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From hydroxyurethane methacrylates to hybrid non-isocyanate polyurethanes (HNIPU)

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Keywords

Cyclic carbonate; hydroxyurethane; methacrylate; radical polymerization; thermosets

Abstract

New hybrid PHU networks were quantitatively synthesized by radical polymerization of new HydroxyUrethane MethAcrylate (HUMA) prepolymers. These HUMA were synthesized in several steps. Firstly, bis cyclic carbonate PPO (PPOBC-380) was reacted with two different diamines (EDR-148 and EDA) in excess. Then, these end-functionalized hydroxyurethane prepolymers were converted into end-functionalized hydroxyl prepolymers by ring opening of ethylene carbonate. Finally, a methacrylate function was grafted to the hydroxyl functions. All these steps were performed at room temperature. These prepolymers were thermally either homopolymerized or copolymerized using benzylmethacrylate or poly(ethylene oxide) bisphenol A dimethacrylate as comonomers, leading to new hybrid non-isocyanate polyurethane networks with various properties.

Introduction

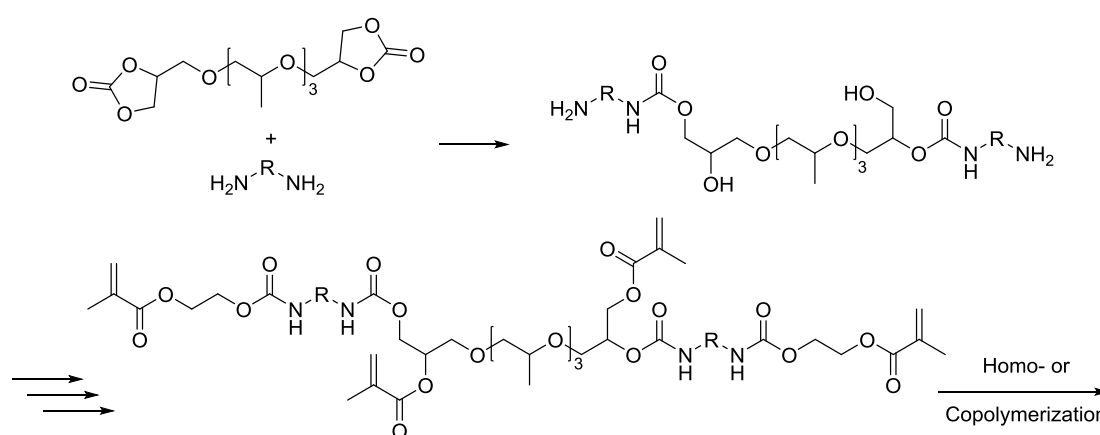
Polyurethane chemistry is well-known since this class of polymers is encountered in many applications such as adhesives, foams, binders, elastomers and coatings ...¹ The synthesis of polyurethanes requires hydroxyl and isocyanate functions to yield urethane groups. However,

recently emerged concerns about the impact of isocyanates on health and environment.² Therefore, it became highly desirable for industry to avoid isocyanate monomers in the synthesis of polyurethanes. Research on Non-isocyanate polyurethanes (NIPU) recently gained increasing interest in both academic and industry communities.^{3–10} Furthermore, the aminolysis reaction of cyclic carbonates emerged recently as one of the most practical and promising routes for the synthesis of NIPUs. These resulting polymers are called PolyHydroxyUrethanes (PHU) due to the presence of primary and secondary hydroxyl groups near the urethane function.^{11–14} Nonetheless, the reactivity of the aminolysis reaction is lower than the corresponding reaction between hydroxyl groups and isocyanates. To overcome this issue, the synthesis of reactive PHU prepolymers has become a promising route. In a first step, end-functionalized PHU oligomers are obtained by reaction between cyclic carbonates with diamines or aminoalcohols. Thus, in a second step, hybrid-PHUs can be obtained by copolymerization or cross-linking thanks to reactions between reactive PHU oligomers and various functional groups, such as epoxy, acrylic or maleimide monomers.^{15–17}

Polyurethane acrylates are currently widely used for coating applications and are notably obtained by UV-light processes. They exhibit excellent mechanical and chemical properties such as high abrasion resistance, toughness or tear strength.^{18–22} Moreover, thanks to various reactive diluents, their properties can be easily adjusted depending on the desired requests. Furthermore, the micro-phase separation of the urethane segments, mainly governed by the soft segment, enables the control of the mechanical properties of the thermosets.²³ Additionally, polyurethane methacrylates were also developed in order to obtain high glass transition temperatures and to improve the stability of the prepolymers.²⁴ Polyurethane methacrylates are major curing agents providing solvent-resistance, mechanical strength and UV or thermal curing ability.^{22,25,26}

When moving to NIPU, few literature is provided for Hydroxyurethane methacrylate (HUMA) monomers having only one HU unit. They are synthesized from the ring opening reaction of ethylene carbonate by an amine followed by the grafting of methacrylic moiety. For example, these methacrylate monomers were investigated for their ability to react under UV-light. Consequently, they were used to create coatings either as raw materials or reactive diluents.^{27,28} Furthermore, functional latexes were prepared by emulsion copolymerization of HUMA with methyl methacrylate (MMA) and butyl acrylate (BA).^{29,30} Finally, the same methodology was performed using a diamine *i.e.* obtention of hydroxyurethane dimethacrylate end groups which were copolymerized with methyl acrylate using AIBN to obtain crosslinked polymers consisting of hard polyurethane segments and soft poly(meth)acrylate segments.³¹ To the best of our knowledge, no Hydroxyurethane methacrylates (HUMA) prepolymers were thermally synthesized and used to form hybrid-PHU thermosets.

Therefore, in this work, the study was focused on an innovative approach of synthesis of HUMA prepolymers which were crosslinked under thermal treatment without the use of initiator to yield hybrid-PHUs. The present prepolymers were synthesized by carbonation of a poly(propylene oxide) (PPO) diepoxide providing a dicarbonate. For the ring-opening reaction of cyclic carbonates, two different amines were used: ethylenediamine (EDA) for its short aliphatic chain and (ethylenedioxy)diethylamine (EDR-148) for its longer and more flexible aliphatic chain. The radical homopolymerization and copolymerization of synthesized HU methacrylates with benzyl methacrylate and poly(ethylene oxide) bisphenol A dimethacrylate comonomers were examined (Scheme 1). The thermal and thermo-mechanical properties of these hybrid PHU networks were investigated by TGA, DSC, DMA and gel content analyses.



Scheme 1: General synthetic pathway.

Experimental part

1) Materials

Poly(propylene glycol) diglycidyl ether ($M_n=380$ g/mol) (PPO-DGE-380), tetrabutyl ammonium bromide, 4-dimethylaminopyridine, methacrylic anhydride, ethylene carbonate and benzyl methacrylate were supplied by Sigma-Aldrich and were used without purification. Dimethylformamide (DMF), dichloromethane (DCM) and ethyl acetate (EtOAc) were purchased from VWR Chemicals. Deuterated solvent $CDCl_3$ was obtained from Eurisotop for NMR analyses. Poly(ethylene oxide) bisphenol A dimethacrylate ($M_n \sim 805$ g/mol determined by 1H NMR), ethylenediamine (EDA) and (ethylenedioxy)diethylamine (EDR-148) were respectively supplied by Sartomer, Thermo Fisher and Huntsman.

2) Analytical Methods

NMR analyses: Proton nuclear magnetic resonance (^1H NMR) analyses were performed in deuterated chloroform (CDCl_3) using a Bruker Avance 400 MHz NMR spectrometer at a temperature of 25 °C. NMR samples were prepared as follows: 10 mg of product experiment in around 0.4 mL of CDCl_3 . Spin multiplicity is shown by s = singlet, d = doublet, t = triplet, m = multiplet.

Thermogravimetric analyses (TGA) were performed using a TG 209F1 apparatus (Netzsch) at a heating rate of 10 °C/min. Approximately 10 mg of sample was placed in an platinum crucible and heated from room temperature to 700 °C under nitrogen atmosphere ($60 \text{ mL}\cdot\text{min}^{-1}$).

Differential scanning calorimetry (DSC) analyses were carried out using a NETZSCH DSC200F3 calorimeter. Constant calibration was performed using indium, *n*-octadecane and *n*-octane standards. Nitrogen was used as the purge gas. Approximately 10 mg of sample were placed in perforated aluminum pans and the thermal properties were recorded at $50 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ to observe the glass transition temperature. The T_g values were measured on the second heating ramp to erase the thermal history of the polymer. All the reported temperatures are middle values.

Dynamic Mechanical Analyses (DMA) were carried out on Metravib DMA 25 with Dynatest 6.8 software. Samples were tested according to uniaxial tension mode while heating at a rate of $3 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ from $\approx T_g - 50 \text{ }^\circ\text{C}$ to $T_g + 50 \text{ }^\circ\text{C}$, at a frequency of 1 Hz with a fixed strain of 10^{-5} m. These conditions have been chosen to study the elastic behavior of the materials.

Fourier-Transform Infrared Spectroscopy (FTIR): FTIR spectra were recorded on a Thermo Scientific Nicolet 6700 FTIR apparatus by using OMNIC software from 650 to 4000 cm^{-1} . A drop was applied on top of the ATR modulus and 32 scans were made with a resolution of 4.

Size Exclusion Chromatography (SEC) were carried out using a Polymer Laboratories PL-GPC 50 system with two columns of 300 mm (column PL mixed C $5\mu\text{m}$, $2.102\text{--}2.106 \text{ g/mol}$ at $35 \text{ }^\circ\text{C}$. THF is used as an eluent with a flow of 1.0 mL/min . The internal standard used was toluene and the injection volume was $20 \mu\text{L}$. The detection is done using an interferometric refractometer. The calibration was made using a Varian Poly(methyl methacrylate) range.

Titration of the epoxy equivalent weight by ^1H NMR: The Equivalent Weight (EW) is the amount of product needed for one equivalent of reactive function. It was determined by ^1H NMR using an internal standard (benzophenone). A known weight of product and benzophenone was poured into an NMR tube and $500 \mu\text{L}$ of CDCl_3 were added. It was determined using the Equation 1 by comparing the integral of the protons of the benzophenone and the integral of the reactive function.

$$\text{Equation 1} \quad EW = \frac{\int \text{PhCOPh} * H_{\text{function}}}{\int \text{function} * H_{\text{PhCOPh}}} * \frac{m_{\text{function}}}{m_{\text{PhCOPh}}} * M_{\text{PhCOPh}}$$

\int_{PhCOPh} : integration of the benzophenone protons; \int_{function} : integration of the protons of the reactive function; H_{function} : number of protons of the reactive function; H_{PhCOPh} : number of protons of the benzophenone; m_{function} : weight of the product; m_{PhCOPh} : weight of the benzophenone; M_{PhCOPh} : molecular weight of the benzophenone

Swelling index: Three samples of around 30 mg each were separately put in DCM for 24 h. The swelling index (SI) was calculated using the Equation 2 where m_2 is the mass of the material after swelling in DCM and m_1 is the initial mass of the material.

$$\text{Equation 2} \quad SI = \frac{m_2 - m_1}{m_1} \times 100$$

Gel content: After SI measurements, the three samples were dried in a ventilated oven at 70 °C for 24 h. The gel content (GC) was calculated using the Equation 3, where m_3 is the mass of the material after drying and m_1 is the initial mass of the material.

$$\text{Equation 3} \quad GC = \frac{m_3}{m_1} \times 100$$

3) Synthesis routes

a) Synthesis of poly(propylene oxide) dicarbonate (PPOBC-380)

In a round-bottom flask poly(propylene oxide) diglycidyl ether (PPODGE-380) (1 eq, 200 g) and TBABr (5 mol%) were dissolved in EtOAc (300 mL). The solution was introduced onto a reactor and the atmosphere was replaced with CO₂ (P=15 bar). The solution was heated at 80 °C with continuous stirring for 48 h. Then, the crude mixture was washed several times with water and brine. The pure product PPOBC-380 was obtained as an oil (yield=87%). ¹H NMR (400 MHz, CDCl₃): δ : 1.07–1.18 (m, 7H), 3.30–4.00 (m, 18H), 4.35–4.55 (m, 4H), 4.74–4.86 (m, 2H)

b) Synthesis of amino end-functional hydroxyurethane prepolymers

10 g of PPOBC-380 were used with 5 eq of EDR-148 and 3 eq of EDA by using Equation 4. The ring-opening of cyclic carbonates with amines was carried out without solvent at room temperature and stirred overnight. The amines were not removed and used as reactive diluents. The products were respectively called PPOAM-EDR and PPOAM-EDA for the HUMA prepolymer obtained from EDR and EDA.

$$\text{Equation 4} \quad m_{\text{amine}} = \frac{x \times AHEW}{Eq \times CEW}$$

x: carbonate product weight; AHEW : amine hydrogen equivalent weight; CEW: carbonate equivalent weight; Eq: equivalent of amine.

c) Synthesis of hydroxyl end-functional hydroxyurethane prepolymers

As a typical procedure, PPOAM-EDR (27 g) was dissolved in DCM (200 mL) with ethylene carbonate (1 eq). The reaction was stirred during 24 h. After the complete consumption of ethylene carbonate was confirmed by ^1H NMR, the solvent was removed under vacuum without further purification. The same procedure was used for PPOAM-EDA and the final products were called PPOOH-EDA and PPOOH-EDR.

d) Synthesis hydroxyurethane methacrylates (HUMA)

As a typical procedure, to a solution of PPOOH-EDR (37 g) in DMF (150 mL), 10 eq of methacrylic anhydride and 0.3 eq of DMAP were added at 5 °C. The reaction was allowed to stir during 48 h. The reaction mixture was washed with saturated sodium carbonate solution and DCM until complete removal of the methacrylic anhydride. If required, 10 %wt NaOH solution was used to promote the elimination of the methacrylic anhydride.

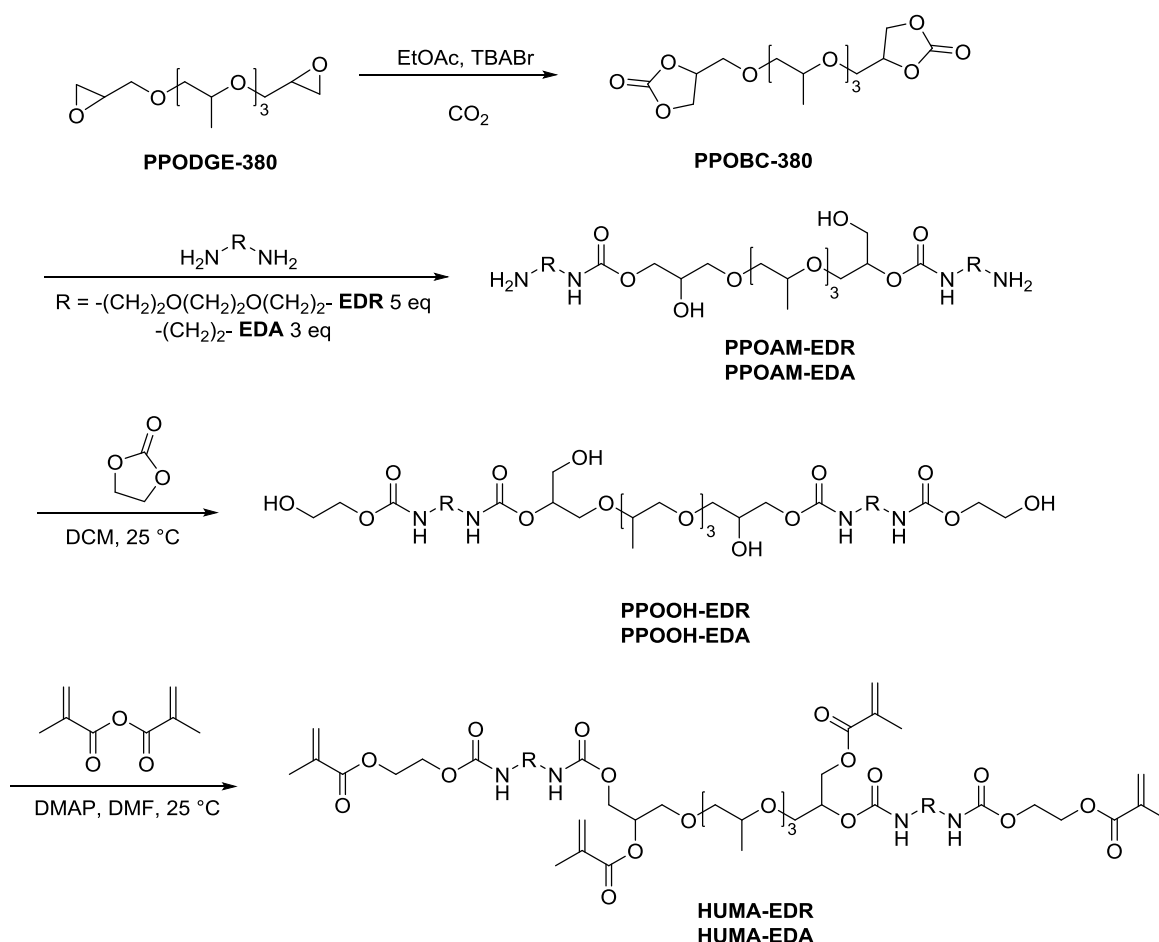
4) Polymerization routes

The polymers (homo- or copolymers) were cured using the following heating rate: 1 h at 80 °C, 1 h at 100 °C, 1 h at 120 °C and 24 h at 150 °C. This procedure was used to avoid the formation of bubbles. The thermosets were copolymerized with 50 mol% of benzylmethacrylate or poly(ethylene oxide) bisphenol A dimethacrylate.

Results and discussion

1) Synthesis and characterization of hydroxyurethane methacrylate (HUMA) prepolymers

The synthesis of HUMA prepolymers is a 4-step reaction presented in Scheme 2.



Scheme 2: Reaction scheme of the synthesis of hydroxyurethane methacrylate (HUMA) prepolymers.

a) Synthesis of poly(propylene oxide) dicarbonate (PPOBC-380)

The initial step consisted in the carbonation of epoxy rings into five-membered cyclic carbonates. The starting material was a poly(propylene oxide) diglycidyl ether (PPODGE-380). The carbonation was carried out in EtOAc in presence of tetrabutylammonium bromide as previously reported to provide the desired dicarbonate PPOBC-380 in quantitative yield.¹⁶ To accurately determine the carbonate functionality *i.e.* the carbonate equivalent weight (CEW), ¹H NMR titration was used with benzophenone as internal reference.

b) Synthesis of amino end-functional hydroxyurethane prepolymers (PPOAM)

The synthesis of amino end-functional hydroxyurethane prepolymers was performed at room temperature in bulk without any catalyst. Two different amines were used: a short aliphatic amine (ethylene diamine *i.e.* EDA) and a more flexible amine containing 3 ethylene oxide units (*i.e.* EDR) to respectively yield PPOAM-EDA and PPOAM-EDR. Indeed, the ring-opening aminolysis of cyclic carbonates is well-known for the synthesis of hydroxyurethanes.³² Thus, an excess of amines was used in presence of PPOBC-380: 5 eq for EDR and 3 eq for EDA as depicted in Scheme 2. Reaction was performed under stirring at room temperature for 16h. The use of amine in excess guaranteed the

functionalization of HUMA prepolymers with amine end groups and make the reaction mixture less viscous. This methodology is well known in the polycondensation chemistry.³³ With lower excess of amine, step growth polymerization can occur and create longer chain polymers. Furthermore, the amine functionality *i.e.* the amine equivalent weight (AHEW) was determined by ¹H NMR titration. The AHEW value of PPOAM-EDR is 190 g.eq⁻¹ whereas it is 661 g.eq⁻¹ for the PPOAM-EDA. These values correspond to the molecular weight obtained by SEC. Indeed, the PPOAM-EDA presents a higher molecular weight (PMMA equivalent) than the PPOAM-EDR (3,200 vs. 2,300 g.mol⁻¹).

The aminolysis of the PPOBC-380 was thoroughly monitored by ¹H NMR. This synthesis step was easily observed by the entire disappearance of the signal of the protons a₁ in α position of the carbonate function at 4.3 ppm to form all the characteristic signals of the hydroxyurethane HU (Figure 1-(a, b, c)). At 4.8 (l₂) and 4.0 ppm (f₂) the protons of the pendant (primary and secondary) hydroxyls and at 4.0 and 3.4 ppm the protons of the carbamate functions can be observed. The triplet localized at 2.8 ppm is a mixture of the free unreacted amine and the amine grafted on the PPOBC-380 (Figure 1 – (c)). As for EDR prepolymer, the same method was followed for the monitoring of the reaction steps. In the spectrum of the PPOAM-EDA, the signals of the free amine (singlet at 2.8 ppm – a) and the amine which has reacted (multiplet at 2.85 ppm – a₂) are not overlapped unlike in the spectrum of the PPOAM-EDR (Figure 2 – (a, b, c)). Consequently, two different aminotelechelic hydroxyurethane products were obtained: PPOAM-EDR and PPOAM-EDA. No removal of the free amines was performed as the residual amines can be used as reactive diluents. Moreover, the free amine function will react during the following steps, as the prepolymers formed, and they will be fully included into the final crosslinked network.

c) Synthesis of hydroxyl end-functional hydroxyurethane prepolymers (PPOOH)

To functionalize these PPOAM with methacrylate, another step was required to obtain hydroxyl end-groups. Thus, the ring-opening reaction of ethylene carbonate by the previously synthesized PPOAM permitted to provide: PPOOH-EDR and PPOOH-EDA with diols end-groups. These reactions were performed at room temperature in DCM during 24 h. Concerning the EDR prepolymer, the triplet from the –CH₂– in α-position of the amine group (a₂ & a) at 2.8 ppm disappeared for the benefit of the protons a₃ and b₃ respectively at 4.3 and 3.9 ppm revealing full conversion into urethanes and formation of the terminal primary hydroxyl (Figure 1 – (c, d)). For the EDA prepolymer, the multiplet at 2.85 ppm and the singlet at 2.8 ppm from the –CH₂– in α-position of the amine group (a₂ & a) disappeared revealing quantitative conversion of the amines into urethanes. Thus, a hydroxyl functionality of 2 was proved for the end groups.

d) Synthesis of HUMA prepolymers

The last step was the methacrylation of PPOH using methacrylic anhydride and DMAP, which is a common way of methacrylation.^{27,28} These reactions were performed at room temperature for 48 h in DMF. An excess of 10 eq of methacrylic anhydride was employed to allow the conversion of every hydroxyl group including the pendant ones. Titration of both HUMA by ^1H NMR to control the methacrylate equivalent weight (MEW), highlighted the conversion of all the hydroxyl groups including the ones from the pendant groups. The signals of the protons in α -position of the hydroxyl groups a_3 , h_3 and n_3 disappeared in the spectrum of the final EDR prepolymer. Moreover, the presence of the methacrylate substituents was exhibited by the appearance of a singlet at 1.8 ppm and multiplets at 5.45 and 5.95 ppm (Figure 1 – (e)). Concerning the EDA prepolymer, the signals of the $-\text{CH}_2-$ in α -position of the hydroxyl groups a_3 , f_3 and l_3 shifted as well. The addition of methacrylate groups was displayed by the presence of a singlet at 1.9 ppm and two multiplets at 5.65 and 6.1 ppm (Figure 2 – (e)). The calculation of the MEW confirmed the oligomerization of the EDA prepolymer. Indeed, MEW value is higher for EDA prepolymer than for the EDR prepolymer (347 g.eq^{-1} for the EDA prepolymer vs. 269 g.eq^{-1} for the EDR prepolymer) which has shortest chains with less pendant hydroxyl groups (see Supporting Information). The calculation of EW involves the methacrylated amine, coming from the free amine and the methacrylated prepolymers. No residual methacrylic anhydride or methacrylic acid were present thanks to the purification performed.

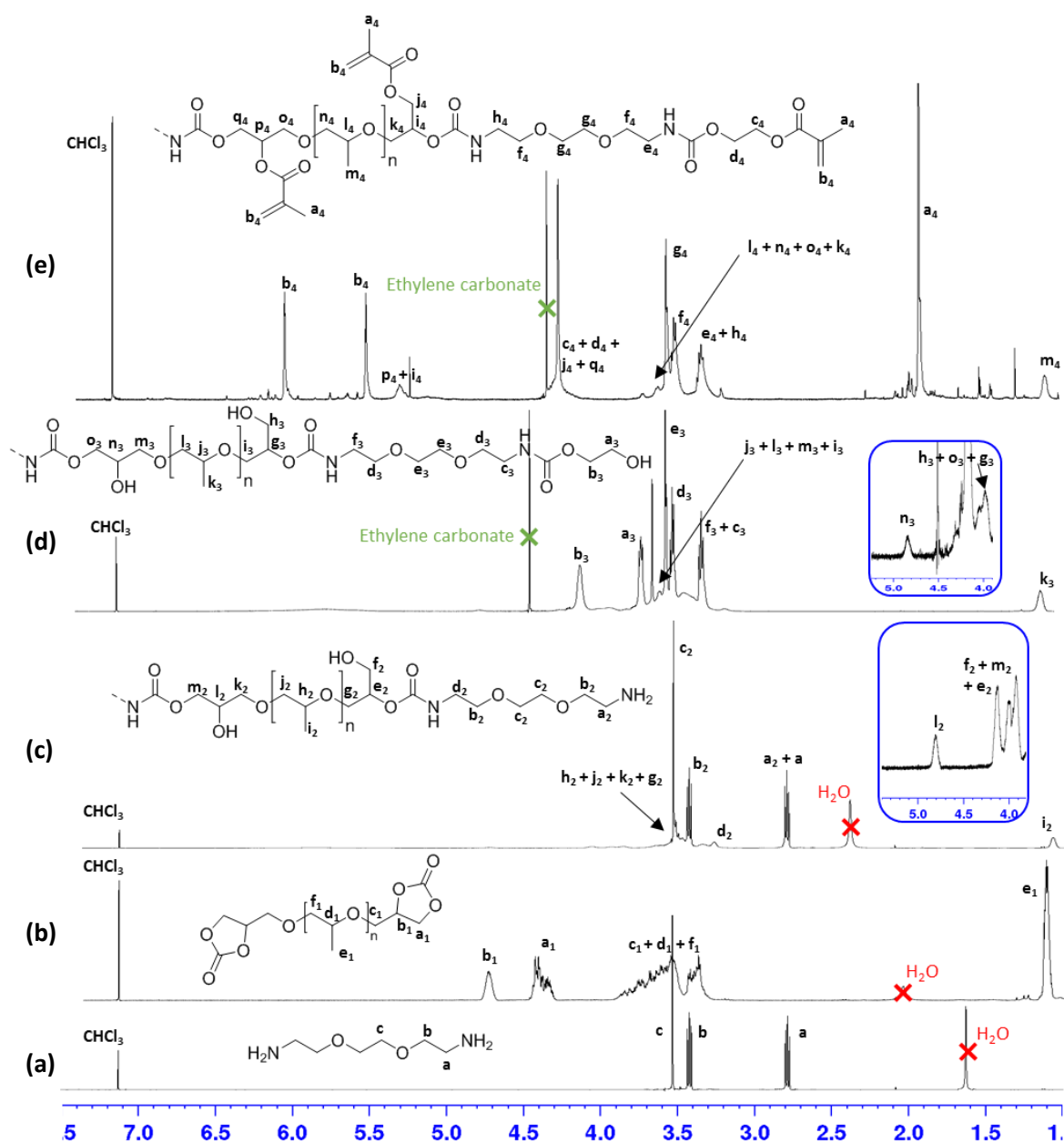


Figure 1: ^1H NMR spectra of the starting reagents: (a) EDR-148; (b) PPOBC-380; the intermediate prepolymers: (c) PPOAM-EDR; (d) PPOOH-EDR and the final methacrylate (e) HUMA-EDR prepolymer.

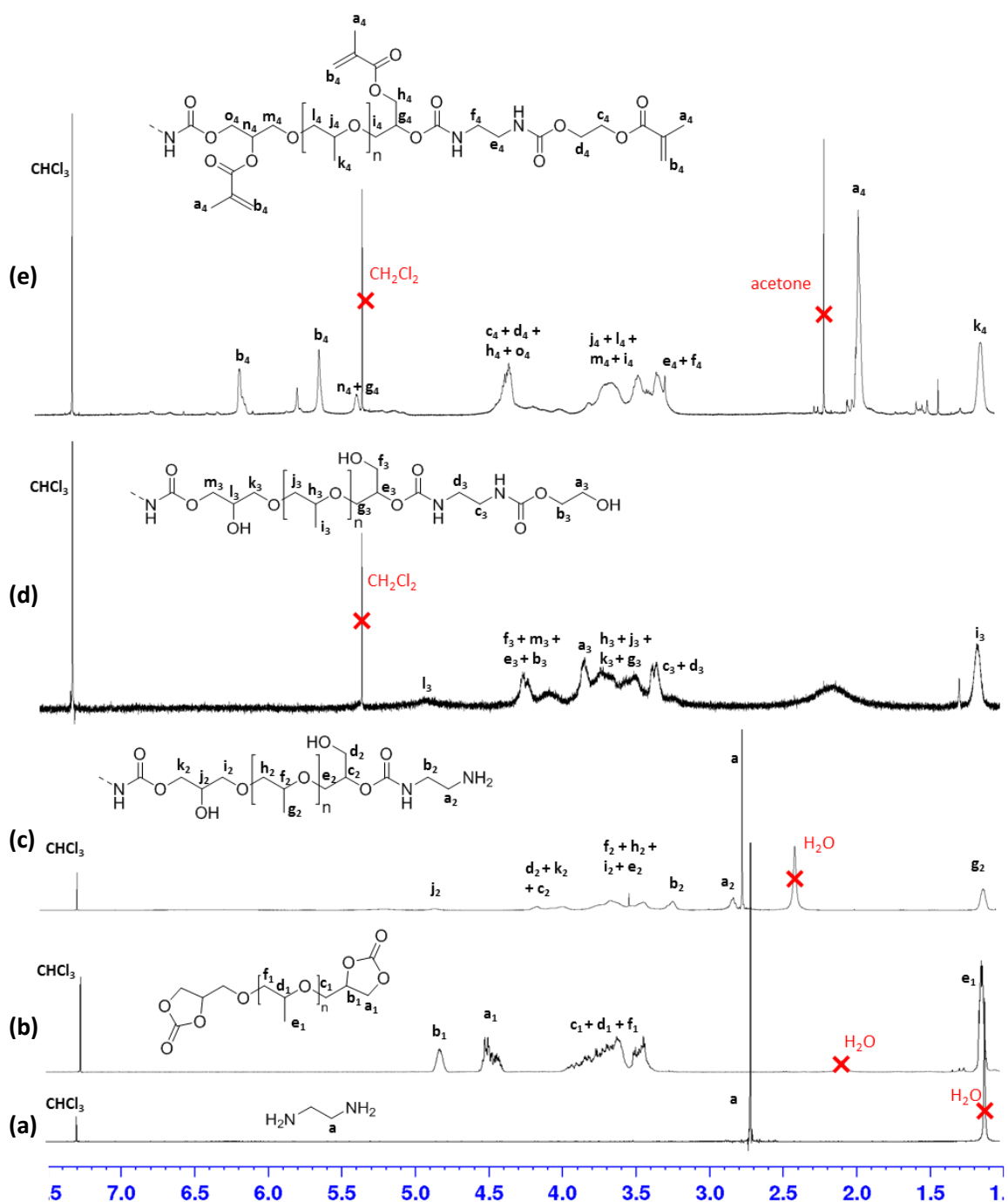


Figure 2: ^1H NMR spectra of the starting reagents: (a) EDA; (b) PPOBC-380; the intermediate prepolymers: (c) PPOAM-EDA; (d) PPOOH-EDA and the final methacrylate (e) HUMA-EDA prepolymer.

2) Synthesis of PHU thermosets

These prepolymers were then progressively crosslinked 1 h at 80 °C, 1 h at 100 °C, 1 h at 120 °C and 24 h at 150 °C to avoid the creation of bubbles. No initiator was required. Indeed, the crosslinking was performed owing to a thermal way exclusively. Different processes were performed for the crosslinking of these prepolymers. The first one is a radical homopolymerization of the HUMA prepolymers, the second one is a radical copolymerization between HUMA prepolymers and

benzylmethacrylate or poly(ethylene oxide) bisphenol A dimethacrylate (Figure 3). The various formulations are depicted in Table 1. The benzyl methacrylate (BM) was chosen for its low functionality and in order to improve both the thermal stability and the rigidity of the final polymers with its high aromatic content. On the contrary, the poly(ethylene oxide) bisphenol A dimethacrylate (PEOBM) has long poly(ethylene oxide) chain which could decrease the glass transition temperature and aromatic rings with a higher degree of functionality.

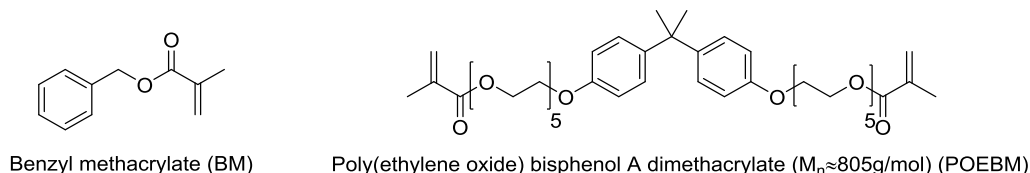


Figure 3: Structure of the benzylmethacrylate BM (left) and poly(ethylene oxide) bisphenol A dimethacrylate PEOBM (right).

Table 1: Formulations used for the thermosets

	HUMA-EDA (% mol)	HUMA-EDR (% mol)	PEOBM (% mol)	BM (% mol)
PHU1	100	--	--	--
PHU2	50	--	--	50
PHU3	50	--	50	--
PHU4	--	100	--	--
PHU5	--	50	--	50
PHU6	--	50	50	--
PEOBPM	--	--	100	--

To determine the conversion of the prepolymers into thermosets, FTIR analyses were performed. As an example with the homopolymerization of the HUMA-EDR prepolymer, the methacrylate function was fully converted. Indeed, the IR band of methacrylate function at 1640 cm^{-1} completely disappeared as highlighted in Figure 4. Furthermore, no enthalpy signal was observed during the first heating ramp of the DSC analyses of PHU4, proving that the methacrylate functions were fully reacted.

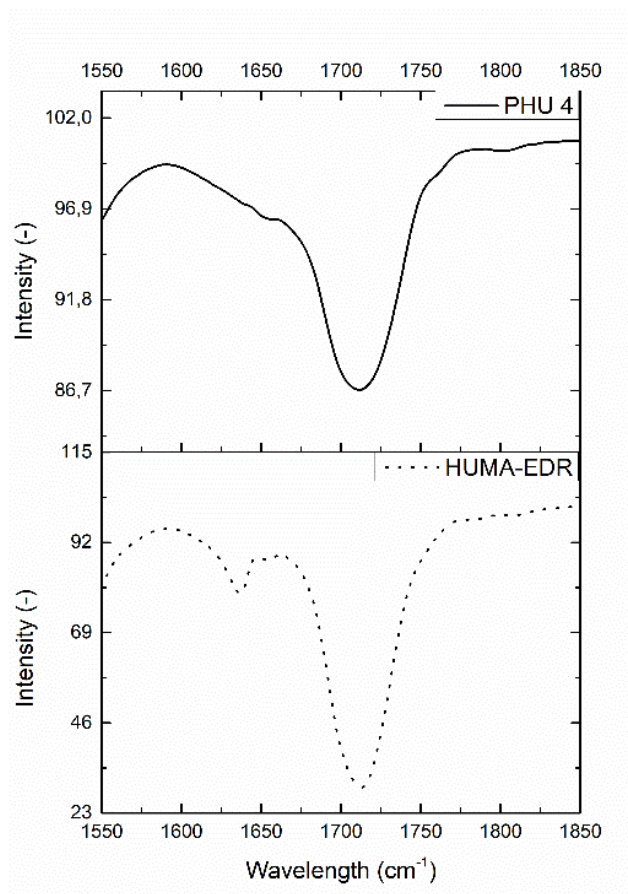


Figure 4: IR spectra of the PHU4 and the HUMA-EDR (magnification between 1550 and 1850 cm^{-1})

3) Characterization and properties of thermosets

After homopolymerization or copolymerization, the physico-chemical and thermo-mechanical properties of the materials were evaluated (Table 2).

Table 2: Thermo-mechanical properties of cured materials.

	GC (%)	SI (%)	T_g (°C)	$T_{d5\%}$ (°C)	Char yield (%)	T_α (°C)	E'_{glassy} (Pa)	E'_{rubbery} (Pa)
PHU1	78	744	43	251	19	72	$1.7 \cdot 10^9$	$6.5 \cdot 10^6$
PHU2	81	382	52	245	15	70	$1.1 \cdot 10^9$	$7.7 \cdot 10^6$
PHU3	84	365	41	259	8	56	$1.8 \cdot 10^9$	$1.2 \cdot 10^7$
PHU4	100	296	69	281	3	109	$1.8 \cdot 10^9$	$3.5 \cdot 10^7$
PHU5	97	136	55	280	22	62	$1.8 \cdot 10^9$	$2.7 \cdot 10^7$
PHU6	97	248	23	301	0	31	$9.1 \cdot 10^8$	$1.9 \cdot 10^7$
PEOBPM	77	342	-7	353	0	1	$9.6 \cdot 10^7$	$6.8 \cdot 10^5$

First, the degree of crosslinking was characterized with the gel content (GC) measurements. The calculation methods were described in the Experimental Section. Gel content corresponds to the residual mass of materials after immersion in DCM and drying. With values above 97 %, EDR-based PHUs are totally crosslinked. It means that no free species remain trapped in the network. The EDA-based PHUs present lower GC values. This could be due to the presence of non-crosslinked oligomer chains. However, no enthalpies were observed during the heating ramp in DSC analyses meaning that the curing is fully achieved. The swelling index gives information on the crosslinking density. Indeed, high values correspond to a high penetration of solvent. The HUMA-EDA prepolymer has a lower mass than the HUMA-EDR prepolymer because of the higher excess used for the synthesis of the PPOAM-EDR prepolymer. Thus, for the EDA-based materials, the highest SI is for the PHU1. Indeed, they were composed of long chains with large spaces between crosslinking nodes and demonstrated the highest value of swelling index. The use of benzylmethacrylate, for the synthesis of PHU2, brings the crosslinking nodes closer whereas the use of BPA dimethacrylate, for the synthesis of PHU3, creates more crosslinking nodes and avoid the penetration of the solvent. The conclusions are the same for the EDR-based materials. As expected, the EDA-based materials exhibit higher values than the EDR-based materials because of the larger distance between the nodes.

The thermal stability of the materials were evaluated by TGA. The thermal stability of those materials was measured between room temperature and 700°C and results are shown in Figure 5. All the materials present 5 % degradation temperature values above 250 °C. The copolymerization with benzylmethacrylate (PHU2, PHU5) or poly(ethylene oxide) bisphenol A dimethacrylate (PHU3, PHU6) did not increase the thermal stability. However it had a great impact on the char yield. The PHU1 exhibited 19 % of char yield compared to 3 % for the PHU4. This difference comes from the presence of PEO chain from the EDR-148 which reduces thermal stability.^{34,35} When the copolymerization was performed with benzylmethacrylate (PHU2 and PHU5), the char yield was improved thanks to the presence of aromatic rings in the network. On the contrary, the use of poly(ethylene oxide) bisphenol A dimethacrylate (PHU3 and PHU6) conferred lower thermal stability due to PEO chain.

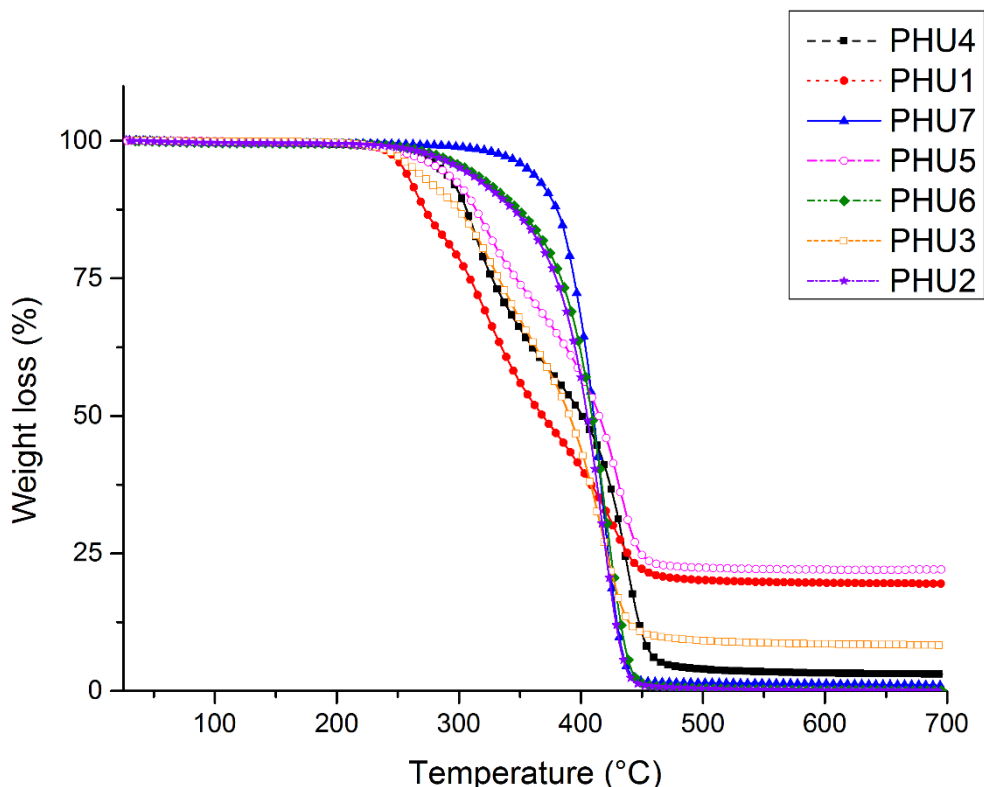
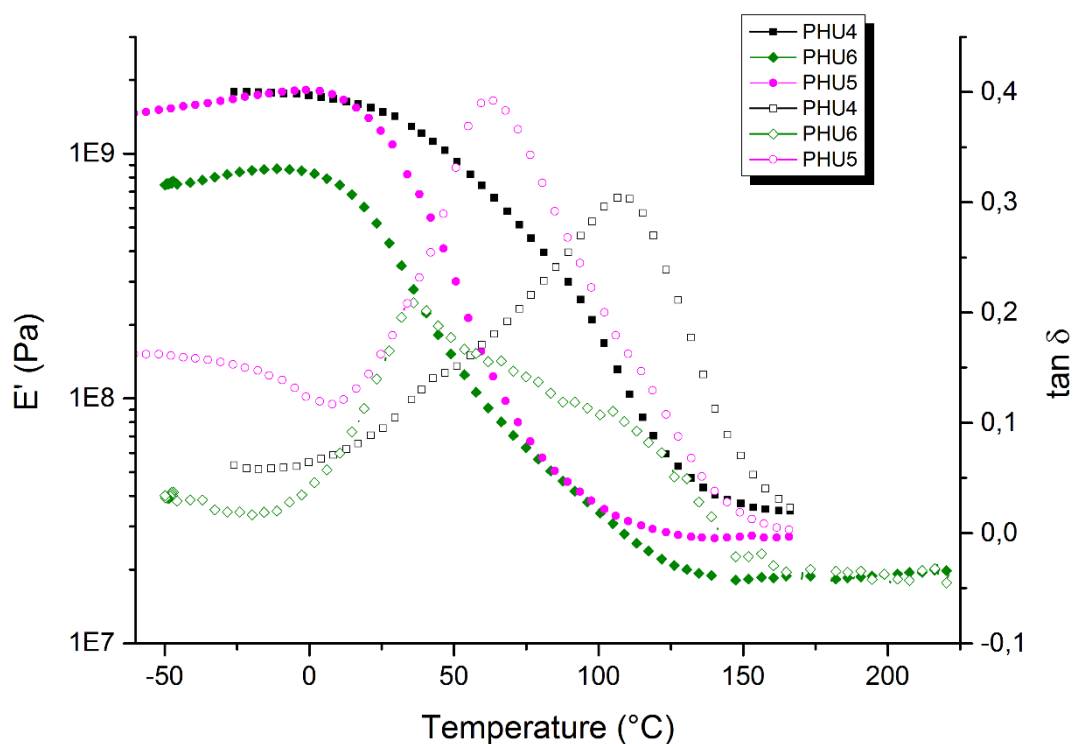


Figure 5: TGA curves

Then, the glass transition temperatures were evaluated at a 50 °C/min heating rate. Indeed, lower heating rates did not allow to observe any glass transition temperature, which could be due to the heterogeneity of the structure of these hybrid materials. Higher glass transition temperatures were obtained for the EDR-based materials. Indeed, as explained previously, the HUMA-EDR, with shorter chain length, tend to increase T_g value. This is particularly due to the high NH/carbonate ratio during synthesis of end-functionalized prepolymers. Indeed, PHU4 exhibit a higher T_g than PHU1. The copolymerization with benzylmethacrylate (PHU2 and PHU5) presents different effects. Indeed, the presence of aromatic groups could increase T_g by π -stacking interactions, but could also act as a bulky group which favors chains mobility and decrease T_g value. π -stacking interactions are less favored in the case of EDA-based materials because of the longer chain which drive away the benzyl moieties. However, when the copolymers with poly(ethylene oxide) bisphenol A dimethacrylate (PHU3 and PHU6) exhibited lower T_g values that the corresponding homopolymers (PHU1 and PHU4). Indeed, the high flexibility of POE chain lowers the T_g values. The glass transition temperature value of POEBPM is -7 °C. Furthermore, PHU6 is more affected because for the formulation of this material, more amount of PEOBM is needed compared to PHU3 (316 mg for PHU3 vs. 405 mg for PHU6).

Thermo-mechanical properties measured with DMA showed the same trend and confirmed those thermal analyses (Figure 6). The alpha transition temperature measured on the top of the tangent delta curve followed the same trend than glass transition temperature values. Similarly, the Young moduli measured in the glassy domain were in the same range (around 1.10^9 Pa) demonstrating the good mechanical properties of the materials. The values of Young moduli in the rubbery domain also followed the same trend but PHU3 and PHU4 presented the highest values highlighting their higher rigidity. Furthermore, the EDR-based materials were more rigid than the EDA-based materials thanks to the shorter chain lengths of the HUMA prepolymers. Furthermore, the DMA analyses highlighted the heterogeneity of these materials with the high width of the $\tan \delta$ curves.



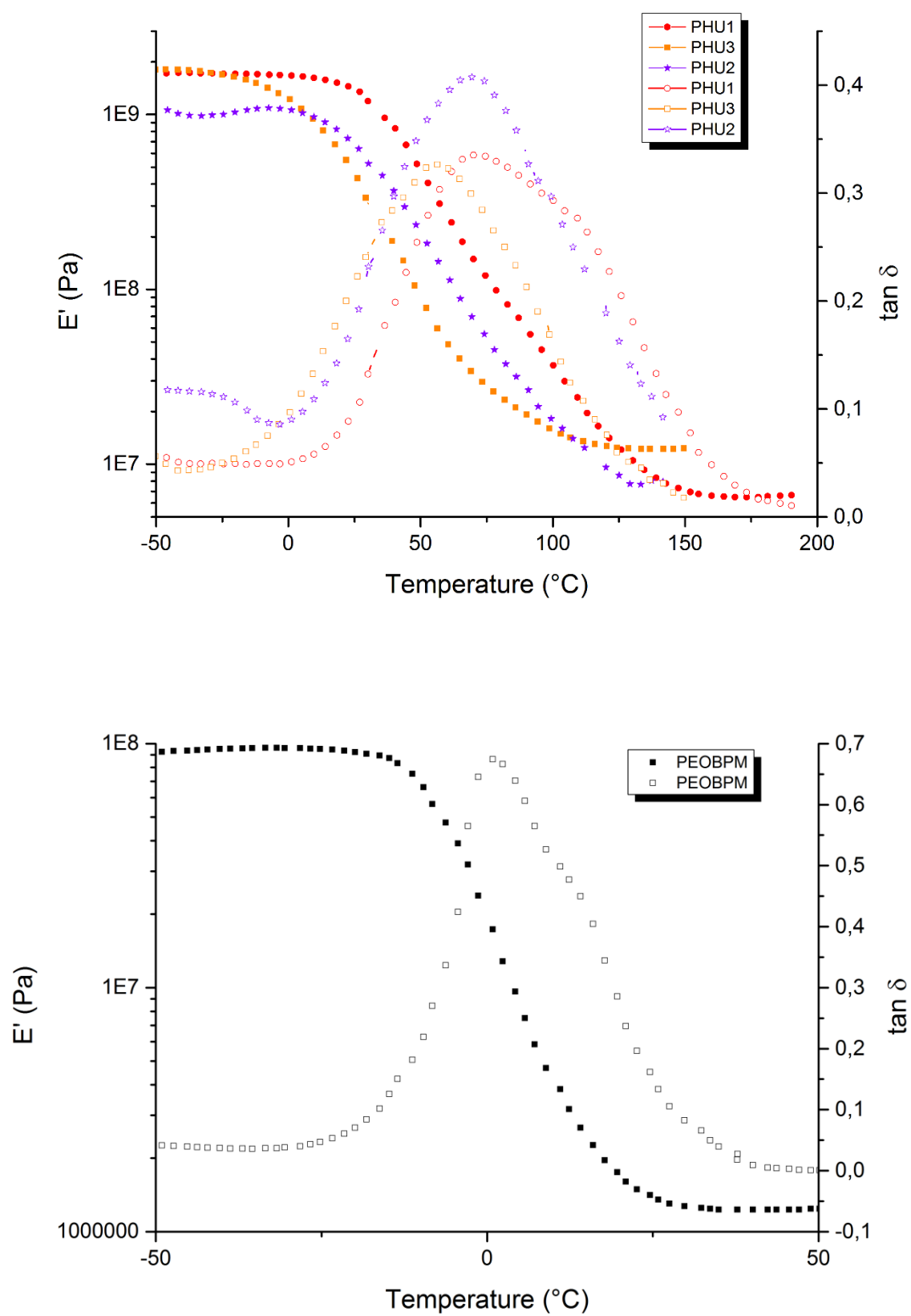


Figure 6: E' and $\tan \delta$ of DMA curves of the cured materials.

Conclusion

In this paper, we synthesized for the first time two new hydroxyurethane methacrylate (HUMA) prepolymers. These both HUMA were synthesized by aminolysis of bis cyclic carbonate PPO with different amines (EDA and EDR-148) followed by methacrylation. These HUMA interestingly present hydroxyurethane groups obtained without isocyanate and several reactive methacrylic functions available for further radical polymerization. These HUMA were then thermally homo- and copolymerized with different ratios of benzylmethacrylate and poly(ethylene oxide) bisphenol A dimethacrylate. These thermosets exhibited glass transition temperatures between 30 and 110 °C. The copolymerization with benzylmethacrylate yielded materials with higher rigidity and thermal resistance. Whereas POEBM allowed to reduce T_g values and improved flexibility of materials. In conclusion, HU methacrylate (HUMA) prepolymers were synthesized and allow to obtain quantitatively cross-linked hydroxyurethane networks with good thermo-mechanical properties.

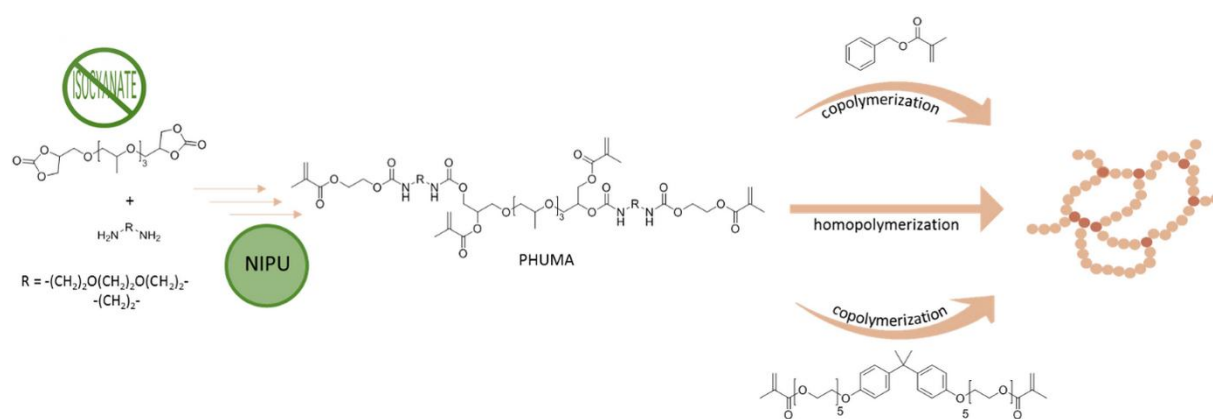
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Graphical Abstract



From Hydroxyurethane methacrylates to hybrid non-isocyanate polyurethanes (HNIPU)

Supporting Information

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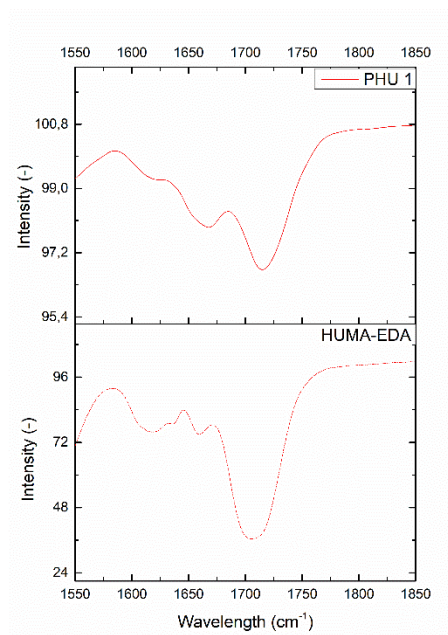
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I. Equivalent weight

Reactants	CEW ^a (g.eq ⁻¹)	AHEW ^a (g.eq ⁻¹)	MEW ^a (g.eq ⁻¹)
PPOBC-380	190	-	-
PPOAM-EDR	-	190	-
PPOAM-EDA	-	661	-
HUMA-EDR	-	-	269
HUMA-EDA	-	-	347

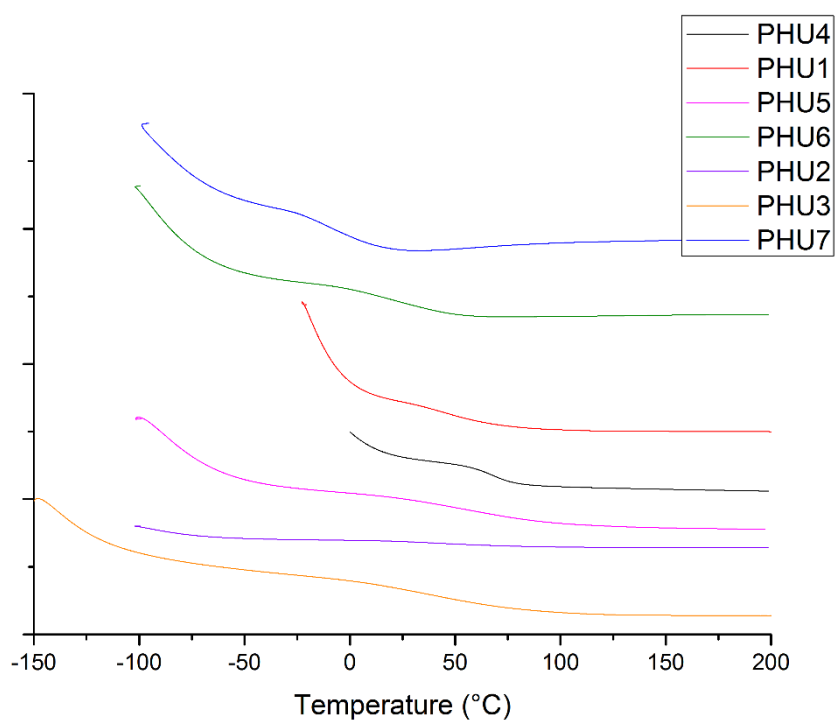
^aCEW, AHEW and MEW were determined by ¹H NMR using benzophenone as internal reference.

II. FTIR analyses

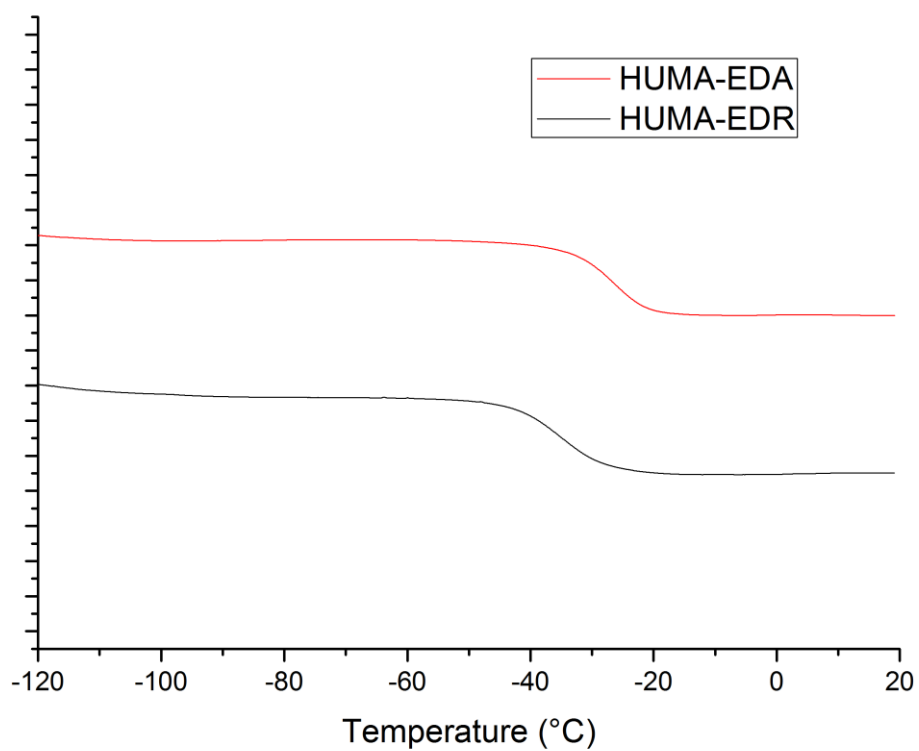


III. DSC analyses

1. Crosslinked materials

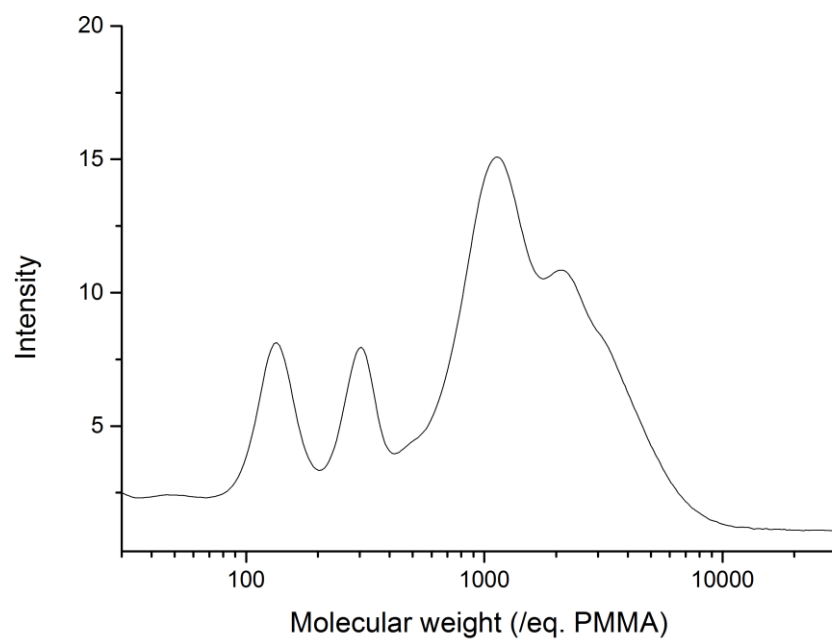


2. HUMA prepolymers



IV. SEC analyses

1. HUMA-EDA



2. HUMA-EDR

