Macromolecules

Ultrahigh T_g Epoxy Thermosets Based on Insertion Polynorbornenes

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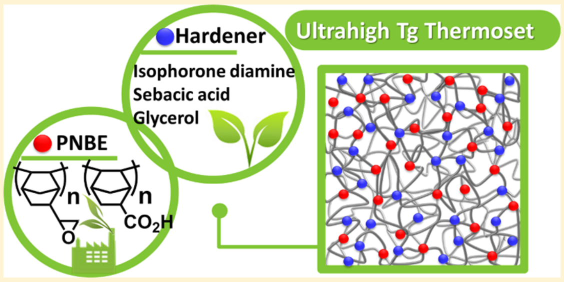
Supporting Information

ABSTRACT: Thermosetting materials (thermosets) are widely used organic materials derived from 3D-network forming monomers. Achieving high glass transition temperature (T_g) thermosets is often a challenging task due to the complexity of designing efficiently and cheaply monomers which are rigid enough to prevent molecular motions within the thermoset. We report here a very simple route to prepare epoxy thermosets with T_g as high as 350 °C, based on insertion polynorbornenes. The epoxy monomer (PNBE(epoxy)) is prepared by the epoxidation of poly(5-vinylnorbornene) obtained by catalytic insertion polymerization of 5-vinylnorbornene. PNBE(epoxy) can be cross-linked with simple biosourced compounds. Alternatively, polar insertion polynorbornene can also be used as cross-linker in the formulation of an epoxy resin, once again resulting in epoxy resins with T_g higher than 300 °C and devoid of degradation at this temperature. Thus, this study clearly demonstrates the viability of catalytic polymerization to access epoxy thermosets with ultrahigh T_g.



INTRODUCTION

Thermosetting materials, also referred as thermosets, are 3D-network molecules obtained by cross-linking multifunctional monomers. They are widely used for a myriad of applications, from the everyday convenience products (e.g., cements, adhesives, protective coatings, automotive applications) to high-tech applications in the aerospace and microelectronics industries. Among these materials, epoxy resins occupy a preponderant position because of the possibility of tuning their mechanical and thermal properties by changing the precise composition of the resin. These resins are constituted of a reactive molecule containing epoxide functionalities (called the epoxy monomer) and a cross-linker which can react with the epoxy monomer to lead to the formation of a 3-D network. Despite more than 50 years of epoxy chemistry, the number of epoxy monomers commercially available is actually quite limited. The majority of the monomers derive from diglycidyl ether of bisphenol molecules such as bisphenol A (BPA), F, or S or of oligomers of phenol−formaldehyde (Novolac).[1] The resulting resins have glass transition temperatures (T_g) which are usually lower than 250 °C. The T_g is a fundamental characteristic of any thermoset, higher T_g's being actively sought for a variety of high-performance applications. Out of concern for an improved sustainability, and also sparked by the fact that BPA is a known endocrine disruptor,[2] the quest for novel epoxys has aroused the interest of numerous research groups.[3] For example, 1,4-butanediol diglycidyl ether (BDE) and glycerol diglycidyl ether (GDE) are derived from reaction of epichlorhydrin with butanediol and glycerol, which can all be produced from the biomass. However, the T_g of the resulting epoxy resins prepared with such monomers are low.[3] Recently, it has been shown that phenyl-based epoxy monomers can be replaced by furan-based ones, leading to thermosets with T_g up to 193 °C.[4]

In order to achieve high T_g epoxy resins, it is necessary to use rigid building blocks for which molecular motions are as restricted as possible and to achieve high cross-link density during the curing process. For example, rigid-rod cross-linkers (such as sulfanilamides) have been shown to yield epoxy resins with T_gs which are higher than those cured with a flexible cross-linker.[5] However, the T_gs remain lower than 250 °C. Highly rigid fluorinated polyimides end-capped by maleic anhydride can even be used as cross-linker, leading to epoxy resins with T_g's comprised between 250 and 300 °C.[6] With the exception of this polyimide example, to our knowledge, no epoxy resin with a T_g as high as 300 °C has ever been reported. Considering the difficulty and cost associated with the preparation of fluorinated polyimides,[7] an alternative route based on simple and readily accessible synthons would be highly preferable.

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Our work is based on the realization that insertion polynorbornene (PNBE) obtained by the catalytic polymerization of readily available norbornene (NBE) leads to a rigid polymer with T_g as high as 350 °C.[8,9] Substituted NBEs bearing polar groups can be obtained in a single step by a simple Diels—Alder reaction using fundamental organic molecules such as dicyclopentadiene (DCPD), acrylic acid, or butadiene as feedstocks (Figure 1). Once polymerized, they lead to the formation of highly functionalized PNBEs which can be used for the preparation of ultrahigh T_g epoxy resins. Two routes were explored in this report. In the first one (route A, Figure 2), poly(5-norbornene-2-carboxylic acid) (PNBE(CO_2H)) was used as cross-linker of bio-based epoxy formulations. In the second (route B, Figure 2), a substituted PNBE (PNBE-(epoxy)) was used as epoxy monomer, using simple and inexpensive hardeners. In all cases, epoxy thermosets with T_g comprised between 250 and 350 °C were obtained. Thus, we have demonstrated that by using the catalytic polymerization of substituted NBEs, very high T_g epoxy thermosets can be prepared from widely available synthons, using a remarkably simple synthetic route. We envision these novel ultrahigh T_g epoxy will find application in high-power electronics, composite fabrication, structural adhesive applications, and other applications where thermosets have to endure elevated temperatures.

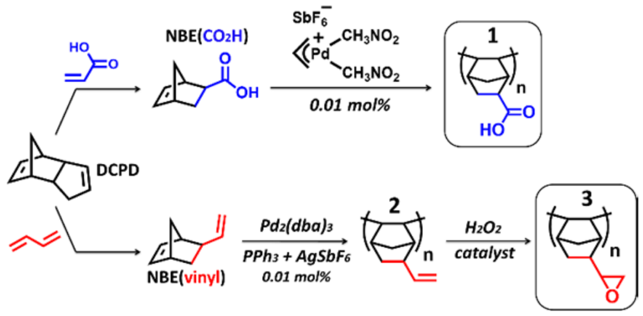

Figure 1. Overview of synthesis of the functionalized polyNBEs.

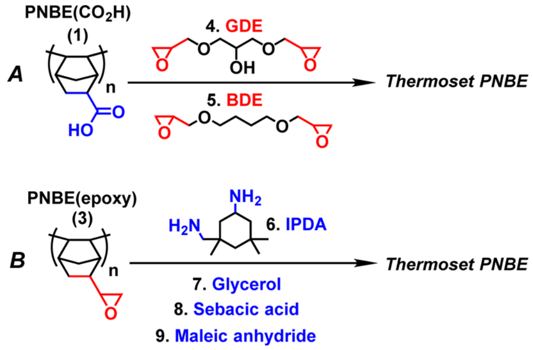

Figure 2. Overview of the synthesis of the thermosets.

■ EXPERIMENTAL METHODS

Materials. Allylpalladium chloride dimer, tris(dibenzylideneacetone) dipalladium(0), silver hexafluoroantimonate, triphenylphosphine, acrylic acid, DCPD, hydrogen peroxide, formic acid, acetic acid, hydroquinone, butanediol diglycidyl ether (BDE), glycerol diglycidyl ether (GDE), isophoronediamine (IPDA), glycerol, sebacic acid, 5-vinyl-2-norbornene, 2,4,6 tris(dimethylaminomethyl)phenol (DMP 30), zinc nitrate hexahydrate (ZN), benzyl tetramethylamonium hydroxide (BTH), tetrahydrofuran (THF), dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), toluene, ethyl acetate, methanol, and deuterated solvents for NMR were all purchased from Sigma-Aldrich. Solvents and liquid monomers used for polymerization were dried over molecular sieves and deoxygenated by bubbling nitrogen.

Synthesis of Functionalized NBEs (Figure 1). *Synthesis of NBE(CO_2H).* In a 50 mL round flask equipped with a condenser, acrylic acid (10.9 g, 150 mmol, 2 equiv) and hydroquinone (165 mg, 1.5 mmol, 1 mol %) were heated under stirring until it began to boil (150 °C). DCPD (10 g, 75 mmol, 1 equiv) was then added in a single portion, and the mixture was stirred at 170 °C until the reflux stopped and the reaction mixture turned brown (around 16 h). The ^1H NMR spectrum of this mixture showed 95% yield of 5-norbornene-2-carboxylic acid (40% *exo*) which was purified by simple distillation to yield a colorless liquid (bp = 153 °C at 5 mmHg).

Synthesis of Functionalized PolyNBEs (Figure 1). *Synthesis of PNBE(CO_2H) (Polymer 1).* In a 250 mL round-bottom flask equipped with a condenser and under a nitrogen flow, $[PdCl(C_3H_5)]_2$ (26 mg, 71.06 μmol, 142.12 μmol of Pd, 1 equiv) and NBE(CO_2H) (40% *exo*, 100 g, 724.63 mmol, 5100 equiv) were mixed and heated at 70 °C until the full solubilization of the $[PdCl(C_3H_5)]_2$ yellow crystals. Then, $AgSbF_6$ (60 mg, 174.61 μmol, 1.23 equiv) were added under vigorous stirring at 70 °C. The reaction was kept for 36 h at 70 °C. At the end of the reaction, the flask contained a cracked solid. This solid was collected and broken with a spatula to form a small powder. The solid was purified using a Soxhlet apparatus with water as solvent until the amount of residual monomer was below quantification by ^1H NMR. As an alternative to the Soxhlet extraction procedure, once the polymerization reaction was performed, the cracked solid was washed with ethyl acetate via vigorous stirring. When ethyl acetate is added, the large pieces are broken into a thin powder which was filtered and washed on ethyl acetate on a Buchner filter. The polymer was dried at 50 °C under vacuum overnight. Yield (46 g, 46%). M_n = 105 000 g/mol, PDI = 1.7.

Monomer Recovery. The liquid solution recovered after the filtration was concentrated on the rotary evaporator and was purified by simple distillation to yield a colorless liquid (bp =153 °C at 5 mmHg). NBE(CO_2H) was collected to be used again. Yield: 44 g, 81%.

*Synthesis of PNBE(Vinyl) (Polymer **2**).* In a 250 mL round-bottom flask, tris(dibenzylideneacetone)dipalladium(0) (76 mg, 0.083 mmol, 0.166 mmol of Pd, 1 equiv), $AgSbF_6$ (68.2 mg, 0.198 mmol, 1.19 equiv), and triphenylphosphine (43.5 mg, 0.166 mmol, 1 equiv) were solubilized in 100 g of toluene at 70 °C. Then, 5-vinyl-2-norbornene (100 g, 832 mmol, 5000 equiv) was added under vigorous stirring and heated at 70 °C for 72 h. A black viscous solution was obtained. The polymer was precipitated with 600 mL of methanol and washed three times with methanol. Then the gray powder was filtered and dried under vacuum at room temperature overnight. Yield: 85 g, 85%. M_n = 17 400 g/mol, PDI = 2.8.

*Synthesis of PNBE(Epoxy) (Polymer **3**). Procedure A.* In a 500 mL round-bottom flask, polymer **2** (15 g, 0.10 mol, 1 equiv) was dissolved in 120 mL of dichloromethane. Then successively acetic acid (4.7 g, 0.08 mol, 0.8 equiv), formic acid (28 g, 0.61 mol, 6.1 equiv), and H_2O_2 (30% w:w in water) (74 g, 0.65 mol, 6.5 equiv) were added under vigorous stirring and stirred for 24 h. During addition, the temperature was kept at 0 °C by cooling with an external ice/water bath. During reaction, the solution turned white, and a white supernatant foam was formed. At the end of the reaction, the solution was precipitated into acetone under vigorous stirring and then rapidly filtered over a filter paper. The solid was collected and washed twice with acetone. Then the white thin powder was dried under vacuum at room temperature for 18 h. Yield: 85%. M_n = 19 600 g/mol, PDI = 2.1.

Procedure B. In a 50 mL round-bottom flask equipped with a magnetic stirrer and a condenser, 1 g (6.7 mmol) of polymer **2** and 33 mg (0.13 mmol, 2 mol %) of MTO (methyltrioxorhenium(VII)) were dissolved in 10 mL of CH_2Cl_2. To this solution were added dropwise 64 μL (0.8 mmol, 12 mol %) of pyridine followed by 4.1 mL (75 mmol, 6 equiv) of 30% w/w aqueous H_2O_2. During the addition the

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temperature was kept at 15 °C by cooling with an external cold water bath. The mixture was stirred at room temperature for 42 h. Then, the polymer was precipitated in acetone (100 mL) and washed three times with acetone. The polymer was finally dried under vacuum overnight at room temperature, leading to the formation of polymer **4** as a fine white powder (75% yield).

Preparation of PolyNBEs Thermosets (Figure 2). *Sample Preparation.* The thermosets were prepared in either a clean silicon mold which was 2 in. in length, 1 in. in width, and 0.4 in. in height or an aluminum mold depicted in Figure S1. The polymer and 90% of the volume of the solvent were mixed together until a homogeneous solution was obtained. Then, the solution was centrifuged (3500 rpm for 10 min). In some cases, the dissolution of the polymer required moderate heating, but once dissolved, the solution could be used at room temperature without polymer precipitation. Then, the other component (nonpolymeric cross-linker or epoxy monomer) and the catalyst, dissolved in the remaining 10% of solvent, were added to the polymer solution. The solution was then mixed for 4 min with a vortex stirrer at room temperature. The solution was then immediately poured into the mold, which was then placed into the oven. The curing procedure was as indicated in the Table S1.

Solvent-Free Preparation. Polymer **3** and hardener (IPDA, **6**) were manually mixed until a homogeneous viscous solution was obtained. The resulting solution was poured into the mold (see Figure S1 or S2), heated at 70 °C for 12 h and then at 150 °C for 4 h, and postcured at 190 °C for 4 h. Note on the curing rate: a very slow curing process was deliberately chosen in order to prepare coatings which are free of defects (such as cracks or bubbles), as shown in Figures S1 and S2. Such procedure is necessary to ensure that mechanical measurements be reproducible. Visually acceptable coupons are nonetheless obtained at significantly faster curing rates such as 3 °C/min with 1 h plateau at 80 °C and 1 h plateau at 110 °C before reaching the final temperature (180 °C).

Characterization. *Nuclear Magnetic Resonance.* The ^{1}H NMR spectrum was recorded on a Bruker Ultrashield 300 MHz spectrometer at ambient temperature. ^{1}H chemical shifts were referenced to the solvent signal.

Gel Permeation Chromatography. The molecular weight distributions of the polymers were determined by gel permeation chromatography (GPC) using a Viscotek instrument equipped with one PL-Gel mixed A LS 20 μm column, one PL-Gel mixed B LS 10 μm column, and one polypore 5 μm column, a Wyatt DSP refractometer, and a Wyatt Dawn light scattering detector. For the PNBE(vinyl) and PNBE(epoxy) polymers, elution was performed in THF at 40 °C, and all samples were analyzed using a dn/dc of 0.16 and 0.20, respectively. For PNBE(CO_2H), elution was performed at 40 °C in DMF containing 1 g/L of LiCl (dn/dc = 0.04).

Differential Scanning Calorimetry. Differential scanning calorimetry measurements (DSC) of solid polymers were performed on a DSC823e (TOPEM modulation) equipped with an FRS5 sample cell, a sample robot, a Julabo FT400 intracooler, and an HRS7 sensor from Mettler Toledo. Samples were heated from 50 to 300 °C at a rate of 10 °C/min, and data were analyzed with STAR software. The data associated with the second heated ramp are shown.

Fourier Transform Infrared Spectroscopy. The solid polymers FTIR spectra were recorded on a Nicolet 6700 Spectrometer equipped with Smart ATR accessory (ThermoSci).

Dynamic Mechanical Thermal Analysis (DMTA). The DMTA analysis were performed on a TA Q800 dynamic mechanical thermal analysis using a single cantilever on a clamped sample over a temperature range of 30−340 °C with a 5 °C/min heating ramp. Samples of 17.6 × 14.5 × 2.0 mm were analyzed, using an aluminum or silicon mold as described above (see Figure S1).

Thermomechanical Analysis (TMA). The TMA analysis was performed on a TA Q400 instrument over a temperature range of 30−340 °C with a 5 °C/min ramp. Sample sizes were identical to those of DMTA.

Tensile Test. An aluminum mold was used as shown in Figure S2 to prepare dogbones following testing standard of ASTM D638, and tensile test was performed on an Instron 5569 machine with the crosshead speed of 1 mm/min.

Thermogravimetric Analysis. The samples were analyzed by TGA-MS using a TA Q500 instrument coupled to a Discovery MS, with a temperature range from 30 to 1000 °C at a 20 °C/min rate.

Swelling Experiments. A piece of the cross-linked polymer was precisely weighted (W_{dry}, 150−350 mg) and was immersed in NMP at room temperature for several days. The plastic piece was blotted dry on filter paper and weighed to determine the wet mass W_{wet}. This step was repeated every day to obtain the swelling evolution over time.

$$W_{\text{up}}\ (\text{wt}\ \%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100$$

■ RESULTS AND DISCUSSION

Our novel thermoset platform stems from the chemistry of functional norbornenes (NBEs), which are derived from Diels−Alder reactions between an essential C5 feedstock, DCPD, and fundamental synthons such as acrylic acid or butadiene (Figure 1). Both acrylic acid[10] and butadiene[11] can be prepared from bio-based feedstocks if necessary. These Diels−Alder reactions can be performed in the absence of organic solvent[12] and lead to the formation of the primarily *endo* substituted NBE (kinetic isomer), which can be collected by simple distillation. In our hands, the solvent-free reaction of acrylic acid and DCPD leads to the formation of 5-norbornene-2-carboxylic acid, NBE-(CO_2H), in ≥95% yield prior to distillation. As starting materials for the novel thermoset platform, we used NBE-(CO_2H) (*endo*:*exo* = 60:40) and 5-vinyl-2-norbornene (NBE-(vinyl) *endo*:*exo* = 75:25). The 1,2-insertion polymerization of NBE leads to a saturated polymer with extremely high T_g (≥350 °C, too high to be measured accurately) and unique optical and mechanical properties.[8,13,14] The polymerization of substituted NBE's was historically plagued by the lack of reactivity of the *endo* isomer, but a novel rectification−insertion polymerization mechanism was recently discovered whereby the low reactivity *endo* isomer is converted *in situ* into the more reactive *exo* isomer.[15] Using this mechanism, the solvent-free polymerization of NBE(CO_2H) catalyzed by (η^3-allyl)$PdSbF_6$ (0.01 mol % relative to monomer) leads to the formation of PNBE(CO_2H), **1**, in 45% yield. The polymerization stops because the polymer/monomer mixture reaches a gel point. The polymer can be purified by Soxhlet extraction with water. The recycled NBE(CO_2H) is pure enough to be used for another polymerization without any change in yield. Thus, the preparation of polymer **1** from widely available starting materials (DCPD and acrylic acid) did not require any organic solvent.

Known catalytic systems reported for the polymerization of NBE(vinyl) have either very low reactivity or react with both of the double bonds present on the monomer leading to an ill-defined polymer structure.[16,17] The rectification−insertion polymerization catalyst, (η^3-allyl)$PdSbF_6$, leads to the formation of cross-linked polymers. We tested several other nickel- or palladium-based catalysts which were found to react with the pendant double bonds (see Supporting Information) either via insertion or via chain transfer. Recently, Wakatsuki et al. discovered that the catalyst $Pd(dba)_2/PCy_3/CPh_3[B(C_6F_5)_4]$ efficiently polymerizes NBE(vinyl) in the absence of side reaction for the pendant double bond,[18] leading to a very high molecular weight polymer ($M_n \geq 200\,000$ g/mol). In solution, this polymer is extremely viscous, rendering any postfunctionalization step difficult unless a huge excess of organic solvent is

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Table 1. Main Characteristics of the Epoxy Materials Derived from Functional Polynorbornenes

expt	mon	cross-linker	wt %[a]	T_g[b] (°C)	E'[c] (MPa) 40 °C	E'[c] (MPa) 250 °C	CTE[d] (ppm/°C) 40 °C	CTE[d] (ppm/°C) 250 °C
route A (PNBE(CO_2H) as cross-linker)								
1	4	1	26–74	≥350	4100	690	107	142
2	5	1	26–74	≥320	2000	685	135	133
route B (PNBE(epoxy) as epoxy monomer)								
3	3	7	92–8	240	1100	<100	89	151
4	3	7	75–25	235	2400	<100	154	591
5	3	8	69–31	245	1550	110	121	185
6	3	6	76–24	≥340	3130	1240	52	59
7	3	6	62–38	≥340	2700	900	75	18
8	3	9	81–19	≥340	3150	912	72	66

[a] Weight compositions correspond to the relative weight of epoxy monomer to cross-linker. [b] Measured as the peak of the tan δ peak in DMTA. [c] Storage modulus as measured in DMTA. [d] Coefficient of thermal expansion as measured in TMA.

used. We discovered that the catalyst $Pd_2(dba)_3$:$AgSbF_6$:PPh_3 (1:1.2:1) leads to the formation of a low molecular weight polymer, **2** (M_n = 12 000 g/mol, PDI = 2.2), which contains one pendant double bond per inserted monomer, as measured by ^1H NMR. Using 0.01 or 0.02 mol % of the catalyst, the polymer is obtained in 45% or 85% yield, respectively (Figure 1). Once again, the unreacted monomer can be collected by distillation and reused for further polymerization. Epoxidation of **2** can be accomplished using H_2O_2/formic acid/acetic acid in yields as high as 85%. Alternatively, the epoxidation can also be performed using H_2O_2 as oxidizing agent with 2 mol % of methyltrioxorhenium(VII) as catalyst in 75% isolated yield.[19,20] Characterization by ^1H NMR and GPC indicates that more than 95% of the pendant double bonds are epoxidized (Figure S3) without any alteration of the molecular weight distribution of the polymer (Figure S4).

An epoxy thermoset is obtained upon cross-linking of an epoxy monomer containing at least two epoxide functionalities with a cross-linker molecule. In this work, we found that polymers **3** and **1** can serve as epoxy monomer and cross-linker, respectively (Figure 2). Below, we refer to them as epoxy monomers even though they are in fact multifunctional reacting species. Upon thermally reacting polymer **1** with either GDE (**4**) or BDE (**5**), two bio-based epoxy monomer, thermosets with $T_g \geq 350$ °C (Table 1) are obtained. Using DMTA, the precise value of the T_g (corresponding to the maximum of tan δ peak) cannot be determined (Figure 3) as the thermosets start to degrade in air before T_g is attained (see below). The T_g onsets (measured at the base of the tan δ peak) of the thermosets prepared with **4** and **5** (Figure 2) are respectively 285 and 304 °C. These values are extremely high when compared to the T_g's of thermosets prepared by reaction of **4** or **5** with a bisphenol containing cross-linker, bisphenol A diamine with the same ratio epoxy/hardener (68 and 12 °C, respectively, Figure S26). The mechanical properties of the thermosets measured by DMTA (Table 1 and Figure 3) indicate a high storage modulus, even at 250 °C.

PNBE(epoxy) (**3**) as epoxy monomer can be cross-linked with IPDA (**6**), glycerol (**7**), sebacic acid (**8**), and maleic anhydride (**9**), which are all bio-based cross-linkers (Figure 2). Importantly, polymer **3** is soluble in **6**, thus precluding the need of organic solvent to prepare the thermoset. At room temperature, the mixture of **3** and **6** does not cross-link for up to a week, as shown by the absence of viscosity increase. Thus, it is possible to prepare solvent-free formulations based on **3** and **6** with relatively long pot-lives. Again, once cured, the thermosets exhibit very high T_g and excellent mechanical properties (Table 1 and Figure 3). Comparative thermosets in which polymer **3** is replaced by diglycidyl ether of bisphenol A, DGEBA, exhibit T_g's which are all less than 100 °C (Figure S26). Using IPDA and maleic anhydride as cross-linkers, the peak of the tan δ curve is not attained at 350 °C (Figure 3B), a temperature at which the sample starts to degrade (see below). For experiments 1, 2, 6, and 7, a small tan δ peak (≤0.1) is observed at ca. 120 °C. This subglass peak is due to the presence of a beta transition, as confirmed by dielectric spectroscopy (results not shown) and also by the fact that it occurs while the storage modulus remains high (at T_g, the storage modulus falls below 100 MPa). Therefore, the PNBE-

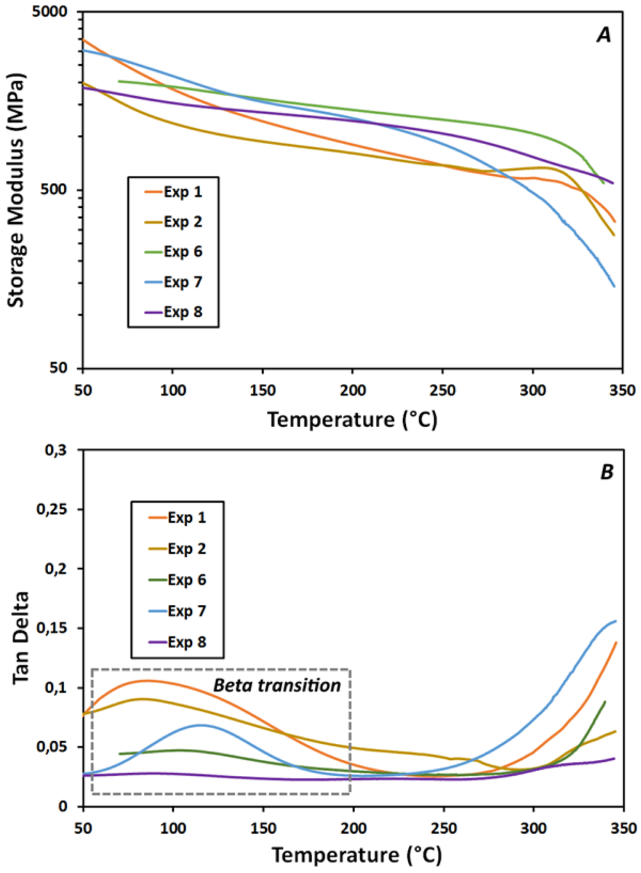

Figure 3. Storage modulus (A) and tan δ (B) of several thermosets (Table 1) as measured by DMTA (50−340 °C).

based thermosets exhibit very high T_g's and storage moduli. These remarkable thermomechanical properties can be ascribed to the high rigidity of the bicyclic backbone with hindered internal rotations as well as to the very high cross-link density achieved with these multifunctional PNBEs (see Figure 4).[21,22]

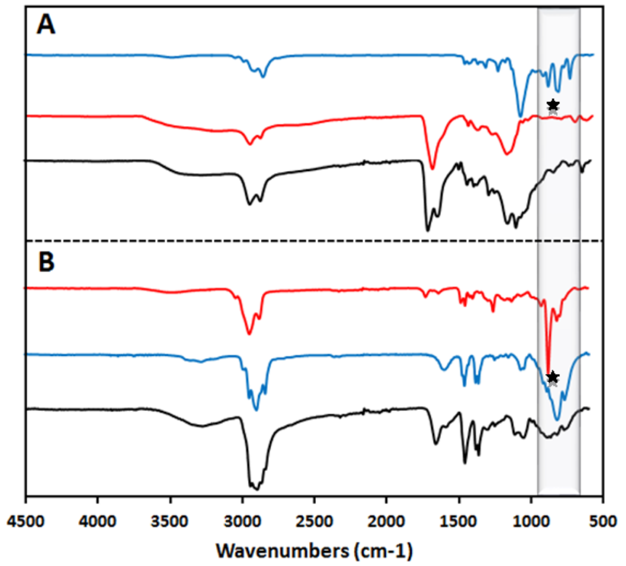

Figure 4. (A) FTIR spectra of top: BDE (5), middle: polymer 1, bottom: thermoset sample 2 (Table 1). (B) FTIR spectra of top: polymer 3, middle: IPDA (6), bottom: thermoset sample 6 (Table 1). Note the disappearance of the epoxide band at 874 cm^{-1} (starred peak).

The disappearance of the characteristic epoxide band at 874 cm^{-1}, as observed by FTIR spectroscopy (Figure 4 for characteristic examples and Supporting Information for each formulation) is indicative of the complete conversion of the epoxide ring upon reaction during curing. The thermosets are also found to be impervious to swelling, as shown by less than 1.5% swelling after 1 week of immersion in NMP whereas all the starting materials are soluble in NMP. The disappearance of the 874 cm^{-1} band and the absence of swelling are indicative of the high cross-linking degree achieved in these samples.

The PNBE thermosets possess very high thermal stability. With the exception of samples 1, 3, and 4, the onset of degradation in air, defined at the point where the weight change derivative dWt_{change}/dT is greater than 0.05%/°C, is comprised between 340 and 360 °C (Figure 5). Thermosets 1, 3, and 4 have onsets of degradation above 280 °C. These samples are prepared with monomers (GDE) or cross-linkers (glycerol) which contain free hydroxyl (OH) groups. The ring-opening of an epoxide by an hydroxyl group is known to be slow compared to the reaction of an amine with an epoxide.[23] Once it is ring-opened, the epoxide is itself transformed into an alcohol, which can again react with another epoxide. Thus, only a fraction of the hydroxyl (OH) groups of glycerol initially introduced in the formulation are consumed. Therefore, compared to the other samples, thermosets prepared with glycerol (samples 3 and 4) have a lower cross-link density and lower thermal stability, as shown by lower mechanical properties and thermal stability (Figure 5). Nonetheless, these properties remain very high in comparison to conventional epoxy thermosets.

The mechanical properties of the PNBE thermosets were further examined by TMA analysis (Table 1), thus allowing to determine the coefficient of thermal expansion (CTE). For adhesive and coating applications, low values of CTE which remain constant over a wide temperature range are desirable in order to minimize the risk of stress cracking due to a CTE mismatch between a low-CTE substrate and the thermoset. Remarkably, the PNBE thermosets exhibit a constant and low CTE values over a wide range of temperatures, as shown by a linear TMA curve (Figure 6). The small inflections in the TMA curve (indicated by stars in Figure 6) correspond to the onset of T_g, in agreement with the values measured by DMTA (Figure 3). For glycerol-containing thermosets (experiment 3), T_g is observed ca. 50 °C higher, resulting in high CTE values at 250 °C (Table 1). All other themosets have constant and low CTE values in the range 50−275 °C, indicative of a remarkable dimensional stability.

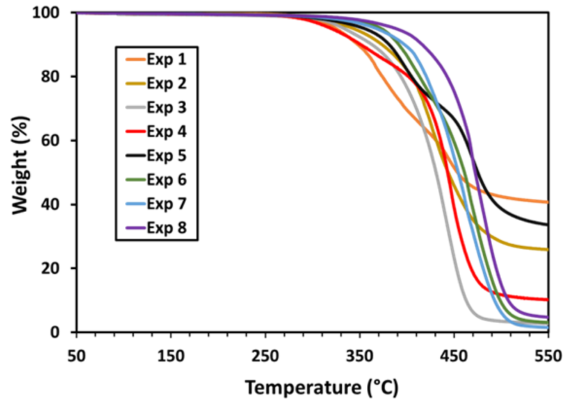

Figure 5. TGA spectra of several obtained thermosets (Table 1). Analysis performed under nitrogen flow. All samples were heated to 200 °C prior analysis in order to dehydrate them.

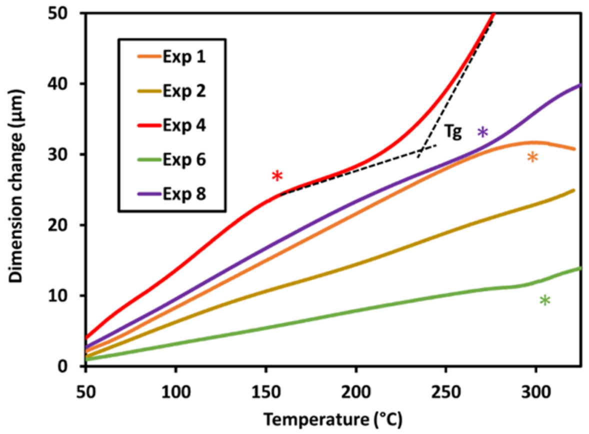

Figure 6. TMA analysis of five different thermosets (Table 1), with the T_g onset indicated by a star.

Thermosets 6 and 7 (Table 1) have been selected to perform a tensile test analysis because of their high thermomechanical properties. As measured by tensile testing, the Young's moduli of thermosets prepared in experiments 6 and 7 are 2.83 ± 0.18 and 3.21 ± 0.12 GPa, respectively (average of four dogbones). The fracture in sample 6 is brittle, as shown by SEM analysis of the broken sample (Figure S24), whereas the fracture of sample 7 is ductile (Figure S25). This behavior can be explained by the higher amount of rigid PNBE in sample 6 compared to sample 7.

The thermosets based on either PNBE(CO_2H) or PNBE-(epoxy) have to our knowledge the highest T_g's ever reported for epoxy thermosets. They also offer unique mechanical properties, as illustrated by the low CTE at 250 °C and very high storage moduli (as high as 4 GPa at room temperature for experiment 1 and 1.2 GPa at 250 °C for sample 6). They also contain as much as 38 wt % of IPDA (**6**) or 26 wt % of GDE (**4**) or BDE (**5**) which are all bio-based and renewable. Furthermore, the synthesis of PNBE(CO_2H) from starting materials (acrylic acid and DCPD) to isolated polymer did not require any solvent and did not generate any waste. Thus, these polymers offer a convincing proof of principle that green chemistry principles can be used to design a bisphenol-free epoxy platform with a set of properties which exceeds those of conventional containing epoxys.

■ CONCLUSIONS

To conclude, one of the most important challenges currently facing synthetic polymer chemists is to design novel materials with properties surpassing those of existing materials while using synthetic routes which are acceptable in terms of environmental, cost, and safety constraints as well as societal expectations. In order to address this challenge, we demonstrated here that catalytic PNBEs form a versatile platform for the facile construction of epoxy resins with unsurpassed thermomechanical properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.5b02648.

Synthesis of polymers **1**–**3**, of all thermosets, pictures, and analytical details (NMR, FTIR, DMTA, TMA, AFM, SEM) (PDF)

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Notes

The authors declare no competing financial interest.

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