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## Photo-crosslinked coatings from an acrylate terminated **non-isocyanate polyurethane (NIPU)** and reactive diluents

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### ABSTRACT

**Non-isocyanate polyurethane** acrylate coatings (NIPUAs) were prepared by photocrosslinking of mixtures of an acrylate terminated NIPU oligomers (A-OI) and reactive (meth-)acrylate diluents. A-OI were prepared by a transurethane polycondensation pathway followed by an acrylation reaction of the resulting hydroxy chain-ends. The influence of the reactive diluent content and chemical structures on the thermal and mechanical properties of these coatings has been investigated. The obtained materials exhibited thermal stabilities above 255°C, Young modulus ranging from 2.6 to 9.2 MPa, tensile strength from 2.69 to 25.5 MPa and elongation at break from 56 to 470 %.

### KEYWORDS:

Polyurethane, non-isocyanate, NIPU, transurethanization, coating, acrylates, UV-Curing, reactive diluent.

## INTRODUCTION

Polyurethanes (PUs) are a class of very important polymer materials possessing versatile properties allowing them to be used in various application fields. Polyurethane acrylate systems (PUAs) are based on acrylate-terminated prepolymers that are crosslinked to afford protective coatings displaying very good abrasion and chemical resistances and very flexible mechanical properties.<sup>1,2</sup>

The attention towards UV-curable coatings is continually increasing owing to their fast curing and low energy consumption.<sup>3</sup> Their formulations are usually composed of three major components: photoinitiator, reactive oligomer and reactive diluent.<sup>4</sup> The reactive diluent decreases the viscosity of the formulation and copolymerizes with the oligomer. The chemical structure of the oligomer defines the viscoelastic properties of the final crosslinked material.<sup>5</sup>

Epoxy acrylate, polyester acrylate and urethane acrylate oligomers (PUAs) are commonly used in the preparation of free radical UV-curable coatings.<sup>6</sup> PUAs are conventionally prepared by acrylation of telechelic polyurethane oligomers, synthesized by the conventional reaction between polyols and toxic diisocyanates, which are obtained from diamines and toxic phosgene.<sup>7</sup> During the two last decades, some research groups have proposed alternatives to prepare PUA materials by non-isocyanate and non-phosgene routes (NIPUAs).<sup>8-18</sup>

Recently, the photo-curing of poly(hydroxyurethane) acrylate (PHU) oligomers, obtained by the polyaddition of cyclic dicarbonate with diamine monomers followed by acrylation have been studied.<sup>12,13,16,18</sup> However, as far as we know, the photo-crosslinking of NIPUA oligomers obtained by the transurethane polycondensation, which is one of the most promising free isocyanate pathways to polyurethanes, has not yet been described.<sup>19-25</sup> This pathway consists in the reaction of dialkyl dicarbamates<sup>19-22</sup> or dihydroxyethyl dicarbamates<sup>23-25</sup> with diols, in presence of organic or organo-metallic catalysts. However, with dihydroxyethyl dicarbamates, a weak proportion of urea functions are formed owing to a back-biting side reaction.<sup>23-25</sup> On the other hand, the transurethane polycondensation gives conventional PU structures and not poly(hydroxyurethane) structures (PHUs).<sup>26-28</sup>

In this work, we describe the preparation of UV-curable coatings from several urethane and non-**urethane** reactive diluents and a NIPU-acrylate oligomer (NIPUA), obtained by the transurethane polycondensation approach. The impact of the reactive diluent chemical structure and content on the mechanical and thermal properties of the resulting coatings is investigated.

## EXPERIMENTAL

### Materials

Poly(tetramethylene oxide) (PTMO) of  $M_n = 2000$  g/mol, 1,6-diaminohexane (98%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%), dimethyl carbonate (DMC, 99%, anhydrous), ethylene carbonate (99%, anhydrous), were obtained from Sigma Aldrich. Acryloyl chloride (96%), 4-methoxyphenol (MeHQ, 99%) and triethylamine (99%) were supplied by Fisher Scientific. Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (Irgacure 819) and Ethyl phenyl(2,4,6-trimethylbenzoyl) phosphinate were supplied by BASF. All the other reagents and solvents were used without further purification. The reactive diluents HDDA (hexamethylene diol di-acrylate) and UDMA (urethane diol di-methacrylate) were supplied by Esstech.

### Synthesis

#### Preparation of Dimethylhexane-1,6-dicarbamate (BMC-C<sub>6</sub>)

In a neat round bottom flask equipped with a magnetic stirrer, hexamethylenediamine (1 eq.), TBD (0.1 eq.) and DMC (10 eq.) were added and stirred for 5 h at 80 °C. Then, the reaction medium was cooled to room temperature. Crystallized product (BMC-C<sub>6</sub>) was recovered by filtration (yield > 85 %) and washed by distilled water to remove TBD. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 4.67 (s, broad, 2H; NH), 3.65 (s, 6H; NH(CO)OCH<sub>3</sub>), 3.15 (m, 4H; NHCH<sub>2</sub>); 1.48 (m, 4H; NHCH<sub>2</sub>CH<sub>2</sub>), 1.32 (m, 4H; NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ): 26.2, 29.9, 40.7, 52.0, 157.1 ; IR (ATR): ν~3300 cm<sup>-1</sup> (m; ν<sub>NH</sub>), ~1700 (s, ν<sub>CO</sub> H-bonded) cm<sup>-1</sup>, ~1530 cm<sup>-1</sup> (s, ν<sub>NH</sub> bending).

#### Preparation of hydroxy-terminated NIPU oligomer H-C6-2000

In a three-necked round-bottom flask equipped with a mechanical stirrer, a Dean Stark condenser and connected to a vacuum pump, BMC-C<sub>6</sub> and poly(tetramethylene oxide) of  $M_n = 2000$  g/mol (PTMO 2000) were added at an appropriate molar ratio previously calculated by Carothers theory to reach the desired degree of polymerization. The temperature was progressively risen to 160 °C under nitrogen flow and stirring. Then, 10 mol% of MeOK catalyst in regard to BMC monomer was added. After 1 h of reaction at 160 °C, the reaction mixture was placed under vacuum (400 mbar, 1 h). Finally, the pressure was carefully reduced to 0.5 mbar during 4 h. After cooling down to room temperature under nitrogen flow, H-C6-2000 was recovered without any purification.

#### Preparation of Acrylate-terminated NIPU Oligomer A- C6-2000

H-C6-2000 was introduced in a neat round bottom flask equipped with a magnetic stirrer, under a nitrogen stream. The oligomer was solubilized in anhydrous DCM. Triethylamine (3.5 eq.), previously distilled under KOH pellets, was added to the reaction mixture. After cooling down the mixture to 0 °C using an ice bath, acryloyl chloride (3 eq.) was added dropwise into the reaction mixture. When addition was completed, the mixture was allowed to react during 6 h at room temperature. Filtration of triethylammonium salts was then carried out. After, mixture was washed three times by HCl (1M), NaOH (1M) and finally brine. First organic phase was recovered and the oligomer part remaining into the aqueous phase was extracted by DCM. Treatment was repeated and the organic phases were

combined, dried over  $\text{MgSO}_4$ , and filtrated. Around 300 ppm of 4-methoxyphenol stabilizer was added and solvent was evaporated. Finally, the obtained yellow product was dried using high vacuum at 25°C.

#### *Preparation of the reactive diluent BHECA (Bis(HydroxyEthyl Carbamate Acrylate))*

In a 250 mL 3-necked flask, 24.05 g (0.27 mol) ethylene carbonate and 15.05 g (0.13 mol) of 1,6-hexanediamine were stirred in  $\text{N}_2$  atmosphere at 90 °C for 2 h. Then, the reaction temperature was increased to 120 °C during 5 h. After cooling to room temperature, the obtained white crude product was washed with 150 mL of water, was filtered, and was recrystallized in water (29.39 g, yield: 78 %). Then, this product (23.80 g, 0.08 mol, 1 eq.) was reacted with acryloyl chloride (16.93 g, 0.18 mol, 2.21 eq.), in presence of trimethylamine (19.77 g, 0.20 mol, 2.40 eq.), in DCM for 6h at room temperature. The obtained BHECA was a yellowish solid (yield: 60 %). Then, 5.0 g of BHECA was purified over a flash column, using a DCM/MeOH (97:3) mixture as eluent. A white powder was obtained (3.3 g, purification yield: 66 %).

#### *Preparation of photo-crosslinked NIPU coatings (NIPUAs)*

Formulations were prepared by dissolving A-C6-2000 and the reactive diluent in an appropriate amount of butyl acetate leading to a convenient viscosity. Then, 3.3 wt% of BAPO-TPOL photoinitiator (BAPO-TPOL) were added to the mixture. Formulations were stirred up to 2 hours in order to obtain homogeneous media. Then, the obtained formulations were casted to stiff matte steel "Q-panel" plates supplied by Labomat. After degreasing the plates with a cloth soaked in ethanol (EtOH), two types of coatings were prepared for each type of formulation, i.e. "thin" and "thick" films. In order to obtain thin films, the desired formulation was applied on the top of the plate and wet thickness control was provided using a roll coater. To obtain thick films, slides of an adhesive tape on the borders were used to calibrate the thickness. The plates were then put in a UV conveyor (UV Fusion Light Hammer 6) to perform photo-crosslinking of the NIPU coatings.

### **Measurements and Instrumentation**

$^1\text{H}$  and  $^{13}\text{C}$  NMR analysis were performed on a Bruker 300 Fourier Transform spectrometer at 300 MHz and 75 MHz respectively, in  $\text{CDCl}_3$  solutions containing tetramethylsilane (TMS) as internal standard.

IR spectra were acquired with a FTIR (Perkin-Elmer Spectrum 2000 FTIR), provided with a diamond ATR device (Attenuated Total Reflection). Spectra were recorded from 10 scans in the 500 to 4000  $\text{cm}^{-1}$  range.

Average molecular weights of polymers ( $M_n$  and  $M_w$ ) and dispersity ( $\mathcal{D} = M_w/M_n$ ) were assessed by Size Exclusion Chromatography (SEC). Polymers were dissolved in dichloromethane, filtered (0.45  $\mu\text{m}$ ) and analyzed at 25°C by a Varian PL-GPC50 system provided with two mixed packed columns (PL gel mixed type C). Dichloromethane was used as the mobile phase and PMMA standards (from 875 to 680000  $\text{g mol}^{-1}$ ) were used for calibration.

Thermo-Gravimetric Analysis (TGA) was achieved with a TGA Q500 device (TA Instruments), using a heating rate of 10°C/min under a nitrogen flow. The temperature at 5% of weight loss ( $T_{5\%}$ ) was used as reference to estimate the degradation of polymers.

Differential Scanning Calorimetry (DSC) was achieved with a DSC Q2000 device (TA Instruments), using a heating rate of 10°C/min under a nitrogen flow. The midpoint method was used to evaluate the glass transition temperature (T<sub>g</sub>). Melting temperature (T<sub>m</sub>) was measured at the maximum of the endothermic signal. DSC curves were realized in a temperature range of -80 to 300°C.

The thickness of cross-linked thin films (<50 µm) was measured by magnetic determination using the PosiTector 6000, according to ISO 2808: 2007, with an accuracy of ± 1.0 micron. The device consists of a probe to be applied against the coating, previously deposited on a flat surface. The thickness of the thick crosslinked films (film thickness between 100 µm and 1 mm) was measured with a Digimatic micrometer, with an accuracy given to the nearest micrometer. The coating is clamped by a micrometer screw between the two circular measuring surfaces of the device.

The tensile analyses were performed on a Zwick/Roell device equipped with a 500 N force sensor, two jaws (pneumatic or manual clamping, depending on the type of sample characterized) and a movable crosshead. The tests were carried out in accordance with ISO 527\_3 "Test conditions for films and foils". For each tested coating, between 5 and 15 rectangular specimens were cut out with a scalpel. Specimens with unevenness or notches were systematically removed. The manually clamped jaws limit the width of the specimens to 6 mm, the specimens have the following dimensions: a total length l<sub>3</sub> of 50 mm; a width b of exactly 4 mm; a thickness h always less than 1 mm. The values of b and h were measured precisely at three points and the average of the three measurements were used for the calculations. The distance between jaws L<sub>0</sub> was fixed at 35 millimetres. The test speed u was fixed at 20 mm/min, and the preload value was maintained at 0.05 MPa. After each sample has been broken, the following values shall be determined as a function of the cross-section A (A = b × h, expressed in mm<sup>2</sup>) of the sample: The breaking strength of the material σ<sub>r</sub> (MPa) which corresponds to the stress experienced when the specimen breaks, often equal to the maximum stress; the elongation at break ε<sub>r</sub> (%) which corresponds to the elongation of the material before it breaks; Young's modulus or Elasticity E (MPa) which corresponds to the slope of the stress/strain curve in the range between ε<sub>1</sub> = 0.05% and ε<sub>2</sub> = 0.25% of the elongation of the material considered reversible.

For swelling tests, mass (m<sub>i</sub>) samples of approximately 15 mg (thin films) and 50 mg (thick films) were placed in 4 mL pill dispensers containing 3.5 mL of THF and then placed under magnetic agitation at room temperature for 24 h. The samples were removed from the solvent, dried on the surface with absorbent paper and weighed (m<sub>h</sub>). These samples were then dried in a vacuum oven at 40°C for 24 h and weighed (m<sub>f</sub>).

- The extractables **percentage** (τ<sub>EX</sub>) of the samples was expressed in % as follows:

$$\tau_{EX} = \frac{m_i - m_f}{m_i} \times 100 \quad \text{Eq.1}$$

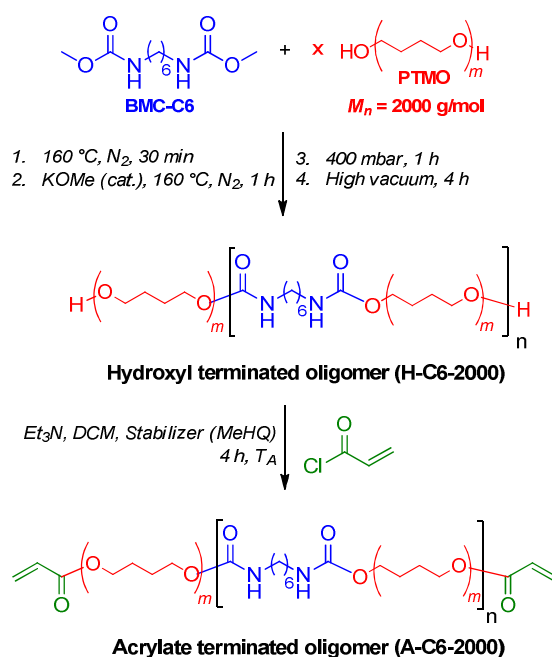
- The swelling (Q) of the samples was expressed in % as follows:

$$Q = \frac{m_h - m_f}{m_f} \times 100 \quad \text{Eq.2}$$

## RESULTS AND DISCUSSION

### Synthesis and characterizations of acrylated NIPU oligomer

Dimethylhexane-1,6-dicarbamate (BMC-C6, Scheme 1), was prepared by a reaction of a large excess of dimethylcarbonate (DMC) (to avoid any cyclization or chain extension) with hexamethylene diamine, in the presence of TBD as catalyst, as previously described.<sup>20-24</sup> The mixture was allowed to react for 6 h at 80°C. The solid monomer was then recovered by crystallization with yield higher than 90%. BMC-C6 can be considered as potentially biobased since hexamethylene diamine<sup>31-32</sup> and DMC<sup>33-34</sup> can be prepared from renewable feedstock. It also can be considered as potential substitute of hexamethylene diisocyanate.



**Scheme 1.** Synthesis approach of acrylated NIPU oligomers.

NIPU oligomer with hydroxyl end-groups (H-C6-2000) was first prepared by a transurethane polycondensation reaction between BMC-C6 and an excess of poly(tetramethylene oxide) (PTMO,  $M_n = 2000$  g/mol) (Scheme 1). PTMO is an interesting polyol since it affords good resistance to hydrolysis and good mechanical characteristics to polyurethane materials.<sup>35</sup>

The targeted  $M_n$  of H-C6-2000 was 5500 g/mol. Thus, the targeted  $X_n$  was deduced from the following equation:

$$M_n = (X_n - 1) \times M_0 + M_{PTMO} \quad \text{Eq.3}$$

With:

- $M_0$  = Molecular weight of the repeating monomer unit =  $(M_{PTMO} + M_{BMC} - 2M_{MeOH})/2$
- $M_{PTMO}$  = Average molecular weight of PTMO.
- $M_{BMC}$  = Molecular weight of BMC.
- $M_{MeOH}$  = Molecular weight of methanol.

Using Carothers' theory,<sup>36</sup> the degree of polymerization " $X_n$ " and the number of repeating units " $n$ ", can be written as follows:<sup>37</sup>

$$X_n = \frac{1+r}{1+r-2rp} = 2n+1 \quad \text{Eq.4}$$

Where  $r$  is the stoichiometric ratio of reagents ( $r < 1$ ), and  $p$  is the conversion of the limiting reagent. If we assume that  $p \rightarrow 1$ , the stoichiometric excess of diols to be used «  $1/r$  » can be calculated as follows:

$$\frac{1}{r} = \frac{X_n + 1}{X_n - 1} \quad \text{Eq.5}$$

The hydroxy-terminated oligomer H-C6-2000 was reacted with acryloyl chloride to obtain the acrylate analogue A-C6-2000. The reaction was conducted in dichloromethane (DCM) at room temperature during 6h. Then, the organic phase was washed several times in acidic and basic aqueous solutions to eliminate by-products. Before evaporation of the organic phase, 300 ppm of methoxyphenol (MeHQ) were added to prevent cross-linking of the recovered product (yield: 76%).

The FTIR spectra (Figure 1) revealed the disappearance of the band at around  $3500 \text{ cm}^{-1}$  arising from stretching vibration of the terminal hydroxyl functions (H-O). We can also observe the C-H bending bands of the acrylate group at around  $1410 \text{ cm}^{-1}$  (in-plane) and  $810 \text{ cm}^{-1}$  (out-of-plane). The stretching vibration band of C=O of the ester-acrylate groups appeared at around  $1725 \text{ cm}^{-1}$ , and was overlapped with the C=O stretching vibration band of the free urethane groups ( $1720 \text{ cm}^{-1}$ ). Other urethane bands are detected at  $1686 \text{ cm}^{-1}$  (H-bonded C=O, stretching) and  $1526 \text{ cm}^{-1}$  (N-H bending). The stretching vibration of N-H bonds of urethane groups appeared at around  $3300 \text{ cm}^{-1}$ .

$^1\text{H}$  NMR spectra (Figure 2) revealed the shift of the signal "6" of the terminal methylene protons owing to the electron-withdrawal effect of the introduced acrylate groups from  $\delta = 3.61 \text{ ppm}$  ((t,  $\text{CH}_2\text{-OH}$ ) to approximately  $\delta = 4.17 \text{ ppm}$  (t,  $\text{CH}_2\text{-OCOR}$ ). The new acrylate proton signals appeared at around  $\delta = 6.39 \text{ ppm}$  (signal "10", dd,  $\text{R-OCOCH=CH}_{\text{trans}}\text{H}$ ,  $^3J_{\text{trans}} = 17 \text{ Hz}$ ,  $2J \approx 1 \text{ Hz}$ ),  $\delta = 6.11 \text{ ppm}$  (signal "9", dd,  $\text{R-OCOCH=CH}_2$ ,  $^3J_{\text{trans}} = 17 \text{ Hz}$ ,  $^3J_{\text{cis}} = 10 \text{ Hz}$ ) and  $\delta = 5.81 \text{ ppm}$  (signal "11", dd,  $\text{R-OCOCH=CH}_{\text{cis}}\text{H}$ ,  $^3J_{\text{cis}} = 10 \text{ Hz}$ ,  $2J \approx 1 \text{ Hz}$ ).  $^{13}\text{C}$  NMR spectra displayed the signals of the two acrylate carbons ( $\delta = 130.5$  and  $128.6 \text{ ppm}$ ), as well as the quaternary carbon of the acrylate ester ( $\delta = 166.3 \text{ ppm}$ ).

A-C6-2000 exhibited waxy solid aspect with  $M_n$  values of 5650 and 11100 g/mol by  $^1\text{H}$  NMR and GPC, respectively. The dispersity determined by GPC was of 2.2.

The percentage of urethane groups and of hard segments within the acrylated oligomer were, respectively, calculated as follows:

$$\%U = \left[ \frac{2 \times n \times M_{\text{urethane}}}{M_n} \right] \times 100 = 3.4\% \quad \text{Eq.6}$$

$$\%HS = \left[ \frac{(M_{\text{BMC}} - 2 \times M_{\text{MeOH}}) \times n}{M_n} \right] \times 100 = 5.0\% \quad \text{Eq.7}$$

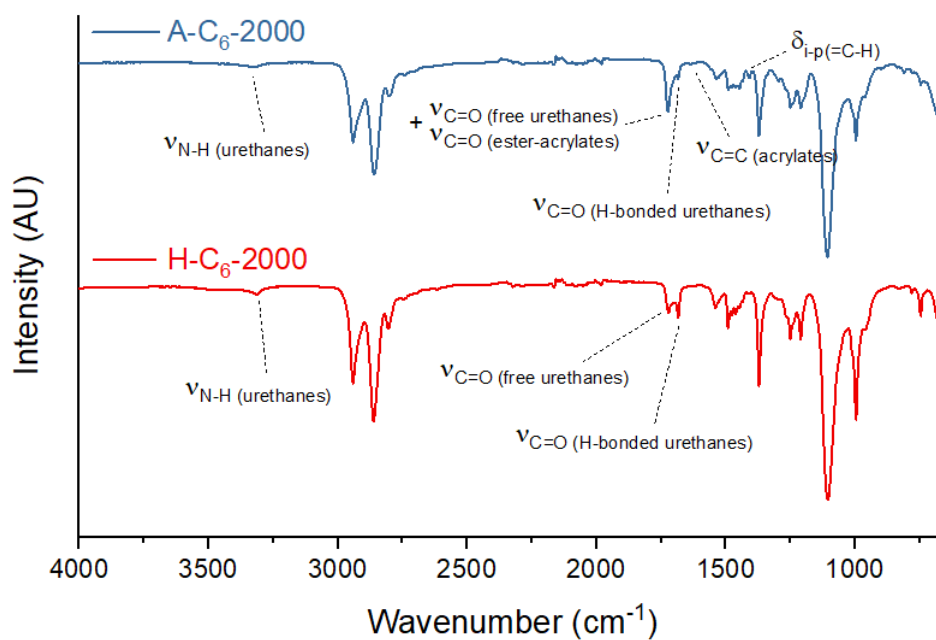


Figure 1: FTIR spectra of the oligomers H-C6-2000 and A-C6-2000.

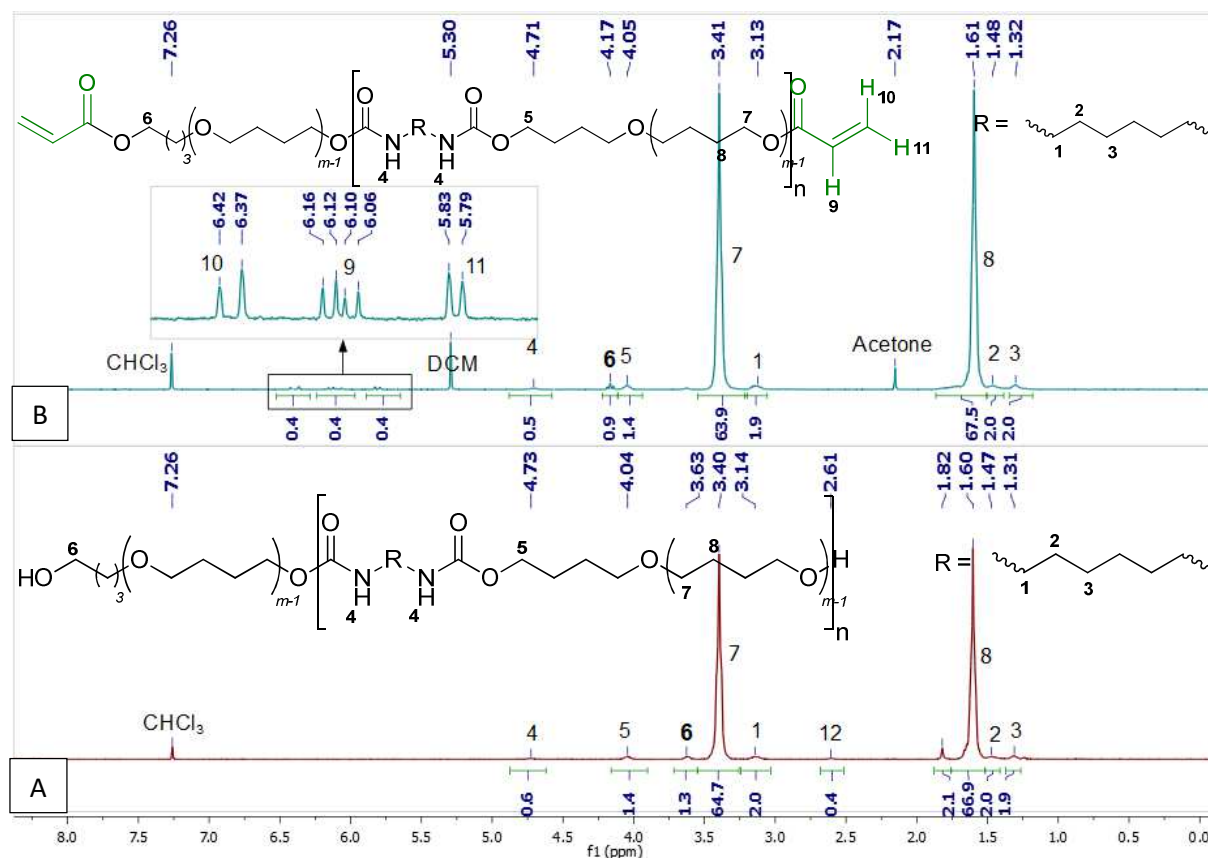
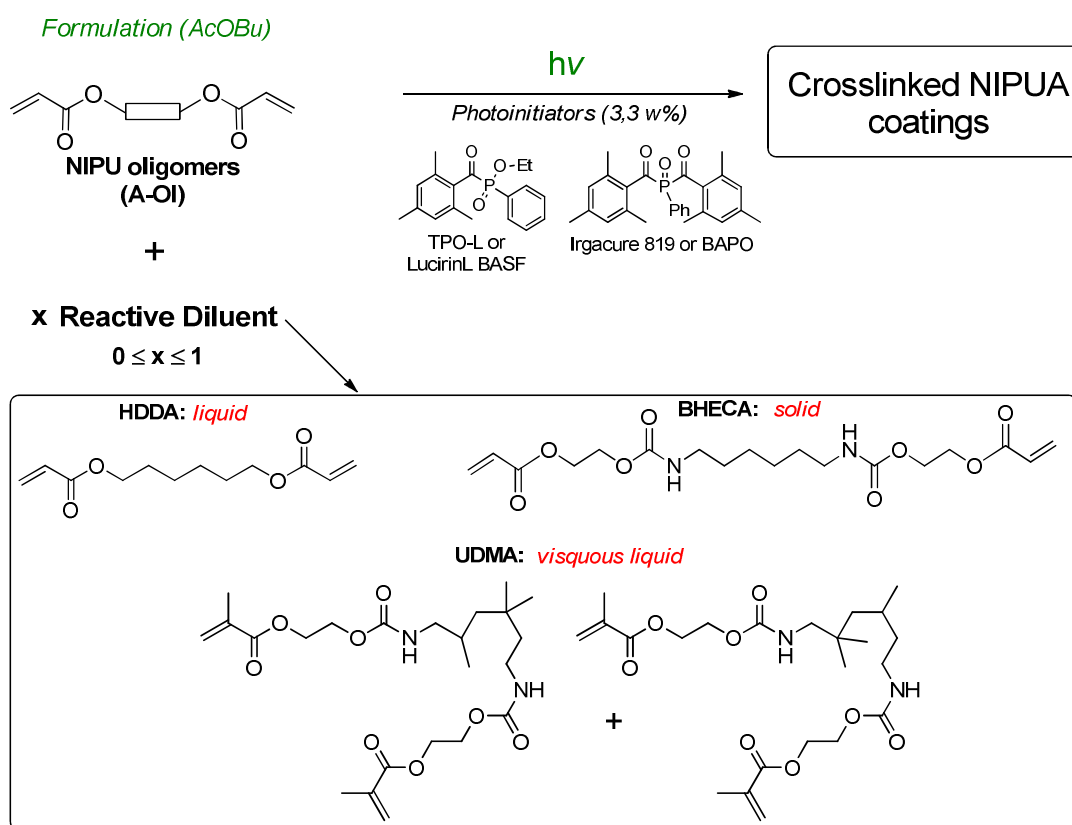


Figure 2:  $^1\text{H}$  NMR spectra of H-C6-2000 (A) and A-C6-2000 oligomers (B).

## Preparation and characterizations of photo-crosslinked coatings

NIPUA coatings were then prepared by photo-curing of the A-C6-2000 oligomer with different proportions of reactive diluents, which were used to reduce viscosity of formulations and tune the cross-linking density of the final coating and its properties.<sup>1</sup> Reactive diluents for free radical photo-curing of coatings are usually acrylic or methacrylic monomers.<sup>38</sup> Generally, unlike multi-functional reactive diluents, mono-functional reactive diluents lead to decreased modulus and increased ductility.<sup>39</sup> A high average functionality leads to high conversion and high crosslink density<sup>40</sup>, increasing material hardness at the expense of flexibility.<sup>41,42</sup> However, a high functionality also can lead to low final conversion owing to gelation phenomenon.

Three reactive diluents were chosen, i.e. HDDA (Hexamethylene Diol Di-Acrylate, Esstech), a commercial diluent widely used in industry;<sup>7</sup> UDMA (Urethane Diol di-MethAcrylate, Esstech) and BHECA (N-hexamethylene dihydroxyethyl carbamate diacrylate), a laboratory-prepared compound. Their chemical structures are shown in Scheme 2. Commercial diluents were liquids. UDMA was more viscous than HDDA. BHECA was a white solid obtained by aminolysis of ethylene carbonate by a default of hexanediamine, then functionalization of the resulting hydroxyl end groups by acryloyl chloride. Its structure has been evidenced by <sup>1</sup>H and <sup>13</sup>C NMR and FTIR (supporting data).



**Scheme 2.** Photo-crosslinking approach of the A-OI oligomers in presence of reactive diluent.

The formulations were prepared in butyl acetate (AcOBu) with a combination of two type I free-radical photoinitiators (TPO-L and BAPO, Scheme 2) at 3.3 wt.%. They were then photo-crosslinked under a UV conveyor equipped with a parabolic mercury vapor lamp. For reproducibility, the light dose received by samples after one pass was adjusted to about 1.2 J/cm<sup>2</sup> (intensity of approx.

10 W/cm<sup>2</sup> in the UVA + UVB + UVC range, constant conveyor speed at 5 m/min. The coatings were prepared in two series of thicknesses, of approximately 30 μm (thin films) and 160 μm (thick films).

The weight percentage of HDDA was varied from 10 to 50 wt.% (NIPUA-H series). Because of the presence of two urethane functions, UDMA and BHECA were used at 20 wt.% but no more (NIPU-U20 and NIPU-B20) to get flexible materials. The obtained coatings exhibited yellowish, transparent, smooth and homogeneous physical appearance. Some pictures are available in the supporting data.

Conversions were calculated by FTIR in ATR mode by monitoring the band at  $\sigma = 1410 \text{ cm}^{-1}$  arising from the C-H bending (in-plane) of the acrylate group. The conversion  $\chi$  was calculated as follows:

$$\chi = \frac{\frac{A_0^{C=C}}{A_0^{ref}} - \frac{A_f^{C=C}}{A_f^{ref}}}{\frac{A_0^{C=C}}{A_0^{ref}}} \times 100 \quad \text{Eq.8}$$

Where  $A_0^{C=C}$  and  $A_f^{C=C}$  are the absorbance values of the band at  $1410 \text{ cm}^{-1}$  ( $\delta(\text{C-H})$ ) of the formulation at initial and final curing times, respectively.  $A_0^{ref}$  and  $A_f^{ref}$  are the absorbance values of the C-H sp<sup>3</sup> stretching bands.

Table 1: Conversion and appearance of NIPUA coatings.

| Coating code <sup>1</sup> | Reactive diluent | C <sub>C=C</sub> <sup>2</sup><br>(meq/g) | DE <sup>3</sup><br>(%) | $\chi$ <sup>4</sup><br>(%) | Aspect <sup>5</sup> | Thickness<br>(thin/thick)<br>(μm) |
|---------------------------|------------------|--|------------------------|----------------------------|---------------------|-----------------------------------|
| NIPUA-H0                  | -                | 0.8                                      | 52                     | 75                         | Y, S, T             | 28 ± 4<br><b>160 ± 11</b>         |
| NIPUA-H10                 | HDDA             | 2.5                                      | 56                     | 87                         | Y, S, T             | 26 ± 4<br><b>176 ± 10</b>         |
| NIPUA-B20                 | BHECA            | 2.5                                      | 54                     | 84                         | Y, S, T             | 22 ± 6<br><b>161 ± 3</b>          |
| NIPUA-U20                 | UDMA             | 2.3                                      | 59                     | 76                         | Y, S, T             | 30 ± 5<br><b>137 ± 10</b>         |
| NIPUA-H20                 | HDDA             | 4.0                                      | 63                     | > 95                       | Y, S, T             | 32 ± 8<br><b>178 ± 4</b>          |
| NIPUA-H30                 | HDDA             | 5.2                                      | 65                     | > 95                       | Y, SR, F, T         | 41 ± 7<br><b>168 ± 8</b>          |
| NIPUA-H40                 | HDDA             | 6.3                                      | 67                     | > 95                       | Y, SR, T            | 33 ± 4<br><b>178 ± 4</b>          |
| NIPUA-H50                 | HDDA             | 7.2                                      | 71                     | > 95                       | Y, SR, T            | 27 ± 8<br><b>205 ± 6</b>          |

<sup>1</sup> Notation: H = HDDA, B = BHECA, U = UDMA. The numbers 10, 20, 30, 40 and 50 are the weight percentages of the reactive diluents within the coatings.

<sup>2</sup> Double bond concentration of the « A-OI + reactive diluent » systems.

<sup>3</sup> Dry extract from AcOBu formulations (the weight percentage of non-volatile matter after solvent evaporation).

<sup>4</sup> Conversion of acrylate double bonds estimated by FTIR.

<sup>5</sup> Y = Yellow, S = Soft, SR = Semi-rigid, F = Fragile, T = Transparent.

The conversion values ( $\times$ ) of acrylate groups are displayed in Table 1. We can observe that conversion increased with the HDDA content within NIPUA-H series. Conversion in the case of the material based on UDMA was lower comparing to conversion of the NIPUA analogue based on BHECA. This may be explained by the lower reactivity of methacrylate comparing to acrylate groups. **An increase of viscosity may also explain this limitation of conversion.** Overall, the obtained conversion values are in consistency with those of PUAs systems.<sup>1,2,43</sup>

The average molecular weights between crosslinked network's knots (acrylate functions) were calculated as follows:

$$M_{c(A-A)} = a \times M_{\text{NIPUA}} + b \times M_{\text{reactive diluent}} \quad \text{Eq. 9}$$

where a and b are the molar ratio of NIPUA and the reactive diluent ( $a+b=1$ ).

The swelling tests were performed in THF as solvent, the values of the extractable ( $\tau_{Ex}$ ) and swelling (Q) percentages are presented in Table 2.  $\tau_{Ex}$  values of NIPUA coatings are below 11 %, and most of them are below 6 %, suggesting that the obtained NIPUAs are well crosslinked. In addition, these coatings were chemically stable in THF. On the other hand, as expected, the swelling percentages of coatings were proportional to  $M_{c(A-A)}$  and ranged from 61 to 313%. Nevertheless, these values are higher in the case of thick films comparing to their thin analogues with roughly same extractible amount. This ambiguous phenomenon could be explained by geometric reasons of the samples.

Table 2: Extractables and swelling percentages of NIPUA coatings.

| Coating code | Reactive diluent | $M_{c(A-A)}^1$ | Thin Films      |          | Thick Films     |          | Obs. <sup>2</sup> |
|--------------|------------------|----------------|-----------------|----------|-----------------|----------|-------------------|
|              |                  |                | $\tau_{Ex}$ (%) | Q (%)    | $\tau_{Ex}$ (%) | Q (%)    |                   |
| NIPUA-H0     | HDDA             | 5650           | 2.4 ± 0.4       | 180 ± 27 | 5.3 ± 1.1       | 313 ± 14 | ND                |
| NIPUA-H10    | HDDA             | 1780           | 4.3 ± 0.3       | 128 ± 6  | 3.8 ± 0.7       | 159 ± 16 | ND                |
| NIPUA-H20    | HDDA             | 1130           | 6.0 ± 1.0       | 59 ± 12  | 6.6 ± 0.3       | 144 ± 5  | ND                |
| NIPUA-H30    | HDDA             | 870            | 2.8 ± 0.2       | 46 ± 2   | 11.4 ± 1.9      | 90 ± 5   | D                 |
| NIPUA-H40    | HDDA             | 720            | 1.7 ± 0.3       | 17 ± 1   | 6.4 ± 1.3       | 70 ± 1   | ND                |
| NIPUA-H50    | HDDA             | 630            | 1.4 ± 1.0       | 17 ± 2   | 2.3 ± 0.3       | 61 ± 7   | ND                |
| NIPUA-B20    | BHECA            | 2000           | 1.5 ± 0.7       | 93 ± 2   | 2.2 ± 0.5       | 221 ± 15 | ND                |
| NIPUA-U20    | UDMA             | 1780           | 5.0 ± 0.3       | 120 ± 5  | 5.7 ± 0.3       | 175 ± 8  | ND                |

<sup>1</sup> Average molecular weight between two acrylate functions.

<sup>2</sup> ND = No or little degradation, D = Degradation, D+ = Significant degradation.

### Thermal properties

The thermal stability of coatings was assessed by TGA under nitrogen atmosphere. The temperatures at 5% of weight loss ( $T_{5\%}$ ) are listed in Table 3, they ranged from 255 to 318°C showing a good thermal stability. Figures 4 and 5 display typical TGA curves and their first derivative curves giving  $T_{\text{max}}$  (temperature at maximum degradation rate) of each step. As for conventional polyurethanes,<sup>8,43</sup>

thermal degradation of NIPUA coatings occurs in two-steps, with degradation of the hard segment parts (HS,  $T_{max} \approx 320 \text{ }^\circ\text{C}$ ) followed by the PTMO soft segment parts (SS,  $T_{max} \approx 410 \text{ }^\circ\text{C}$ ). The A-C6-2000 prepolymer revealed similar two-step degradation profiles.

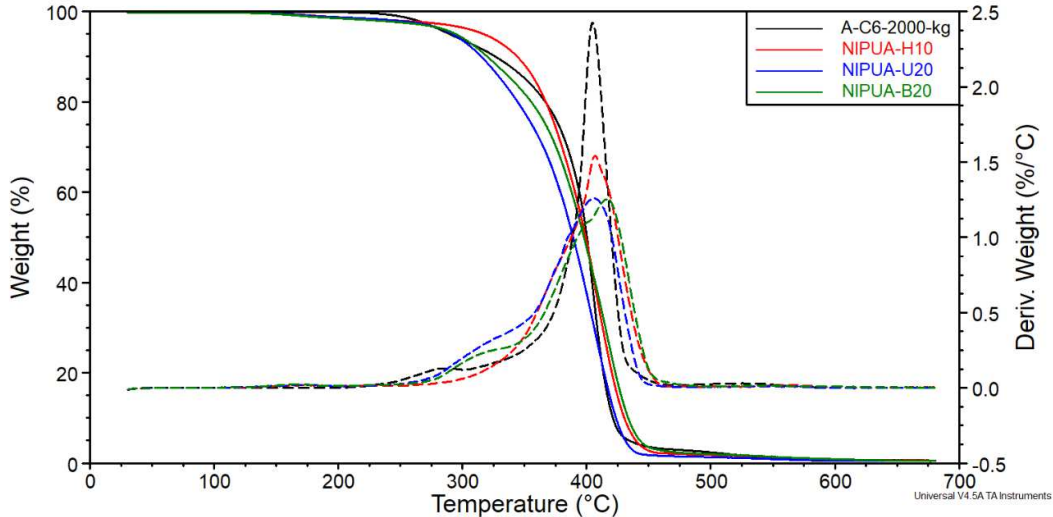


Figure 4: TGA curves (solid curves) and their first derivatives (dashed curves) of A-C6-2000, NIPUA-H10, NIPUA-U20 and NIPUA-B20.

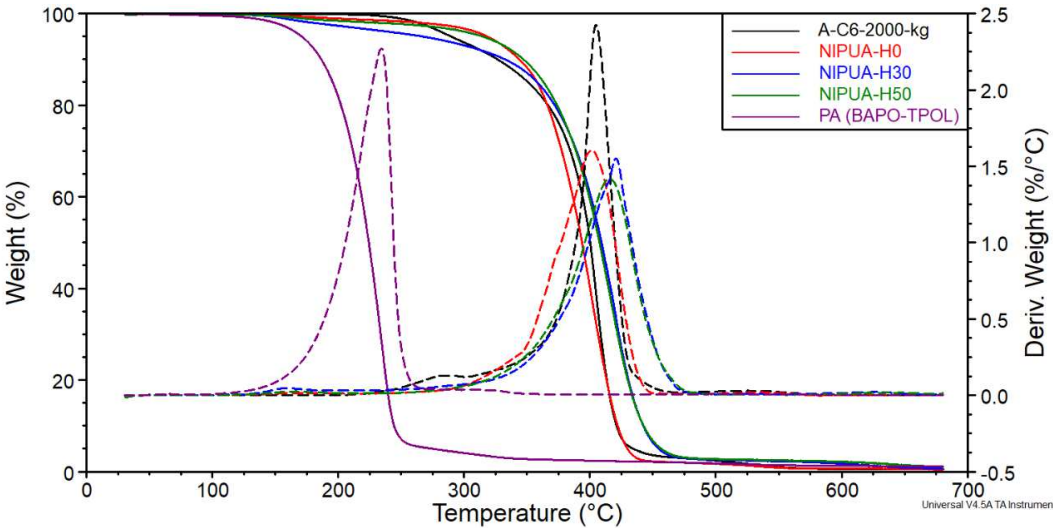


Figure 5: TGA curves (solid curves) and their first derivatives (dashed curves) of A-C6-2000, NIPUA-H10, NIPUA-H30 and NIPUA-H50 as well as BAPO-TPOL photo-initiator.

Table 3: Thermal properties of NIPUA coatings.

| Coating code | Reactive diluent | C <sub>C=C</sub> (meq/g) | T <sub>5%</sub> <sup>1</sup> (°C) | T <sub>c</sub> <sup>2</sup> (°C) | ΔH <sub>c</sub> <sup>2</sup> (J/g) | T <sub>m</sub> <sup>2</sup> (°C) | ΔH <sub>m</sub> <sup>2</sup> (J/g) | T <sub>#</sub> <sup>3</sup> (°C) | ΔH <sub>#</sub> <sup>3</sup> (J/g) |
|--------------|------------------|--------------------------|-----------------------------------|----------------------------------|------------------------------------|----------------------------------|------------------------------------|----------------------------------|------------------------------------|
| A-C6-2000    | -                | -                        | 289                               | -3                               | 75                                 | 23                               | 77                                 | 189                              | 37                                 |
| NIPUA-H0     | -                | 0.8                      | 318                               | -21                              | 46                                 | 13                               | 47                                 | 187                              | 17                                 |
| NIPUA-H10    | HDDA             | 2.5                      | 316                               | -41*                             | 24*                                | 9                                | 30                                 | 183                              | 26                                 |
| NIPUA-H20    | HDDA             | 4.0                      | 255                               | -41*                             | 2*                                 | 10                               | 2                                  | 172                              | 71                                 |
| NIPUA-H30    | HDDA             | 5.2                      | 265                               | -40*                             | 1*                                 | 9                                | 2                                  | 163                              | 100                                |
| NIPUA-H40    | HDDA             | 6.3                      | 260                               | -                                | -                                  | -                                | -                                  | 169                              | 76                                 |
| NIPUA-H50    | HDDA             | 7.2                      | 314                               | -                                | -                                  | -                                | -                                  | 176                              | 48                                 |
| NIPUA-B20    | BHECA            | 2.5                      | 294                               | -43*                             | 21*                                | 9                                | 29                                 | 182                              | 31                                 |
| NIPUA-U20    | UDMA             | 2.3                      | 291                               | -34*                             | 13*                                | 7                                | 18                                 | 184                              | 56                                 |

<sup>1</sup> Determined by TGA.

<sup>2</sup> Determined by DSC. T<sub>g</sub> was not observed for any material.

<sup>3</sup> Exothermic phenomena determined by DSC

\* Cold crystallization

For coatings based on the non-urethane HDDA diluent (NIPUA-H10 to NIPUA-H50) as well as those without any reactive diluent (NIPUA-H0), the degradations of the hard and soft segments were overlapped (Figure 4 and 5) suggesting that the crosslinking reaction increases T<sub>max</sub> of the HS part.<sup>44</sup> However, T<sub>5%</sub> decreased from 318 to 260°C with the increase of HDDA content within the coating up to 40 wt.%, and increased again to 314°C for 50 wt.% of HDDA. This evolution could be ascribed to the presence of volatile compound such as residual solvent within these materials and is in quite consistency with the values of extractable percentages ( $\tau_{Ex}$ , Table 3, thick films). Coatings based on reactive diluents bearing urethane groups (BHECA and UDMA) exhibited intermediate T<sub>5%</sub> (294 and 291°C, respectively) and T<sub>max</sub> values for the urethane degradation step (Figure 4).

The thermal properties of the NIPUA coatings were measured by DSC. Typical DSC curves are presented in Figure 6. The thermal parameters are displayed in Table 3. T<sub>m</sub> value of PTMO soft segments decreased from 23°C (within A-C6-2000 prepolymer) to 13°C after photocrosslinking (NIPUA-H0). This value fell to around 10°C when HDDA is used at 10 to 30 wt.% and was not observed at 40 and 50 wt.%. ΔH<sub>m</sub> values also decreased from 47 to 0 J/g with the increase of HDDA content from 0 to 50 %, i.e. decrease of M<sub>A-A</sub> from 5650 to 630 g/mol. This result suggests that the crystallinity of the soft segments was reduced by increasing the cross-linking density, which is consistent with the literature data.<sup>25</sup> T<sub>c</sub> values decreased from -3 to -21°C after crosslinking of A-C6-2000 in the absence of reactive diluents (NIPUA-H0). In the presence of reactive diluents at 10 to 30 wt.%, cold crystallization was observed at around -40°C, which disappeared for a composition of 40 and 50 wt.%. ΔH<sub>c</sub> values decreased with crosslinking and the content of reactive diluent. NIPUA-U20 and NIPUA-B20 coatings exhibited T<sub>m</sub> values of 7 and 9°C with ΔH<sub>m</sub> values of 18 and 29 J/g, respectively. T<sub>c</sub> values were of -34 and -43°C with ΔH<sub>c</sub> values of 13 and 21 J/g, respectively. They have very close properties

than NIPUA-H10 because of their quite similar crosslinking density ( $M_{A-A}$  around 1800 g/mol). In addition, the glass transition temperatures of the soft segments were not observed at the screened temperature range ( $T > -60$  °C). The literature value of  $T_g$  for PTMO2000 is  $-84$  °C.<sup>45</sup> Increasing the cross-linking density with reactive diluents do not increase the value of  $T_g$  above  $-65$  °C, which suggests nanophase segregation implying limited HS - SS interactions.<sup>46</sup>

The DSC analysis also showed an exothermic phenomenon around  $170$  °C for all the films with enthalpies ranging from 17 to 100 J/g (Table 3 and Figure 6). This phenomenon may also explain why the onset of degradation is observed before  $200$  °C on the TGA curves. The residual photoinitiator underwent degradation around  $170$  °C (Figure 5), which could lead to a restructuring/degradation of the network via chain breaks, restoring mobility to the soft segments, which could then reorganize.<sup>7</sup> This would explain the reappearance of the melting peak of the soft segments at the next heating (Figure 6).

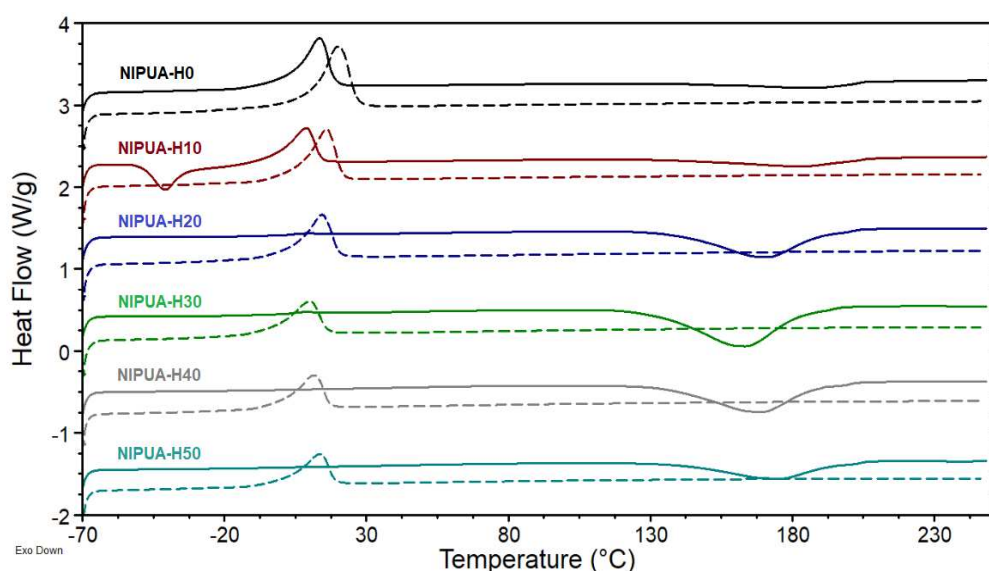


Figure 6: DSC curves of NIPUA-H0 to NIPUA-H50 coatings. 1<sup>st</sup> heating (solid curves) and 2<sup>nd</sup> heating (dashed curves).

## Mechanical properties

The uniaxial tensile tests have been performed on thick NIPUAs films to assess their mechanical properties. The results are displayed in Table 4. Typical stress/strain curves are presented in Figures 7 and 8. A large spectrum of properties was obtained by varying the amount and nature of the reactive diluent. Young modulus (strength properties) varied from 2.69 to 10 MPa, breaking stress ( $\sigma_r$ , strength properties) from 3.62 to 11.2 MPa, and elongation at break ( $\epsilon_r$ , elasticity) from 64 to 470%.

The influence of the cross-linking density on the mechanical properties has been studied on coatings containing HDDA reactive diluent (NIPUA-H series). HDDA content has a considerable impact on the elastic behavior of the material. Indeed, elongation at break drops dramatically (from 470 to 140%) as soon as 10 wt.% of HDDA is added. Conversely, stiffness increases more linearly with the percentage of HDDA content, as shown by Young's modulus values (Table 4).

Table 4: Mechanical properties of NIPUA coatings.

| Coating code | $M_{c(A-A)}^1$<br>(g/mol) | $E^2$<br>(MPa)  | $\sigma_r^2$<br>(MPa) | $\epsilon_r^2$<br>(%) | $C_{C=C}^3$<br>(meq/g) |
|--------------|---------------------------|-----------------|-----------------------|-----------------------|------------------------|
| NIPUA-H0     | 5650                      | $2.69 \pm 0.32$ | $11.8 \pm 3.5$        | $470 \pm 37$          | 0.8                    |
| NIPUA-H10    | 1780                      | $4.06 \pm 0.37$ | $3.62 \pm 1.01$       | $140 \pm 20$          | 2.5                    |
| NIPUA-H20    | 1130                      | $5.78 \pm 0.85$ | $5.34 \pm 2.01$       | $110 \pm 19$          | 4.0                    |
| NIPUA-H30    | 870                       | $10.0 \pm 0.6$  | $5.88 \pm 1.15$       | $66 \pm 8$            | 5.2                    |
| NIPUA-H40    | 720                       | $17.0 \pm 0.7$  | $7.59 \pm 0.93$       | $64 \pm 5$            | 6.3                    |
| NIPUA-H50    | 630                       | $25.5 \pm 0.7$  | $8.43 \pm 0.93$       | $56 \pm 4$            | 7.2                    |
| NIPUA-U20    | 2000                      | $5.80 \pm 0.51$ | $4.51 \pm 1.20$       | $140 \pm 22$          | 2.3                    |
| NIPUA-B20    | 1780                      | $4.21 \pm 0.49$ | $5.54 \pm 1.04$       | $210 \pm 16$          | 2.3                    |

<sup>1</sup> Average molecular weight between two acrylate functions.

<sup>2</sup> E = Young modulus;  $\sigma_r$  = breaking stress;  $\epsilon_r$  = elongation at break.

<sup>3</sup> Double bond concentration in the A-OI oligomer.

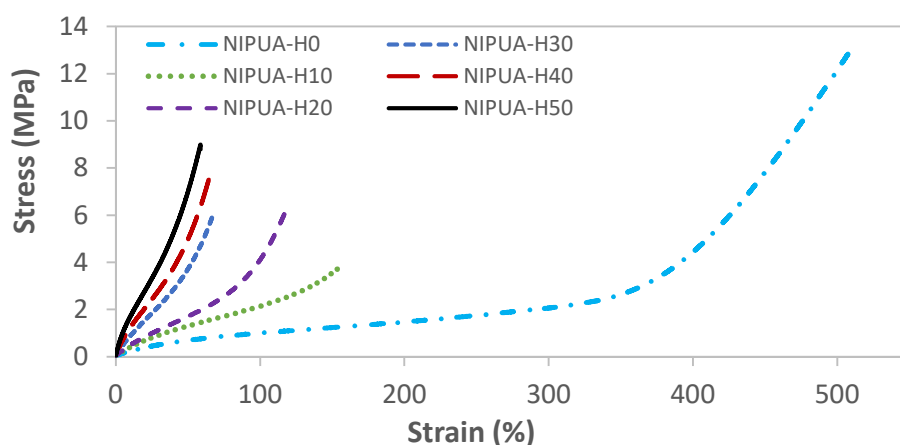


Figure 7: Typical stress/strain curves of the films based on HDDA.

In the case of NIPUA-H0, the high elasticity properties come from the length of the A-OI oligomer ( $M_c = 5650$  g/mol). Above 400% elongation, the high stress at break could result from a crystallization phenomenon induced by the axial deformation, bringing the polymer chains physically closer together and ordering them in relation to each other and thus promoting their interactions.<sup>47</sup> With the introduction of HDDA, the higher cross-linking density generate additional acrylate/soft segment interactions, which could hinder crystallization. This could explain the significant drop in mechanical strength ( $\sigma_r$ ) from approximately 12 to 5 MPa. When the wt.% of HDDA is increased from 10 to 50%,  $\sigma_r$  increases with the cross-linking density as expected.<sup>7</sup>

Properties provided by each type of reactive diluent were compared at the same molar fraction ( $C_{C=C} = 2.3 - 2.5$  meq/g, Table 4). The use of urethane reactive diluent (at 20 wt.%) slightly increases the

overall mechanical properties of the materials (Figure 8). These improvements could be the result of the additional interaction provided by the H-bonds formed by the urethanes with the other compounds in the NIPUAs coatings.<sup>15</sup> The branched structure of UDMA could promote miscibility between HS/SS phases while the symmetrical and linear structure of BHECA could promote phase segregation, which explain their different behavior in terms of elasticity ( $\epsilon_r = 140$  and  $210$  %, respectively).

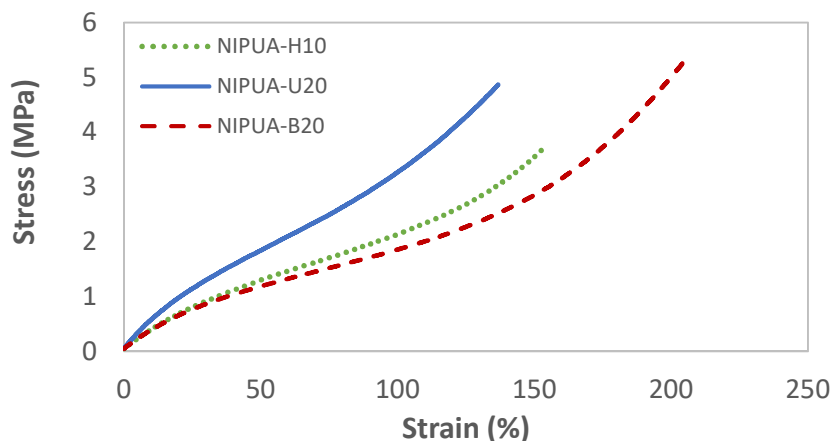


Figure 8: Typical stress/strain curves of films based on various reactive diluents at same hard segment content.

## CONCLUSIONS

A NIPU oligomer with acrylate chain-ends (A-OI) was prepared by transurethane polycondensation reaction of an excess of PTMO2000 with hexamethylene dicarbamate, followed by reaction with acryloyl chloride. Eight NIPU acrylate coatings (NIPUAs) were prepared by photocrosslinking A-OI in formulation with three reactive diluents under a high-intensity UV system. The reactive diluent content and chemical structures had a significant impact on the thermal and mechanical properties of NIPUAs coatings. The obtained properties were in consistency with those of the flexible PUs currently developed on the market ( $T_{5\%} > 255^\circ\text{C}$ ;  $E = 2.69 - 25.5$  MPa,  $\sigma_r = 3.62-11.8$  MPa,  $\epsilon_r = 56 - 470$  %). **Finally, this work evidences the possibility to prepare polyurethane acrylate formulations without using isocyanates. In addition, the advantage of the developed system is that we can tune the length and chemical structure of the acrylate oligomer and reactive diluent as well as the crosslinking density, which offers us a wide range of possible properties.**

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## Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical and time limitations.

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