has reported Sudan-1 as an effective dye for obtaining high resolution pieces in VAT photopolymerization.[28]

Table 5. Optimization conditions and results for the polythiourethane using Sudan-1 (0.05 wt%).

Burn-in layer exposure time (s)	Other layers exposure time (s)	Results
30	20	
	30	

The printing was performed using the optimized conditions (30 s for the burn-in layer and 20 s for other layers), however it was observed that the resolution of the piece was lower. We thought that the incorporation of that dye could reduce the light absorbance of the PBG and thus a print using longer exposure times was used. In this case, when 30 s were used, an increase resolution was appreciated although not substantially improved comparing to the material without the dye.

After optimizing the above-mentioned systems, a more complex piece shown in Figure 30 was printed in order to find the best formulation for printing with the previously optimized conditions for each of the formulations. This piece contains 7 different cones that have diameters of 5 mm, 4 mm, 3 mm, 2.5 mm, 2 mm, 1.5 mm and 1 mm. The dimensions of the base are 1 mm x 15 mm x 10 mm.

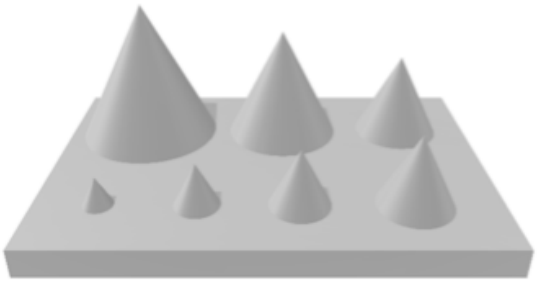


Figure 30. 3D design of the more complex piece.

Table 6. Optimization conditions and results for different polythiourethane systems.

Diluent	Dye	T (ºC)	Burn-in layer exposure t (s)	Other layers exposure t (s)	Layer thickness (µm)	Results
Acetone (30 wt%)	-	25	30	20	50	
					100	
		30	30	15	50	
	Sudan-1 (0.05 wt%)	25	30	30	50	
Methyl lactate (7.5 wt%)	-	25	30	20	50	
-	-	25	30	20	50	

Considering the obtained results, the chosen diluent was acetone, seeing that when using methyl lactate or no diluent the adhesion between layers was not good, and the printed pieces quality was worse than when using acetone. Regarding the dye, although the resolution of the piece improved in the bigger cones, the two smallest cones were missing, furthermore, when adding a dye, a larger exposure time of the layers was needed. Additionally, when using a higher temperature, it was observed that the printing time was shorter, but it lowered the resolution of the piece. Finally, it was shown that 100 μm layer thickness was not suitable for more complex pieces as small featured objects were not achievable.

After selecting the best formulation for printing, a larger size object was printed to show the applicability of this material (Figure 31a).

At first the piece was attempted to print vertically, however, bad results were obtained and it needed more printing time (due to the larger height). So it was decided to print the object horizontally. In order to achieve an appropriate adhesion of the piece to the printing platform, a supporting system was needed. The used support system was automatically suggested by the ASIGA composer software.

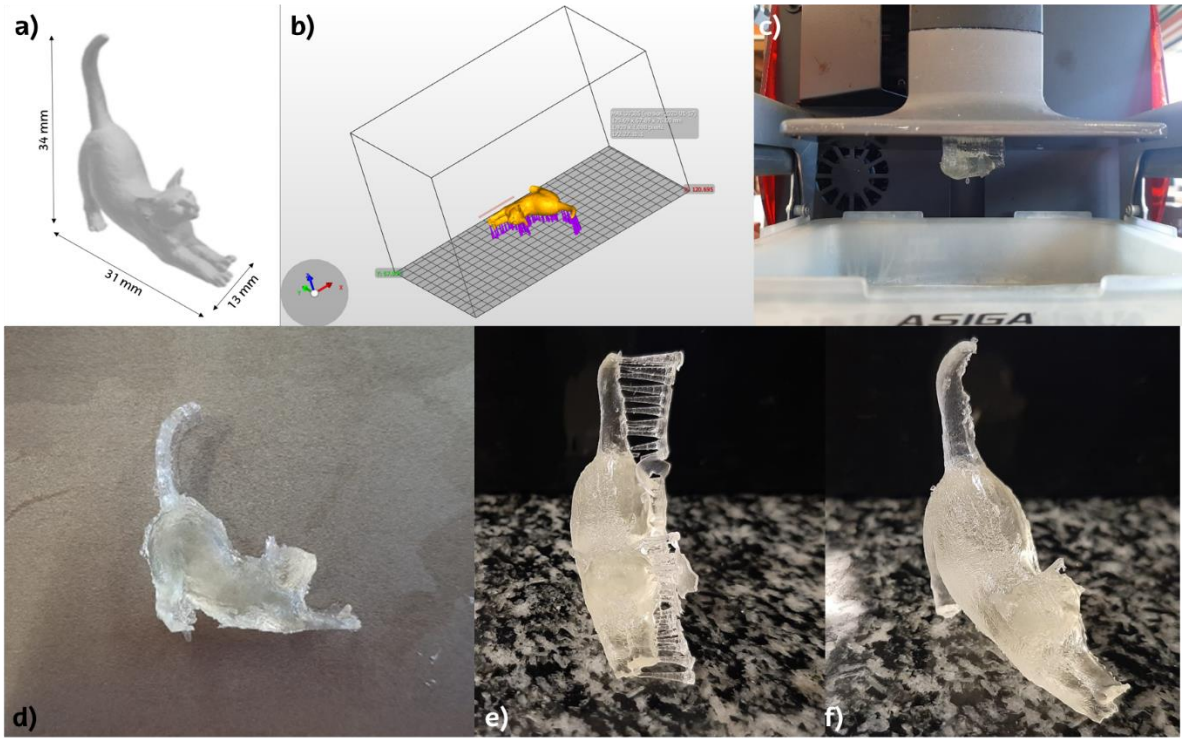


Figure 31. (a) 3D design of the piece, (b) 3D model of the piece and the support structure of ASIGA Composer software, (c) printed piece on the build platform after printing, (d) printed piece after cleaning with ethyl acetate, (e) printed piece with the support structure, (f) final printed piece.

The obtained piece shows a great quality and a reasonable resolution. The piece was obtained in 1 h 18 min which seems to be competitive with the commercial photo-printable resins, demonstrating the use of this polythiourethane system as a competitive candidate for VAT photopolymerization 3D printing applications.

3.4.2 FTIR characterization of the printed objects

When the 3D printing is carried out the sample is irradiated the minimum amount of time in order to get a self-standing layer. However, probably complete conversion of the monomers is not achieved. This observation was confirmed by recording an FTIR spectrum to a printed object. As it can be seen in the Figure 32, the presence of NCO group is detectable suggesting not complete monomer conversion. Nevertheless, after a post-treatment in a 50 ºC

oven for 24 h the complete disappearance of the isocyanate band can be observed.

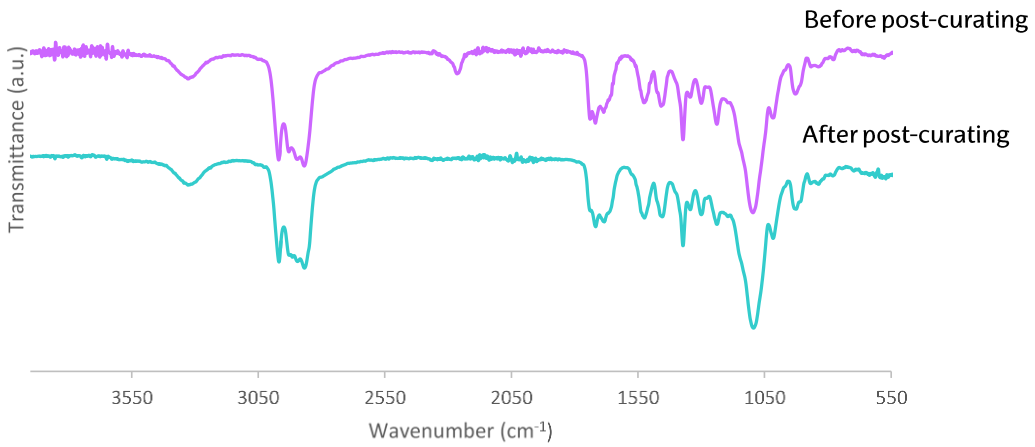


Figure 32. FTIR spectra of the printed polythiourethane before (purple) and after (blue) post-curating.

4 CONCLUSIONS

In this work, polythiourethanes were synthesized as photocurable resins with the aim of developing new materials for 3D printing applications. Overall, this system has proven to have the potential to be a competitive candidate in the field of 3D printing by VAT photopolymerization.

Different PBGs were synthesized, characterized and tested for the thiol-isocyanate reaction. It was found that NPPOC-TMG does not work for this system, as the instability of the system was observed. However, tetraphenylborate salts demonstrated to be an appropriate choice for this work. Besides, it was noted that the polymerization rate of the base catalyzed thiol-isocyanate reaction depends both on the basicity of the basic catalyst and the nature of the thiol.

Various photorheological measurements were performed in order to understand the behavior of the polythtiourethane resins containing the PBGs before and after UV irradiation. These studies confirmed the crosslinking reaction upon UV light irradiation, and the gel times of the materials were obtained.

Materials with different thermal properties were obtained using different thiols and isocyanates, demonstrating the versatility of polythiourethane chemistry

The most important parameters for VAT 3D printing were determined and optimized, achieving the printing of high quality pieces.

5 ONDORIOAK

Lan honetan, politiouretanoak erretxina fotopolimerizagarri gisa sintetizatu ziren, 3D inprimaketa aplikaziotako material berriak garatzeko. Oro har, sistema honek erakutsi du VAT fotopolimerizazio prozesu bidez 3D inprimaketaren arloan hautagai lehiakorra izateko aukera duela.

Tiol-isozianato erreakziorako PBG desberdinak sintetizatu, karakterizatu eta frogatu ziren. NPPOC-TMG-a sistema honetarako baliogarria ez dela aztertu zen, sistemaren ezegonkortasuna ikusi baitzen. Hala ere, tetrafenilboratozko gatzak lan honetarako aukera egokiak direla erakutsi zuten. Gainera, ikusi zen base bidez katalizatutako tiol-isozianato erreakzioaren polimerizazio abiadura katalizatzaile basikoaren eta tiolaren basizitatearen araberakoa dela.

Politiouretanoek UV irradiazioaren aurretik eta ondoren duten portaera ulertzeko, zenbait neurketa fotoerreologiko egin ziren. Azterketa horiek UV argi irradiazioaren ondoriozko erretxinaren sarteatze-erreakzioa berretsi zuten, eta materialen gel-denborak lortu ziren.

Propietate termiko desberdinak zituzten materialak tiol eta isozianato desberdinak erabiliz lortu ziren, politiouretanoen kimikaren moldakortasuna erakutsiz.

VAT 3D inprimaketarako parametro garrantzitsuenak zehaztu eta optimizatu ziren, eta kalitate handiko piezak inprimatzea lortu zen.

6 APPENDIX

^{1}H-NMR characterization

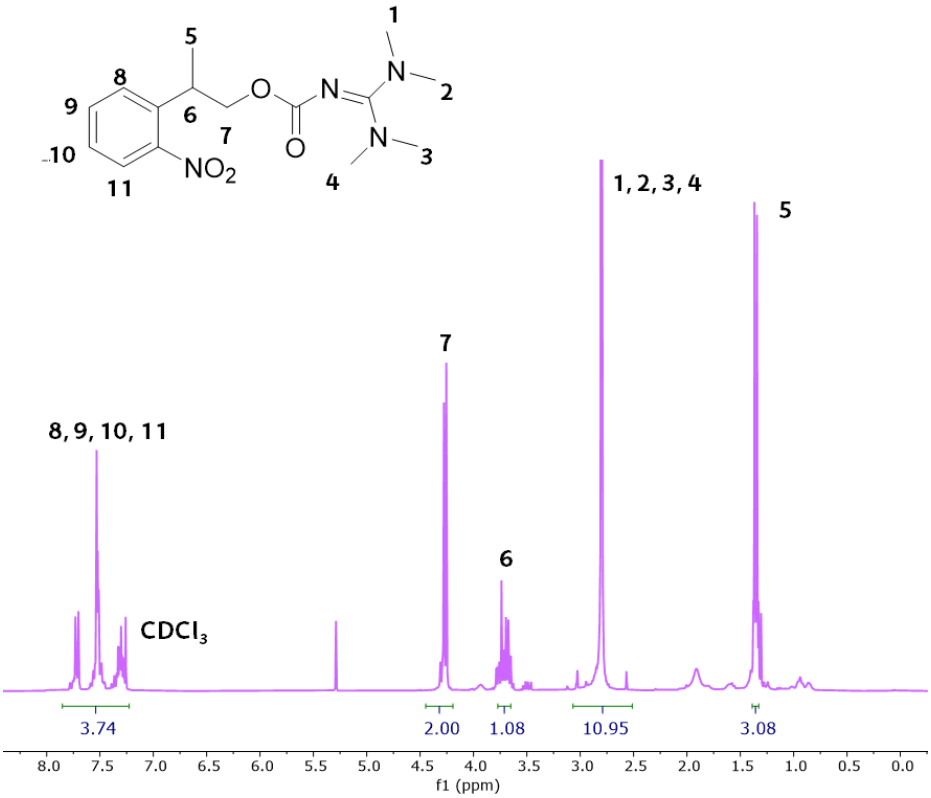


Figure A1. ^{1}H-NMR of 2-(2-nitrophenyl)propan-1-ol.

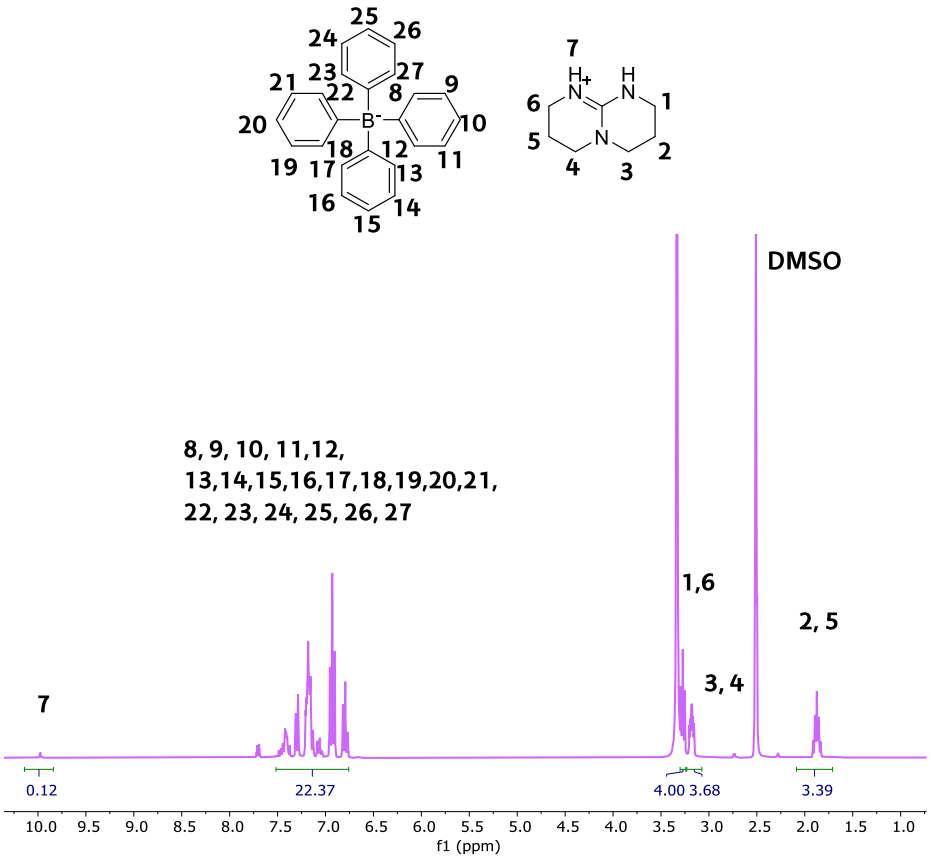


Figure A2. ^{1}H-NMR of TBD·HBPh$_4$.

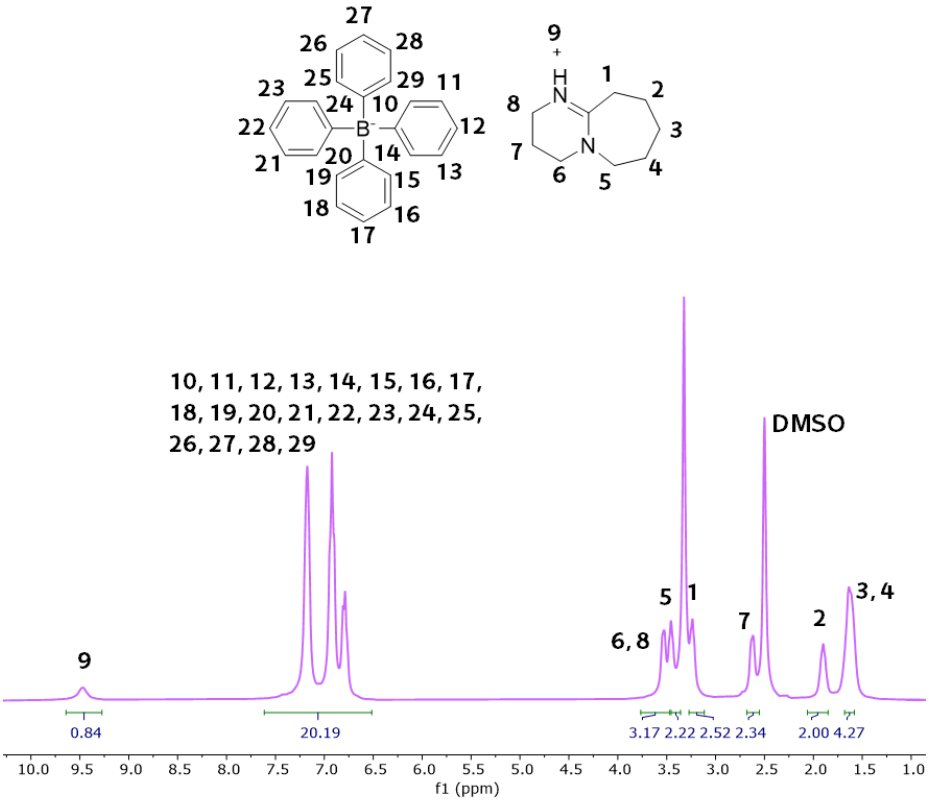


Figure A3. ^{1}H-NMR of DBU·HBPh$_4$.

FTIR characterization

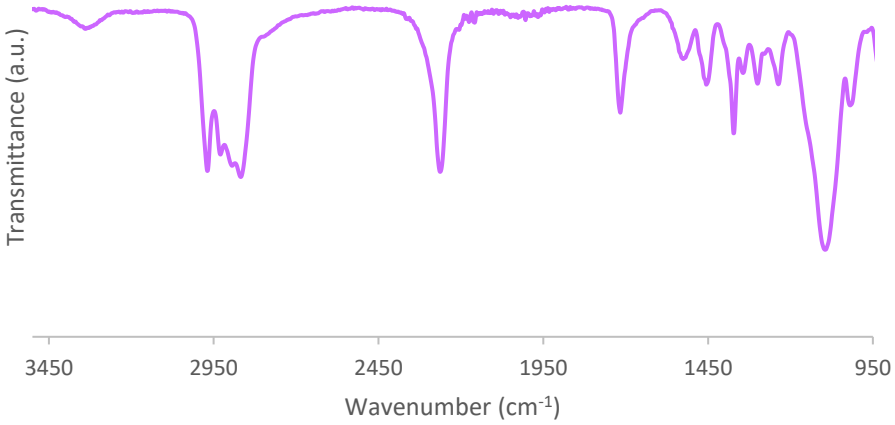


Figure A4. FTIR of PPG-dilPDI (2000).

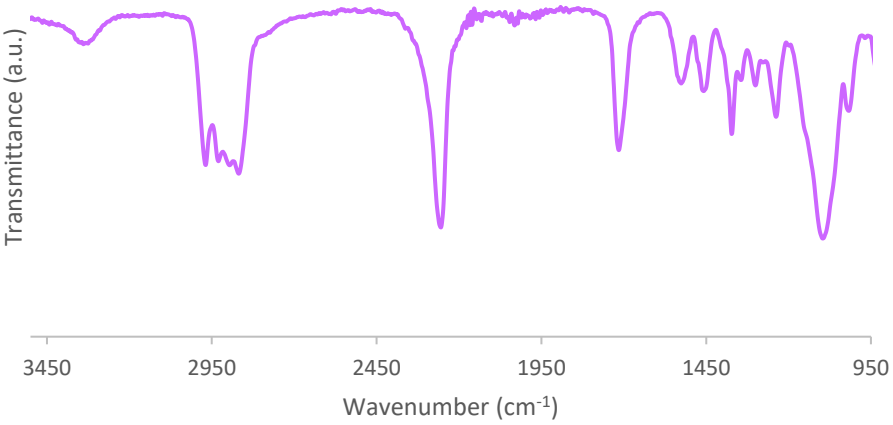


Figure A5. FTIR of PPG-dilPDI (1000).

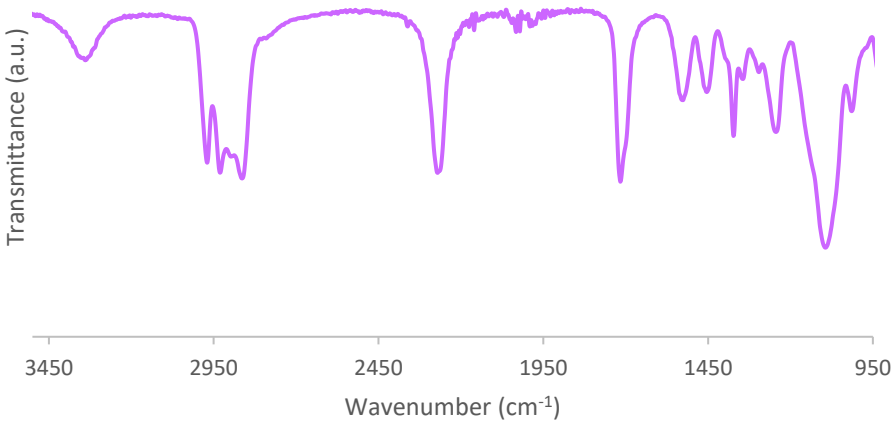


Figure A6. FTIR of PPG-diHDI (1000).

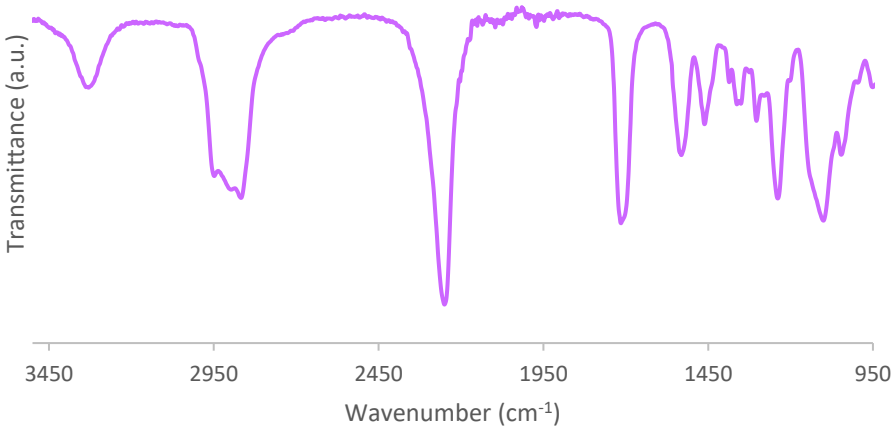


Figure A7. FTIR of PEG-diIPDI (400).

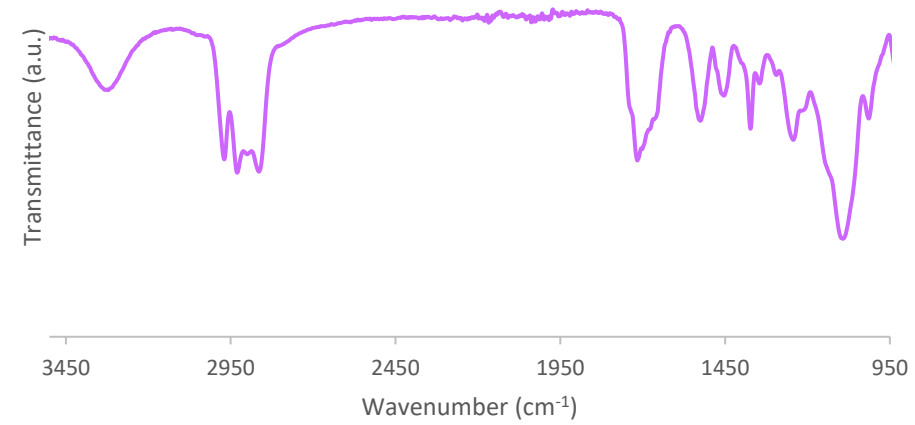


Figure A8. FTIR of the PPG-diIPDI (1000) and TMPTMP containing polythiourethane.

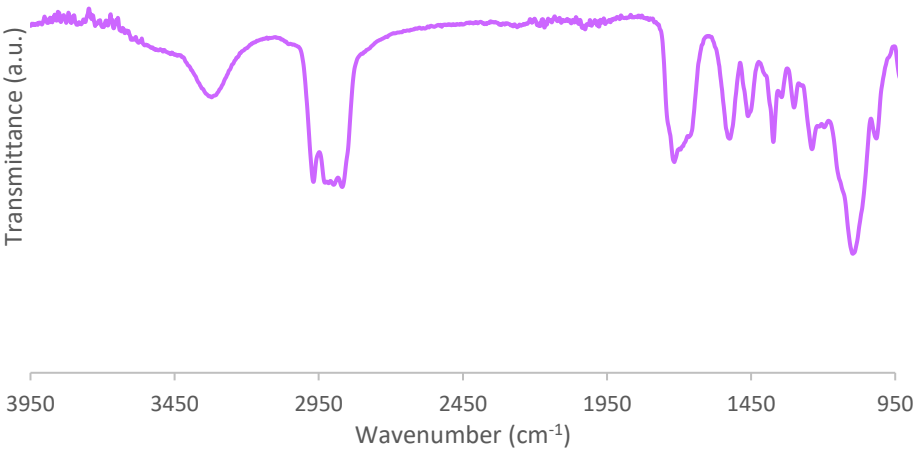


Figure A9. FTIR of the PPG-diHDI (1000) and TMPTMP containing polythiourethane.

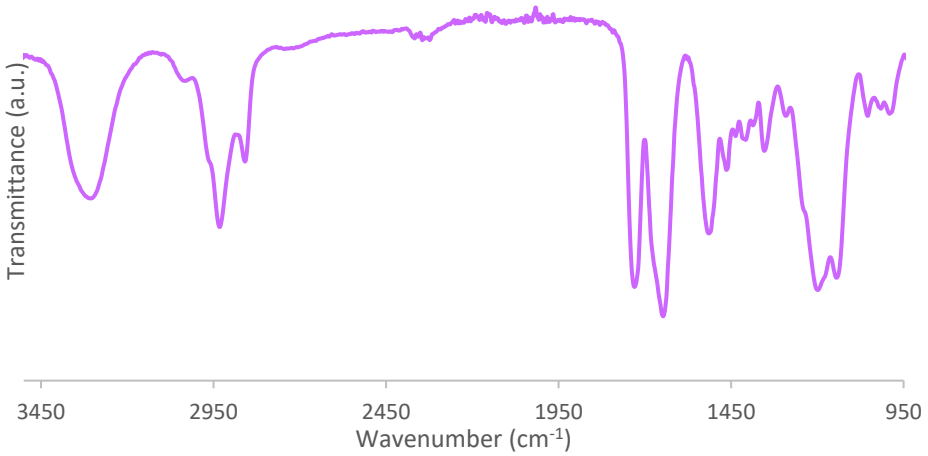


Figure A10. FTIR of the HDI and TMPTMP containing polythiourethane.

Amplitude sweep

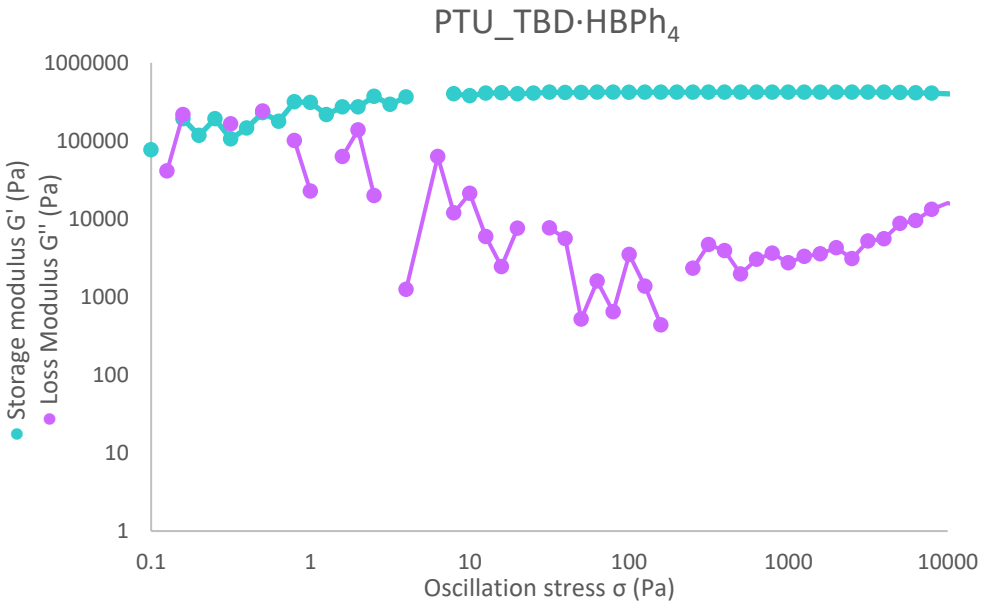


Figure A11. Amplitude sweep of the PPG-diIPDI (2000) and TMPTMP containing reticulated polythiourethane.

TGA

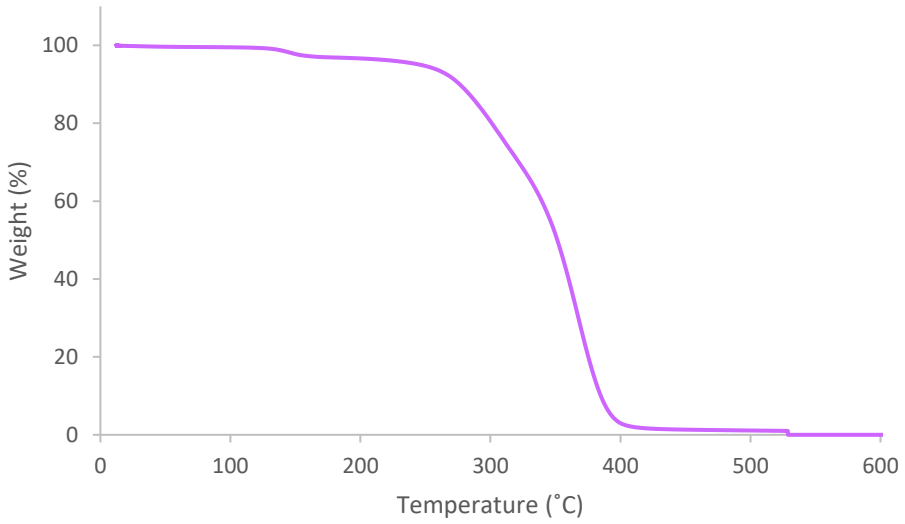


Figure A12. TGA of the PPG-dilPDI (2000) and TMPTMP containing reticulated polythiourethane.

7 BIBLIOGRAPHY

(1) Calignano, F.; Manfredi, D.; Ambrosio, E. P.; Biamino, S.; Lombardi, M.; Atzeni, E.; Salmi, A.; Minetola, P.; Iuliano, L.; Fino, P. Overview on Additive Manufacturing Technologies. *Proc. IEEE* **2017**, *105* (4), 593–612.

(2) Ligon, S. C.; Liska, R.; Stampfl, J.; Gurr, M.; Mülhaupt, R. Polymers for 3D Printing and Customized Additive Manufacturing. *Chem. Rev.* **2017**, *117* (15), 10212–10290.

(3) Sanchez-Rexach, E.; Johnston, T. G.; Jehanno, C.; Sardon, H.; Nelson, A. Sustainable Materials and Chemical Processes for Additive Manufacturing. *Chem. Mater.* **2020**, *32* (17), 7105–7119.

(4) Al Rashid, A.; Ahmed, W.; Khalid, M. Y.; Koç, M. Vat Photopolymerization of Polymers and Polymer Composites: Processes and Applications. *Addit. Manuf.* **2021**, *47* , 102279.

(5) Pagac, M.; Hajnys, J.; Ma, Q. P.; Jancar, L.; Jansa, J.; Stefek, P.; Mesicek, J. A Review of Vat Photopolymerization Technology: Materials, Applications, Challenges, and Future Trends of 3d Printing. *Polymers.* **2021**, *13* (4), 1–20.

(6) Fiedor, P.; Pilch, M.; Szymaszek, P.; Chachaj-Brekiesz, A.; Galek, M.; Ortyl, J. Photochemical Study of a New Bimolecular Photoinitiating System for Vat Photopolymerization 3D Printing Techniques under Visible Light. *Catalysts* **2020**, *10* (3).

(7) Boydston, A. J.; Nelson, A. Chemical Advances in Additive Manufacturing. *Polym. Chem.* **2019**, *10* (44), 5948–5949.

(8) Gamardella, F.; Ramis, X.; De la Flor, S.; Serra, À. Preparation of Poly(Thiourethane) Thermosets by Controlled Thiol-Isocyanate Click Reaction Using a Latent Organocatalyst. *React. Funct. Polym.* **2019**, *134*, 174–182.

(9) Shin, J.; Lee, J.; Jeong, H. M. Properties of Polythiourethanes Prepared by Thiol–Isocyanate Click Reaction. *J. Appl. Polym. Sci.* **2018**, *135* (14).

(10) Li, L.; Chen, X.; Torkelson, J. M. Reprocessable Polymer Networks via Thiourethane Dynamic Chemistry: Recovery of Cross-Link Density after Recycling and Proof-of-Principle Solvolysis Leading to Monomer Recovery. *Macromolecules* **2019**, *52* (21), 8207–8216.

(11) Gamardella, F.; Muñoz, S.; De la Flor, S.; Ramis, X.; Serra, A. Recyclable Organocatalyzed Poly(Thiourethane) Covalent Adaptable Networks. *Polymers.* **2020**, *12* (12), 1–18.

(12) Ellson, G.; Carrier, X.; Walton, J.; Mahmood, S. F.; Yang, K.; Salazar, J.; Voit, W. E. Tough Thiourethane Thermoplastics for Fused Filament Fabrication. **2018**, *45574*, 1–7.

(13) Zivic, N.; Kuroishi, P. K.; Dumur, F.; Gigmes, D.; Dove, A. P.; Sardon, H. Recent Advances and Challenges in the Design of Organic Photoacid and Photobase Generators for Polymerizations. *Angew. Chemie - Int. Ed.* **2019**, *58* (31), 10410–10422.

(14) Sun, X. *Development of Tetraphenylborate-Based Photobase Generators and Sacrificial Polycarbonates for Radiation Curing and Photoresist Applications*; 2008.

(15) Dadashi-Silab, S.; Aydogan, C.; Yagci, Y. Shining a Light on an Adaptable Photoinitiator: Advances in Photopolymerizations Initiated by Thioxanthones. *Polym. Chem.* **2015**, *6* (37), 6595–6615.

(16) Kaupmees, K.; Trummal, A.; Leito, I. Basicities of Strong Bases in Water: A Computational Study. *Croat. Chem. Acta* **2014**, *87* (4), 385–395.

(17) Shin, J.; Matsushima, H.; Comer, C. M.; Bowman, C. N.; Hoyle, C. E. Thiol-Isocyanate-Ene Ternary Networks by Sequential and Simultaneous Thiol Click Reactions. *Chem. Mater.* **2010**, *22* (8), 2616–2625.

(18) Sun, X.; Gao, J. P.; Wang, Z. Y. Bicyclic Guanidinium Tetraphenylborate: A Photobase Generator and a Photocatalyst for Living Anionic Ring-Opening Polymerization and Cross-Linking of Polymeric Materials Containing Ester and Hydroxy Groups. *J. Am. Chem. Soc.* **2008**, *130* (26), 8130–8131.

(19) Kuroishi, P. K.; Dove, A. P. Photoinduced Ring-Opening Polymerisation of l-Lactide: Via a Photocaged Superbase. *Chem. Commun.* **2018**, *54* (49), 6264–6267.

(20) Xi, W.; Peng, H.; Aguirre-Soto, A.; Kloxin, C. J.; Stansbury, J. W.; Bowman, C. N. Spatial and Temporal Control of Thiol-Michael Addition via Photocaged Superbase in Photopatterning and Two-Stage Polymer Networks Formation. *Macromolecules* **2014**, *47* (18), 6159–6165.

(21) Kretschy, N.; Holik, A. K.; Somoza, V.; Stengele, K. P.; Somoza, M. M. Next-Generation o-Nitrobenzyl Photolabile Groups for Light-Directed Chemistry and Microarray Synthesis. *Angew. Chemie - Int. Ed.* **2015**, *54* (29), 8555–8559.

(22) Salmi, H.; Allonas, X.; Ley, C. Polythiourethane Networks Catalyzed by Photobase Generators. *Prog. Org. Coatings* **2016**, *100*, 81–85.

(23) Crivello, J. V.; Reichmanis, E. Photopolymer Materials and Processes for Advanced Technologies. *Chem. Mater.* **2014**, *26* (1), 533–548.

(24) Trinh, T. K. H.; Malval, J. P.; Morlet-Savary, F.; Pinaud, J.; Lacroix-Desmazes, P.; Reibel, C.; Héroguez, V.; Chemtob, A. Mixture of Azolium Tetraphenylborate with Isopropylthioxanthone: A New Class of N-Heterocyclic Carbene (NHC) Photogenerator for Polyurethane, Polyester, and ROMP Polymers Synthesis. *Chem. - A Eur. J.* **2019**, *25* (39), 9242–9252.

(25) Zivic, N.; Sadaba, N.; Almandoz, N.; Ruipérez, F.; Mecerreyes, D.; Sardon, H. Thioxanthone-Based Photobase Generators for the Synthesis of Polyurethanes via the Photopolymerization of Polyols and Polyisocyanates. *Macromolecules* **2020**, *53* (6), 2069–2076.

(26) Figoli, A.; Marino, T.; Simone, S.; Di Nicolò, E.; Li, X. M.; He, T.; Tornaghi, S.; Drioli, E. Towards Non-Toxic Solvents for Membrane Preparation: A Review. *Green Chem.* **2014**, *16* (9), 4034–4059.

(27) Sardon, H.; Engler, A. C.; Chan, J. M. W.; Garc, J. M.; Coady, D. J.; Pascual, A.; Mecerreyes, D.; Jones, G. O.; Rice, J. E.; Horn, H. W.; et al. Organic Acid-Catalyzed Polyurethane Formation via a Dual-Activated Mechanism: Unexpected Preference of N Activation over O Activation of Isocyanates. *J. Am. Chem. Soc.* **2013**, *135*, 16235–16241.

(28) Gastaldi, M.; Cardano, F.; Zanetti, M.; Viscardi, G.; Barolo, C.; Bordiga, S.; Magdassi, S.; Fin, A.; Roppolo, I. Functional Dyes in Polymeric 3D Printing : 2021.