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Remendable thermosetting polymers for isocyanate-free adhesives: a preliminary study

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ABSTRACT

This study describes the synthesis and polymerization of a dicyclocarbonate Diels-Alder (DA) adduct to give a thermoresponsive non isocyanate polyurethane (NIPU). Firstly a model adduct was synthesized by DA reaction between N-methylmaleimide and furfuryl cyclocarbonate ether (FCE). This adduct was characterized by ¹H-NMR and its thermal behavior was studied by ¹H-NMR, and differential scanning calorimetry (DSC). Then a telechelic dicyclocarbonate DA adduct was obtained by DA reaction between an bismaleimide oligomer and FCE in bulk with full conversion. Its thermal behavior was studied by thermogravimetric analysis (TGA) and DSC. The dicyclocarbonate adduct was polymerized by step-growth polymerization with a diamine, Jeffamine EDR148. The polymerization was performed at room temperature (in order to avoid adduct deprotection) with triazabicyclodecene as catalyst. The obtained polymer was characterized by size exclusion chromatography (SEC) and ¹H-NMR. The polymer thermal behavior was fully characterized by three complementary analyses. By DSC, retro-Diels-Alder temperatures could be measured at 90-120°C. By ¹H-NMR kinetic study at 100°C, it could be shown that after 120min at 100°C, 85% of the adducts are deprotected. Finally, by SEC, it was demonstrated that the obtained NIPU polymer chains undergo thermal scission by rDA reaction.

KEYWORDS: polyhydroxyurethane, step-growth polymerization, Diels-Alder, synthesis,

INTRODUCTION

Thermosetting polymers are widely used in coatings, composites and adhesives due to their good mechanical and thermal properties. Indeed they are irreversibly cured into a highly cross-linked network giving an infusible and insoluble material. As a result they cannot be shaped differently, or processed, which

represents a great deal for environmental concerns and particularly for recycling. In response to that concern, remendable polymers have been widely studied over the last decades¹⁻⁴. In particular, it has been pointed out that using remendable adhesives, also as coatings, would lead to a better recycling,

especially for vehicles end-of-life or electronic waste^{5,6}.

Polyurethanes (**PU**s) are very interesting polymer materials allowing a huge variety of industrial applications in paints, coatings, adhesives, sealants and insulation foams. They are widely used in adhesives as they can lead to different properties owing to the various structures of reactants: from soft elastomers to rigid materials. In many adhesives applications PUs are chemically cross-linked which makes the resulting network irreversible. Furthermore, their use in linear polymers is also difficult to recycle due to important H bonds between the chains. Therefore many studies have been conducted on remendable PUs⁷⁻¹⁰.

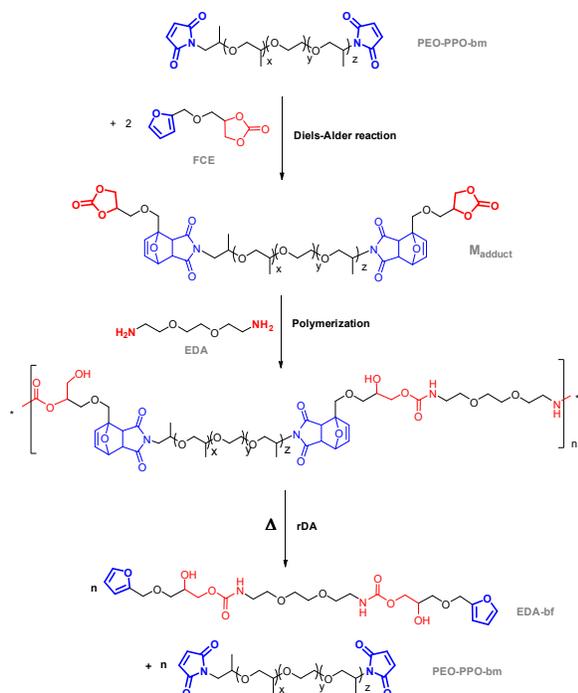
The most efficient way to obtain remendable thermosets is to incorporate reversible bonds which can break on demand using proper stimulus. Several stimuli are possible: temperature, radiations, pH, etc. Practically, temperature is the best option since it can be used easily in industrial process. The urethane bond is itself reversible. Indeed, this bond is stable at room temperature but reversible cleavage occurs at elevated temperatures. In the case of aromatic structures urethane bonds break around 180-200°C to reform alcohol and isocyanate groups¹¹. However their depolymerization temperature is too high and the PU adhesive support could be damaged. Therefore Diels-Alder reaction (**DA**) is a good alternative: it is a well-known thermoreversible system and its use in PU s has been already extensively studied^{9,12,13}.

DA reaction is a [4+2] cycloaddition between a diene and a dienophile leading to an adduct which dissociates under thermic treatment to turn back into the previous diene and dienophile compounds. DA adducts is cleaved at 100-130°C (typically) as they undergo opposite retro-Diels-Alder (**rDA**) reaction. It is a well-known reaction which has already proved its interest in various systems such as self-healing systems¹⁴, thermoreversible materials⁴, or materials having a controlled cross-linking reaction¹⁵. Most of time furane/maleimide

couple is chosen as diene/dienophile because of its good reactivity.

PUs are typically obtained by reaction between a diisocyanate (or polyisocyanate) and compounds having at least two reactive hydrogen atoms, such as hydroxyl groups. As diisocyanates are harmful for human health and its environment¹⁶⁻²⁰, the synthesis of non-isocyanate polyurethanes (**NIPUs**) has recently gained an increasing interest in chemical industry. The most promising alternative is the step-growth polymerization of cyclocarbonates with amines. This pathway permits the formation of poly(hydroxyurethanes)s (**PHU**). These last decades PHUs have been tremendously studied, particularly by Endo²¹⁻²³, Figovsky²⁴⁻²⁶, as well as by our team²⁷⁻²⁹.

However, if the reversibility of PUs has already been studied^{9, 12, 13}, to the best of our knowledge, the reversibility of PHUs has never been studied. Indeed this is all the more difficult since NIPUs syntheses already present challenges, and should generally be carried out at temperatures higher than 50°C. However, reversible linear PHUs present undeniable interest since they allow both to avoid the use of isocyanate and to facilitate the recycling of materials after application. This original study is thus pioneering the synthesis of thermoreversible PHUs by step-growth polymerization of a DA dicyclocarbonate adduct with diamine (Scheme 1). DA dicyclocarbonate adduct was obtained by reaction between furfuryl alcohol and PEO-PPO bismaleimide. All the raw materials are commercially available, which deepens the interest of this system. Firstly, a model adduct has been synthesized to study DA and rDA reaction parameters in order to apply them to PHU synthesis. Then oligomeric dicyclocarbonate adduct was synthesized by DA reaction and polymerized with a diamine. The final polymer was characterized and its thermal behavior was investigated.



Scheme 1: Dicyclocarbonate DA adduct synthesis and its polymerization with a diamine

EXPERIMENTAL

Materials

The Furfuryl alcohol (98%), epichlorohydrine, tetrabutylammonium bromide (TBABr), lithiumbromide (LiBr), butylamine, and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), were purchased from Sigma-Aldrich. N-methylmaleimide (97%) was purchased from ABCR. Ether diamine (EDA) was provided by Huntsman (product Jeffamine EDR148). Polyether bismaleimide (PEO-PPO-bm) was synthesized by Specific Polymers (product's reference SP-1P-9-015). All those products were used without further purification. Solvents were purchased from Sigma-Aldrich.

Nuclear Magnetic Resonance (NMR)

All Nuclear magnetic resonance (^1H and ^{13}C NMR) measurements were recorded on a Bruker AC-400 MHz spectrometer at room temperature in deuterated chloroform (CDCl_3) or dimethylsulfoxide (DMSO) and tetramethylsilane (TMS) as internal reference

for ^1H and ^{13}C NMR chemical shifts.

Size exclusion chromatography (SEC)

Size exclusion chromatography (SEC) was performed on a Varian ProStar Model 210 equipped with an RI refractive index detector. Two PolarGel-L 7.5mm, 600mm combined, were used at 70°C with a $0.8\text{ mL}\cdot\text{min}^{-1}$ flow rate of DMF, calibrated using PEO standards

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) analyses were performed under inert atmosphere with a calorimeter DSC1 from Mettler Toledo. The polymer was weighted in an aluminum pan and consecutively placed in the measurement heating cell. An empty pan was used as reference. All the samples were heated under inert atmosphere from -120 to 100°C at a heating rate of $10^\circ\text{C}/\text{min}$. Three runs were recorded and the glass transition temperature (T_g) values were measured during the second run and confirmed by a third run. T_g s were calculated at the inflexion point of the heat capacity jump.

Thermogravimetric Analysis (TGA)

Thermogravimetric analyses (TGA) were performed using a TGA Q50 W/MFC apparatus of TA Instruments under air and nitrogen flow ($25\text{ mL}/\text{min}$) from room temperature to 500°C at a heating rate of $10^\circ\text{C}/\text{min}^{-1}$. The analysis consisted in registering the weight loss of the sample as a function of temperature.

Analyses

N-methylmaleimide: ^1H NMR (400 MHz, $\text{DMSO}-d_6$): ppm 7.01 (s, 2 H, Hh) 2.86 (s, 3 H, Hi)

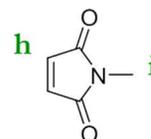


Figure 1: N-methylmaleimide structure

PEO-PPO-bm: ^1H NMR (400 MHz, $\text{DMSO}-d_6$): ppm 6.82 - 7.04 (br.s., 4 H, Hh) 4.21 (m, 2 H, Hi) 3.20 - 3.74 (m, 49 H, Hi') 0.90 - 1.25 (m, 11 H, Hj and Hj')

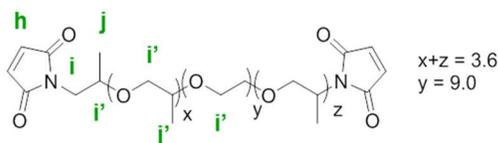


Figure 2: PEO-PPO-bm structure

EDA: ^1H NMR (250 MHz, $\text{DMSO}-d_6$): ppm 3.49 (s, 4 H, H_c) 3.35 (t, $J=5.84$ Hz, 4 H, H_b) 2.55 (t, $J=5.84$ Hz, 4 H, H_a)

The Amine Hydrogen Equivalent Weight is of 37 g/eq (source Huntsman)

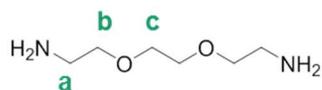


Figure 3: EDA structure

Titration of maleimide functions by ^1H NMR

A specific amount of cyclic carbonate (around 20mg) and a standard (DMSO, around 7mg) were weighted into an NMR tube. Once the ^1H NMR was completed, the characteristic peak of maleimide (6.5ppm) and CH_3 (2.4ppm) of DMSO were integrated. The integration of CH_3 of DMSO was fixed to 600. The maleimide content was calculated according to the equation below, where n_{DMSO} is the number of mole of DMSO in the tube, I_m is the maleimide characteristic peak intensity, I_{DMSO} is the intensity of the DMSO characteristic peak, and m_m is the product weight. The maleimide equivalent weight (MEW) was calculated in triplicate determination (Eq 1).

$$\text{MEW} = \frac{\frac{I_m}{2}}{\frac{I_{\text{DMSO}}}{6}} * \frac{n_{\text{DMSO}}}{m_m}$$

Syntheses

Synthesis of furfuryl glycidyl ether (FGE)

Epichlorohydrine (102g, 1.1mol) and tetrabutylammonium bromide (4.5g) were charged into a 500mL two-necked round-bottom flask equipped with an inlet for dry nitrogen. The system temperature was kept at room temperature while furfuryl alcohol (98g, 1mol) was added dropwise over a period of 45min. The reaction proceeded during 4h and then 150mL of aqueous sodium hydroxide (40% w/w) was poured into the system at 0°C . The

reaction was left overnight, then the product was extracted with ethyl acetate and washed with water several times. The organic layer was collected, dried and solvent was removed using rotary evaporator. A light yellow liquid is collected and then purified by distillation at 110°C under 700mbar, with a 92% yield and a final purity superior to 99% purity. A colorless liquid was obtained in a 60% total yield (Figure 3).

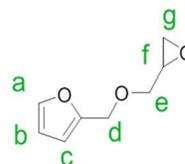


Figure 4: FGE structure

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ ppm: 7.63 (s, 1 H, H_a) 6.43 (b.s, 2 H, H_b and H_c) 4.41 - 4.54 (s, 2 H, H_d) 3.73 (dd, $J=11.5$, 2.6 Hz, 1 H, H_e) 3.29 (dd, $J=11.5$, 6.4 Hz, 1 H, H_f) 2.72 (dd, $J=5.1$, 4.2 Hz, 1 H, H_g) 2.54 (dd, $J=5.1$, 2.3 Hz, 1 H, H_g)

Synthesis of furfuryl cyclocarbonate ether (FCE)

FGE (93g, 0.6mol) is dissolved in DMF with LiBr (2.2g, 5% molar), the amount of DMF is adjusted to 200mL. The mixture is poured in a 300mL reactor, and put under 9bar of CO_2 at 80°C during 5h. DMF is removed by distillation under vacuum. A little amount of ethyl acetate is added and then washed with water to remove LiBr. The organic layer is collected, dried and solvent is removed using rotary evaporator. A dark purple liquid is obtained with a 98% yield.

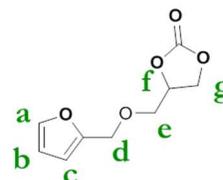


Figure 5: FCE structure

^1H NMR (400 MHz, $\text{DMSO}-d_6$): ppm 7.63 (s, 1 H, H_a) 6.45 (d, $J=6.57$ Hz, 2 H, H_b and H_c) 4.90 - 4.97 (m, 1 H, H_f) 4.42 - 4.58 (m, 3 H, H_d and H_g) 4.24 (dd, $J=8.08$, 6.06 Hz, 1 H, H_d) 3.57 - 3.75 (m, 2 H,

H_e). ¹³C NMR (101 MHz, DMSO-*d*₆): ppm 154.9; 151.0; 143.2; 109.8; 75.3; 68.7; 65.9; 64.3

Synthesis of model adduct

N-methylmaleimide (1eq) is solubilized in THF (50% w), then furan derivative FCE (2eq) is added. The reaction mixture is stirred for three days under reflux (70°C). The exo-adduct is then precipitated in diethyl-ether. The exo-adduct is then isolated by precipitation in diethyl-ether in a 70% yield (from the total amount of adduct).

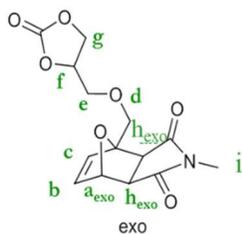


Figure 6: Structure of model adduct

¹H NMR (400 MHz, DMSO-*d*₆): ppm 6.57 (dd, J=5.56, 1.77 Hz, 1 H, H_b) 6.46 (d, J=5.56 Hz, 1 H, H_c) 5.11 (d, J=1.77 Hz, 1 H, H_aexo) 4.91 (m, J=8.46, 6.19, 3.79 Hz, 1 H, H_f) 4.50 (q, J=8.59 Hz, 1 H, H_g) 4.17 - 4.33 (m, 2 H, H_g and H_d) 3.60 - 3.83 (m, 3 H, H_d and H_e) 2.90 - 3.07 (m, 2 H, H_hexo) 2.81 (s, 3 H, H_i). ¹³C NMR (101 MHz, DMSO-*d*₆): ppm 143.3, 137.2, 110.4, 80.3, 75.3, 70.5, 68.6, 66.0, 64.3, 49.7, 48.2, 24.3

Synthesis of M_{adduct}

To achieve DA reaction, a bulk synthesis was chosen: 20.0g of PEO-PPO-bm (1.0 maleimide equivalent) and 9.6g of FCE (1.0 furans equivalent) were mixed in a 200mL pot using mechanical stirring. The mixture was left at room temperature during 20h and then heated at 50°C during 2 days.

M_{adduct} polymerization with EDA

The formulation is calculated for 1.0 cyclocarbonate equivalent (from synthesized adduct M_{adduct}), 1.0 diamine equivalent (from EDA) and 0.05 equivalent of TBD in relation with cyclocarbonate.

First TBD is put in a round bottom flask with M_{adduct} and then DMF is poured (50%w). The mix is stirred during 3min and then EDA is added. The mix is stirred during 16h at room

temperature. Then the polymer is precipitated in ethylacetate at -10°C. After decantation at 0°C, the polymer is isolated (75% yield).

Polymer deprotection monitored by Size Exclusion Chromatography (SEC)

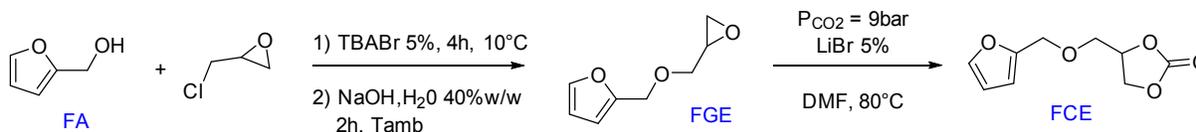
A sample of the polymer (around 60mg) is diluted in SEC eluent (DMF, LiBr 5%*m*) in a hemolysis tube to reach a 10mg/mL dilution. The tube is placed in a 100°C bath. Regularly, a sample of the mixture is removed and put in a vial containing an excess of butylamine. The vial is agitated for several minutes and then analyzed by SEC.

RESULTS AND DISCUSSION

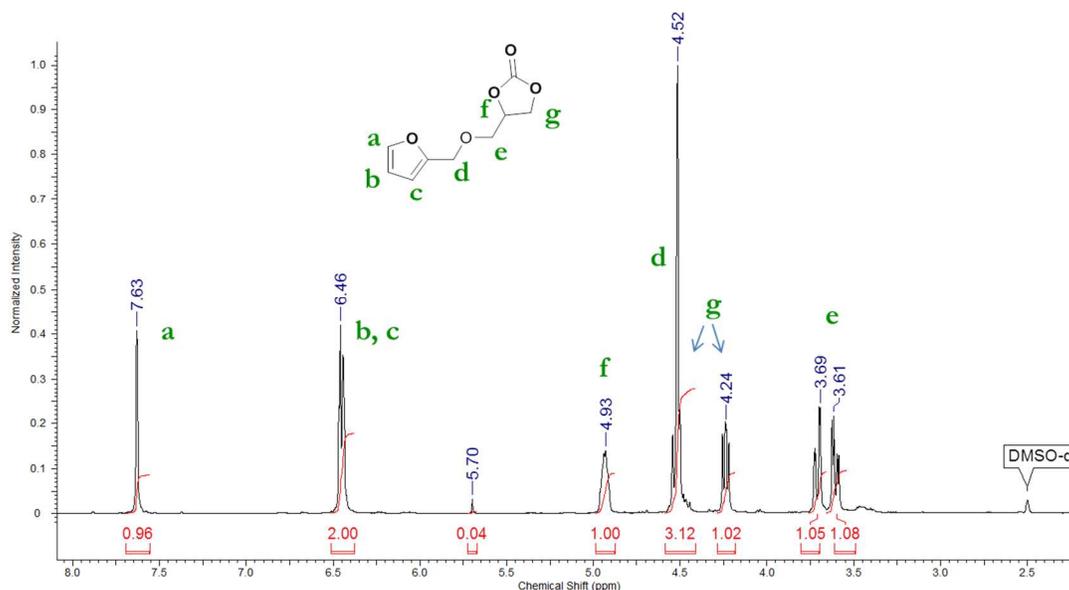
Synthesis of furfuryl cyclocarbonate ether

Firstly furfuryl cyclocarbonate ether (FCE) is synthesized by epoxidation of furfuryl alcohol with epichlorohydrine followed by carbonation of oxirane groups (Scheme 2). Furfuryl alcohol O-glycidylation requires phase transfer catalyst (PTC). Indeed PTC enables the formed furfuryl alkoxide to meet epichlorohydrine, and to speed up the reaction since the formed alkoxide is much more nucleophile than furfuryl alcohol. Glycidylation mechanisms have been already reported in previous works^{30, 31}. FGE is purified by distillation and then carbonated under CO₂ atm. The expected product is confirmed by ¹H NMR, ¹³C NMR and GC-MS.

The ¹H-NMR spectrum shows that expected structure is obtained (Figure 7). The peak of proton CH at 3.1ppm of oxiran of FGE, as described in the experimental part, has disappeared and is replaced by the f signal at 4.9ppm. Moreover, the furanic ring is characterized by two signals a and b at 7.6 and 6.5ppm respectively. The relation between the integrations of a and f signals confirm that the furan derivative is mono-functionalized by cyclocarbonate group. It confirms the quantitative conversion of the carbonation step; all the epoxide groups have been replaced by cyclocarbonate groups

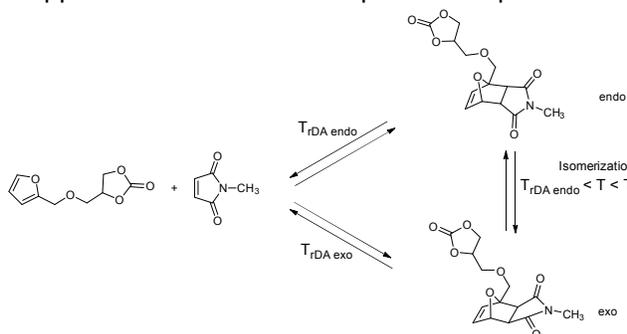


Scheme 2: Furfuryl cyclocarbonate ether (FCE) synthesis

Figure 7: ^1H NMR spectrum of synthesized FCE in DMSO-d_6

Model adduct study

In a second part, a model DA reaction has been conducted to determine FCE reactivity toward maleimides and to study the thermal behavior and rDA parameters of the formed adduct. This model adduct is obtained by reaction of FCE with N-methylmaleimide (Scheme 3). The reaction can be monitored by ^1H NMR: the methyl-group peak at 2.8 ppm is taken as reference. Indeed furan characteristic peak in DMSO-d_6 is at 7.6 ppm, as shown Figure 1, and maleimide double bond characteristic peak is at 6.9 ppm as described in the experimental part.



Scheme 3: Model adduct synthesis by DA reaction between FCE and N-methylmaleimide

Two stereoisomers, the endo and the exo-adducts, are formed during the DA reaction. The first one is the kinetic product and the second one the thermodynamic product³². The exo adduct undergoes rDA reaction at higher temperature than the endo adduct. Therefore, to enhance thermal properties, the exo stereoisomer has to be favored. To obtain a good exo/endo ratio, the reaction is heated at 70°C during 3 days (it has to be mentioned that by heating too much, rDA reaction takes place over DA and a compromise must be found between adduct isomerization and deprotection) (Scheme 3). The exo stereoisomer (Figure 5) is isolated by precipitation in diethyl-ether and analyzed by ^1H -NMR (Figure 8). The DA reaction involves the furanic diene system with the dienophile maleimide double bond. The NMR signals of these groups enable to calculate DA conversion and to identify the

reactants and products. On the NMR spectrum, exo-adduct characteristic peak has been identified at 5.1ppm. Furanic and maleimide group respective signals at 7.6 and 7.0ppm are not present. Also, there is no endo-adduct signal on the spectra (exo-adduct characteristic

peak is expected at 5.2ppm³²). This precipitation step is exo-adduct selective and we isolated pure exo-stereoisomer.

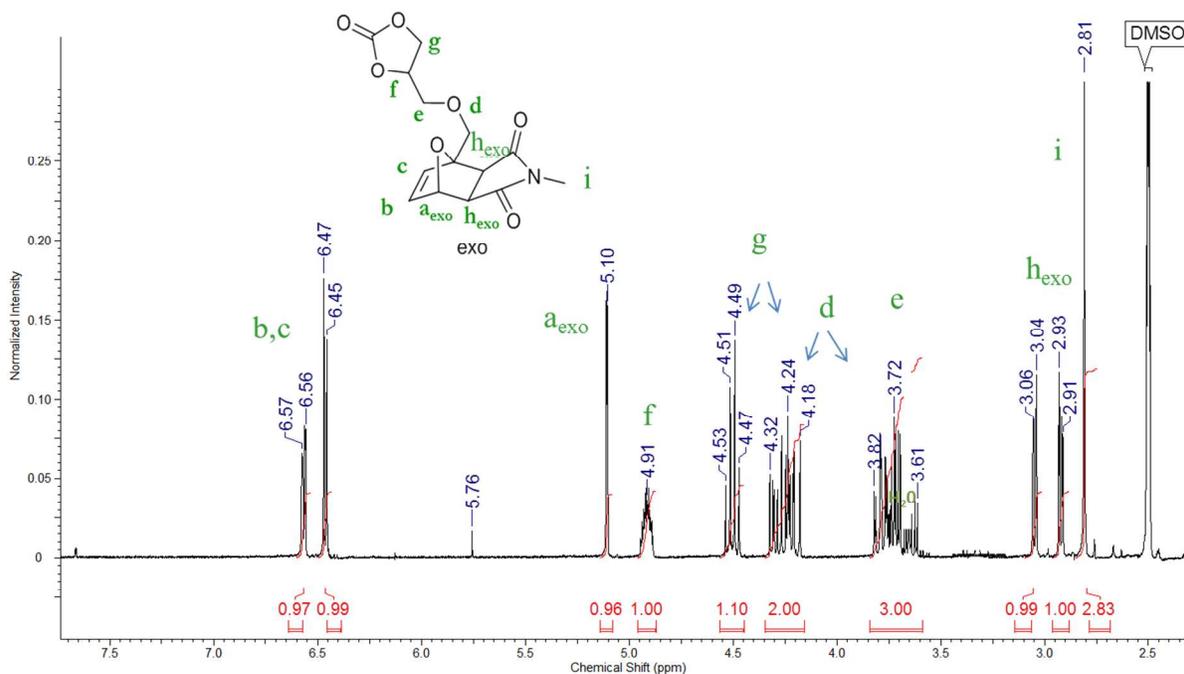


Figure 8: ¹H NMR spectrum of the model adduct exo stereoisomer in DMSO-d₆

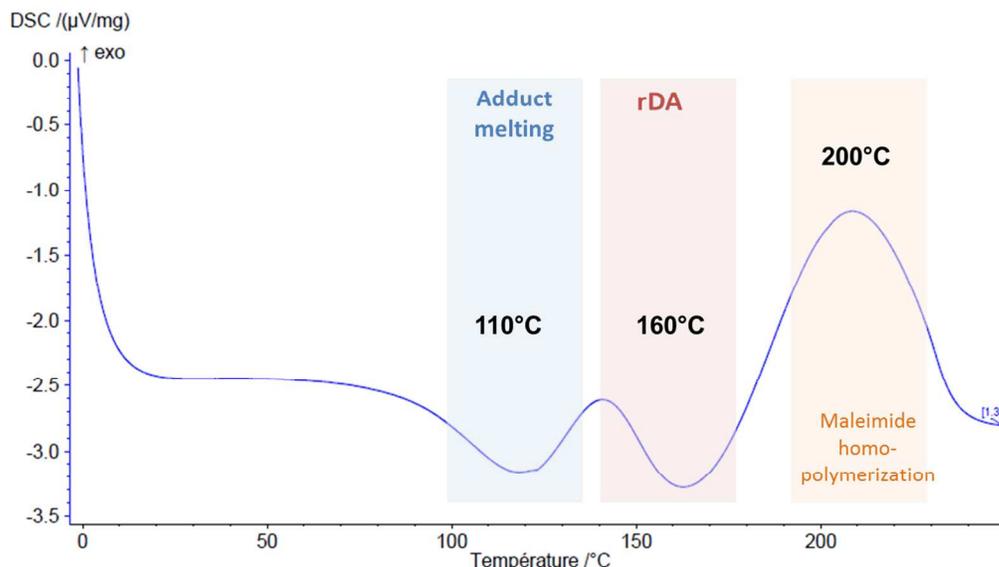


Figure 9: Model adduct DSC thermogram (10°C/min)

DA is an endothermic reaction and so rDA temperature can be measured by DSC. The adduct thermal behavior has been determined

(Figure 9): the first endothermic transition is the adduct melting (at 110°C), then rDA reaction takes place around 160°C. Maleimides are

released by rDA reaction, and they undergo radical homopolymerization at 200°C. The adduct melting transition could be confirmed by visual observation.

DA reaction is a thermodynamic equilibrium between blocked and unblocked forms. The rDA temperature measured by DSC is the temperature where blocked form is no longer stable, and rDA is preponderant. In fact rDA can start at lower temperature but slowly, and therefore a $^1\text{H-NMR}$ kinetic study has been

conducted. The model adduct has been solubilized in DMSO-d_6 , heated at 100°C, and spectrum evolution has been recorded. Furan and maleimide characteristic peaks are at 7.6 and 7.0ppm respectively. The integration of the adduct peak H_a at 5.1ppm is monitored and compared to cyclocarbonate peak H_f of FCE at 4.9ppm as reference peak (Figure 10). The exo-adduct is 90% deprotected after 120min at 100°C in DMSO.

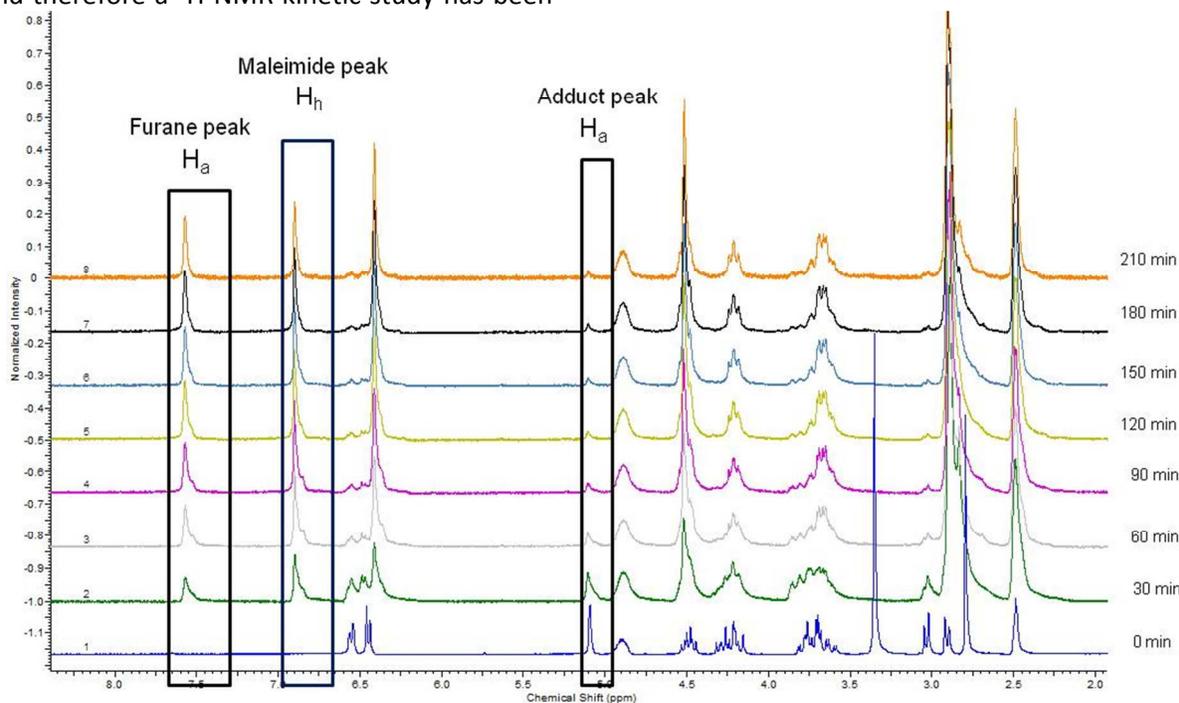


Figure 10: ^1H NMR spectrum of the model adduct at 100°C in DMSO-d_6

This study combines both kinetic and thermodynamic aspects of rDA reaction. It has been showed that the adduct form is no longer stable after 140°C. Moreover, rDA reaction begins at lower temperatures. At 100°C, the exo adduct is cleaved until it reaches the thermodynamic equilibrium allowing 10% remaining exo adduct.

Dicyclocarbonate adduct M_{adduct} synthesis

The target is to synthesize a thermally cleavable dicyclocarbonate, able to polymerize by step-growth polymerization of cyclocarbonates and amines. Such a monomer (M_{adduct}) is obtained by DA reaction between FCE and a bismaleimide

oligomer PEO-PPO-bm. Both reagents are liquid; the reaction is thus performed in bulk at 50°C during 3 days. The conversion by DA reaction is monitored by $^1\text{H-NMR}$ (Figure 11) using the following signals: 7.6ppm for furan; 6.8ppm for maleimide; 5.2 and 5.1ppm for endo and exo adducts respectively; using the group between 1.0 and 1.3ppm as signal reference.

The DA reaction is quite slow, and in order to reach the maximum conversion, reaction is left under stirring during 3 days. Moreover, 50°C is an intermediate temperature allowing both to speed up DA reaction and to favor the exo adduct formation. On the $^1\text{H-NMR}$ spectrum of the final product (Figure 11), the furanic

characteristic peak at 7.6ppm has been identified as well as characteristic peaks of adducts a_{endo} and a_{exo} . The integration ratios allow to determine a DA conversion higher than 99%. A ratio endo/exo is calculated, using a_{endo} and a_{exo} integrations, to determine the proportion of each stereo-isomer. Endo/exo ratio is equal to 1/4. The complete conversion

of all maleimides and furanes means that all cyclocarbonates are telechelic which is essential for the following polymerization step. In order to enhance polymer molar mass, it is important to control the stoichiometry and use only telechelic monomers. M_{adduct} can be polymerized without further purification.

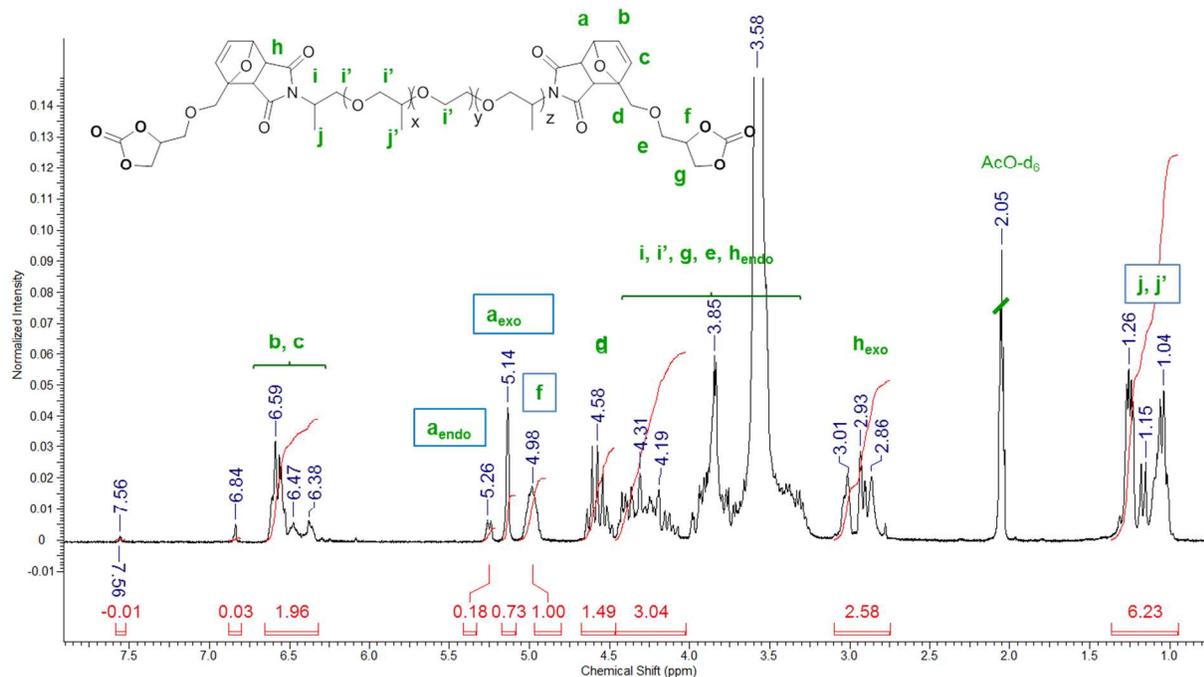
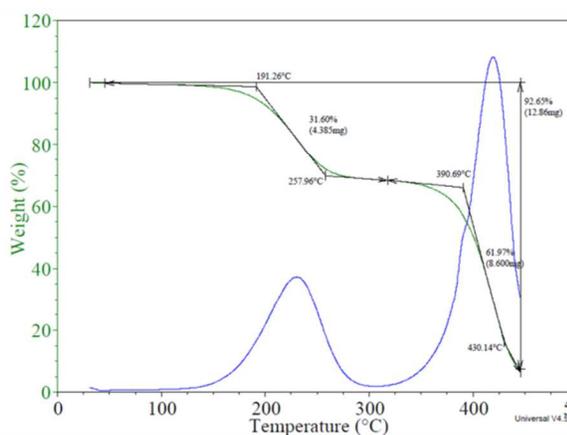
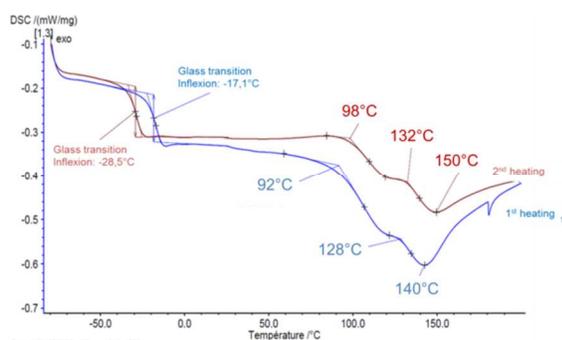


Figure 11: M_{adduct} $^1\text{H-NMR}$ spectrum in AcO-d_6

M_{adduct} thermal behavior is characterized by TGA and DSC. Firstly, TGA thermogram (Figure 12) exhibits a 32% weight loss beginning at 190°C. This percentage corresponds to the theoretical amount of FCE released after rDA reaction. The vaporization temperature of FCE is 170°C, therefore this first weight loss can be attributed to the release of FCE after rDA reaction. The second weight loss at 390°C is due to polyether backbone degradation. Additionally, DSC analysis (Figure 13) shows glass transition temperature at -17°C and two endothermic peaks at 128 and 143°C indicating endo and exo adduct rDA reactions respectively (the exo adduct rDA temperature range is similar to the model adduct rDA). After the first heating, a second heating is performed on the DSC sample after a 1h cooling. The second heating exhibits

the same rDA temperatures than the first one which shows that adducts have been reformed. However, the rDA peak area is smaller, which means that DA adducts have not been completely reformed. The lower glass transition (-28°C) is due to the plasticizing effect of the unprotected FCE in the sample.

Figure 12: M_{adduct} TGA (10°C/min) under airFigure 13: M_{adduct} DSC (10°C/min)

A telechelic dicyclocarbonate adduct has been synthesized and its thermal behavior characterized in DSC. The monomer is cleavable and its thermodynamic rDA temperatures is around 100°C and at 140°C for endo and exo adduct respectively.

M_{adduct} polymerization

The key point is to avoid rDA during polymerization for the synthesis of PHU (Scheme 1). Indeed rDA produces maleimide functions which are highly reactive towards amines. rDA reaction being an equilibrium, maleimide consumption draws the reaction toward deprotection³². Therefore, maleimide groups must remain protected in DA adduct form. In this purpose, adduct polymerization will be carried out at room temperature even if carbonate/amine system low reactivity would require heating. Therefore polymerization reaction needs a catalyst. Triazabicyclododecane

(TBD) is one of the most efficient catalyst for this system^{29, 33}. Jeffamine EDR148 (EDA), is chosen as diamine for its good reactivity towards cyclocarbonates³⁴.

The obtained PHU is analyzed in Size Exclusion Chromatography (SEC) and its chromatogram is reported Figure 17. Its average molar mass is 2,800 g/mol eq PEO (PDI 1.3). This molar mass suggests that the polymerization degree is about 4, which means that there are 4 DA adduct linkages in the polymer's backbone. On ¹H-NMR analysis, the cyclocarbonate peak of proton H_f at 4.9ppm (Figure 11) has disappeared which demonstrates that there are no longer any cyclocarbonate groups. It indicates also that the major part of terminal groups are amines. Moreover, the adduct characteristic signals (*a*_{endo} and *a*_{exo}) are compared to the reference signals (*j*, *j'* at 1.1ppm) which proves that 91% of the initial adducts are still protected after polymerization (Figure 15). It is correlated with a slight increase of the furan signal at 7.6ppm, showing that furans have been released. Also there is no signal indicating maleimide moieties, meaning that they have indeed reacted with amines. This side-reaction has modified cyclocarbonate/amine stoichiometry, lowering the polymer molar mass accordingly to Carothers equation.

Thermal treatment on the obtained polymer would give two rDA products represented Scheme 1: EDA-bf and PEO-PPO-bm. The DSC analysis (Figure 14) exhibits, as previously for M_{adduct} , two endothermic peaks that can be attributed to endo and then exo adduct rDA reactions at 90 and 120°C respectively. There is also an exothermic peak at 140°C meaning that a reaction takes place at that temperature. It could be attributed to Michael addition between maleimides produced by rDA and polymer primary amine end groups.

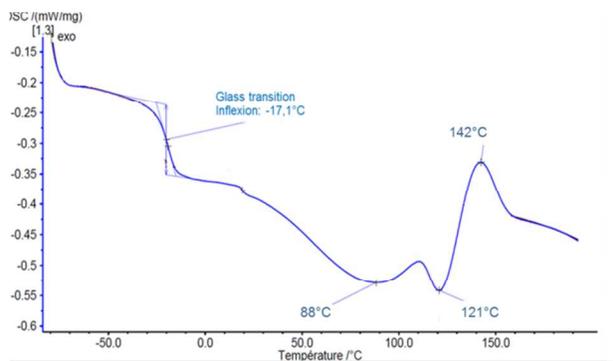
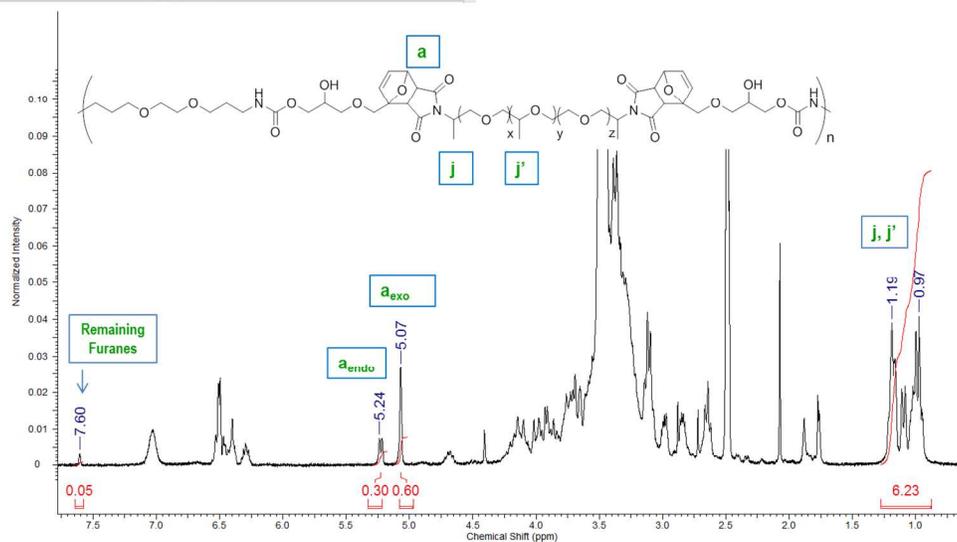
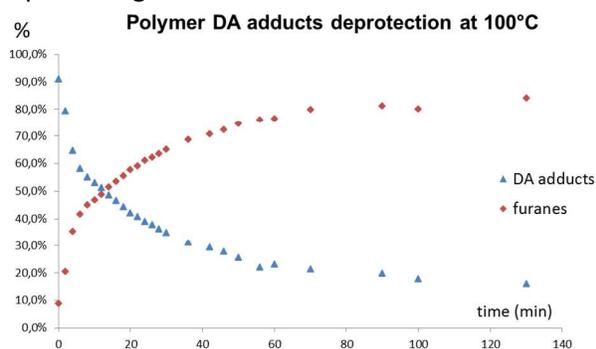


Figure 14: DSC analysis of NIPU (10°C/min)

Figure 15: ^1H NMR spectrum of NIPU polymer in DMSO-d₆

Then a kinetic study of rDA reaction is monitored by ^1H -NMR in DMSO-d₆ and conducted at an intermediate temperature, 100°C. This temperature enables to study endo-adduct deprotection and to determine how exo-adduct are going to react. It is complementary to DSC and offers a better understanding of the adduct behavior. The same method as previously is used to monitor the characteristic signals, and the results are reported Figure 16.

Figure 16: DA adduct deprotection in NIPU polymer at 100°C monitored by ^1H NMR in DMSO-d₆.

DA adducts in the polymer are deprotected at a very similar rate than the model adduct: after 120min, rDA equilibrium is reached at 85% of deprotection. Also, the maleimide signal does not increase at the same rate than furanes. Maleimides are partially consumed by another reaction (unfortunately the polymer signal covers a large portion of the spectrum and does not enable to characterize this reaction). Thus, it can be confirmed that a reaction occurs after rDA.

Chain depolymerization is monitored by SEC. In order to analyze the polymer evolution, a quencher is added before injection in order to stop any reaction to the protected form. A monoamine (butylamine) is used, to react with maleimide by Michael addition. Indeed amine

addition on a maleimide double bond is much faster than DA reaction, and quantitative. Firstly the polymer is heated in DMF, at 100°C. When a sample is removed for analysis, butylamine is added in excess and the mixture is stirred vigorously. The obtained sample is directly analyzed by SEC.

With chromatograms superposition, it can be shown that the initial NIPU polymer is cut to

form the rDA fragments (Figure 17). Indeed when heated, the polymer retention time is longer, which means that its molar mass is decreasing. After 2h at 100°C, it is clear that PEO-PPO-bm (quenched by butylamine) and EDA-bf are the main fragments that remain from the initial polymer.

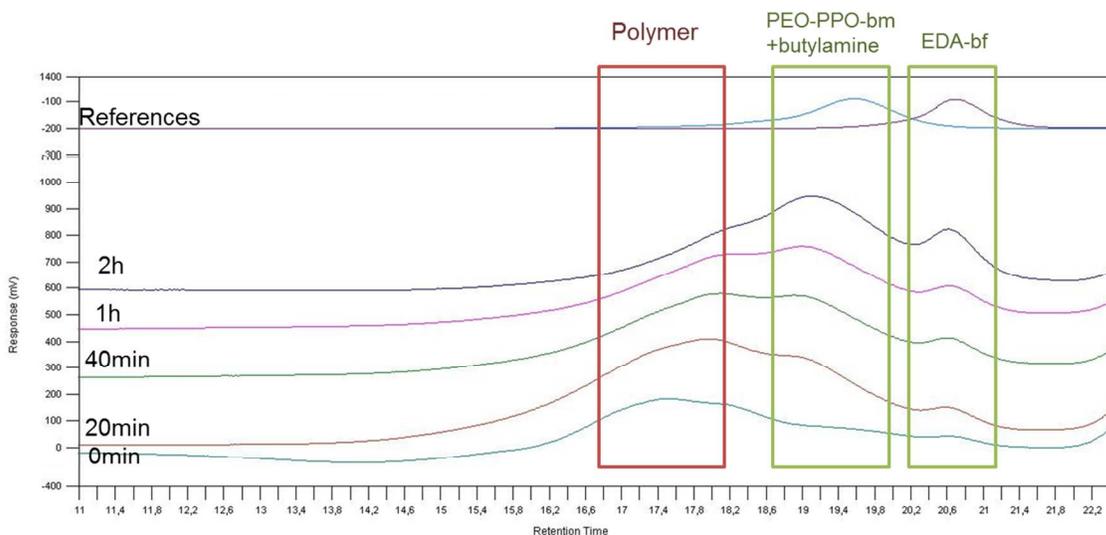


Figure 17: rDA kinetic at 100°C in DMF monitored by SEC

The dicyclocarbonate adduct, M_{adduct} , has been successfully polymerized to form a linear PHU integrating DA adduct in its chain and during polymerization, 91% of initial DA adducts have remained in their protected form. The thermal behavior was then studied by various methods. rDA temperatures have been measured by DSC at 90 et 120°C. By $^1\text{H-NMR}$ kinetic study at 100°C, DA adducts deprotection yield has been calculated: after 120min at 100°C, 85% of the adducts are unprotected. Then, with SEC kinetic study, the break of DA linkages and the release of PEO-PPO-bm and EDA (which are rDA products) has been confirmed.

CONCLUSIONS

A thermo-cleavable NIPU has been successfully synthesized by polymerization of a dicyclocarbonate DA adduct. Two main difficulties emerged for this pathway:

maleimides reactivity towards amines combined with DA adduct sensitivity to temperature. In consequence, the strategy was to bring cyclocarbonate functionality by the furanic compounds and to use a telechelic bismaleimide. Also, a model adduct study engaging N-methylmaleimide and FCE was synthesized and it appeared as a result that DA adduct monomers or within polymer backbone, had a very similar thermal behavior.

The synthesis in high yield of a telechelic cyclocarbonate DA adduct was a key point. The monomer could be polymerized with EDA. The step growth polymerization of cyclocarbonate and amine, despite its low reactivity, was successfully performed at room temperature with TBD catalyst.

rDA reaction has been characterized by three different analyses: DSC, $^1\text{HNMR}$ and SEC. The polymer thermal behavior could be determined. Firstly rDA temperatures are of 90°C and 120°C

for endo and exo isomers respectively. Also, it appears that kinetic parameters are the same between adducts in the polymer chain or in molecular adducts. Deprotection is quite fast: after 120 minutes at 100°C, 85% of the adducts are unprotected. At last, SEC analysis enables to demonstrate that the polymer chains were cleaved by rDA reaction.

This study has been performed on linear PHUs, and thus, constitutes an approach for more complex systems. The concept being validated, the next step is to carry out this study on crosslinked PHUs for thermoremendable adhesives or coatings.

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Figure Legends

Figure 1: Structure of N-methylmaleimide

Figure 2: Structure of ED600bm

Figure 3: Structure of FGE

Figure 4: Structure of FCE

Figure 5: Structure of model adduct

Figure 6: ^1H NMR spectrum of synthesized FCE in DMSO-d₆

Figure 7: ^1H NMR spectrum of the model adduct exo stereoisomer in DMSO-d₆

Figure 8: Model adduct DSC thermogram (10°C/min)

Figure 9: ^1H NMR spectrum of the model adduct kept at 100°C in DMSO-d₆

Figure 10: M_{adduct} ^1H -NMR spectrum in AcO-d₆

Figure 11: M_{adduct} TGA (10°C/min) under air

Figure 12: M_{adduct} DSC (10°C/min)

Figure 13: NIPU polymer DSC (10°C/min)

Figure 14: ^1H NMR spectrum of NIPU polymer in DMSO-d₆

Figure 15: DA adduct deprotection in NIPU polymer at 100°C monitored by ^1H NMR in DMSO-d₆.

Figure 16: rDA kinetic at 100°C in DMF monitored by SEC

Scheme Legends

Scheme 1: Dicyclocarbonate DA adduct synthesis and its polymerization with a diamine

Scheme 2: Furfuryl cyclocarbonate ether (FCE) synthesis

Scheme 3: Model adduct synthesis by DA reaction between FCE and N-methylmaleimide

GRAPHICAL ABSTRACT

Elena Dolci, Guillaume Michaud, Frédéric Simon, Bernard Boutevin, Stéphane Fouquay, Sylvain Caillol

REMEMDABLE THERMOSETTING POLYMERS FOR ISOCYANATE-FREE ADHESIVES: A PRELIMINARY STUDY

Based on a model study, a new bis-cyclic monomer bearing Diels-Alder adduct was synthesized. This monomer was polymerized with a diamine to yield a thermoresponsive polyhydroxyurethane PHU. This PHU is remendable around 100°C by retro Diels-Alder reaction.

