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SUPPORTING INFORMATION

Fully bio-based polyimine vitrimer derived from fructose

Sébastien Dhers,[†] Ghislaine Vantomme[‡,*] and Luc Avérous[†,*]

[†] BioTeam/ICPEES-ECPM, UMR CNRS 7515, Université de Strasbourg, 25 rue Becquerel, 67087 Strasbourg Cedex 2, France; e-mail: luc.averous@unistra.fr

[‡] Institute for Complex Molecular Systems (ICMS), Eindhoven University of Technology, Eindhoven, The Netherlands; e-mail: g.vantomme@tue.nl

Material. Dichloromethane, THF, EtOH, DMF and butylamine were purchased from Sigma Aldrich. 5-(hydroxymethyl)furfural (98%) and Dess-Martin Periodinane (97 %) were purchased from Fluorochem. Priamine 1071 (batch number: 0000487627) was kindly supplied by Croda. All chemicals were used without further purification. Dichloromethane was dried over 3Å molecular sieves over a few days.

Instrumentation. Infrared (IR) spectra were recorded on a Thermo Scientific Nicolet iS210 instrument using a Smart Orbit Diamond. NMR spectra were recorded in $CDCl_3$ on a 400MHz Bruker instrument. DSC analyses have been carried out on a Q200 from TA Instruments, between -50 and 150°C at 5°C/min. TGA analysis has been carried out on a Q5000 from TA Instruments, between 50 and 700°C, ramping at 10°C/min, and at 120°C for 2h for isothermal analysis, both under an air atmosphere.

Rheology experiments were performed on a TA Instruments Discovery HR-3 using ETC parallel plate geometry with 25 mm sample disks. The experiments were performed at different temperatures on the same sample. Arrhenius equations extracted from both stress relaxation and creep recovery represent an average over three experiments. For stress relaxation experiments, a constant axial force of 1N was applied throughout the experiment, and a strain of 2%, comprised in the viscoelastic region, was applied to the material and the relaxation modulus G was followed over time at a constant temperature. Creep experiments were performed using a constant axial force of 5N and a stress of 2000 Pa, and the resulting strain was followed over time at constant temperature. The creep rate ($\dot{\varepsilon}$) was calculated at 800s. Frequency sweep experiments were performed between 0.001 and 100 Hz, using a constant axial force of 1N and a strain of 1%.

Uniaxial tensile tests were performed on a TA Instruments Discovery HR-3 using dog bone-shaped samples at 20°C (effective length 14 mm, width 4.5 mm, thickness 1 mm). The tensile measurements were performed using a preload of 0.05 N and a pulling speed of 50 μm/s until sample failure. The stress σ was recorded as a function of strain ε. Reported values (elongation (%), stress at break (MPa), and Young modulus (MPa)) are the average of three samples. Exhibited tensile curves were selected to be representative of the average values.

Experimental.

Synthesis of FDC. 5-(hydroxymethyl)furfural **HMF** (5.2 g, 41.2 mmol) was taken in 300 mL dry CH_2Cl_2. After dissolution, Dess-Martin Periodinane (21.2 g, 50 mmol, 1.2 eq.) was added and the solution was stirred at room temperature overnight. Then, 200 mL of 1M NaOH were added and the solution was stirred for 1h. The aqueous phase was washed with 3x100 mL CH_2Cl_2 and the organic phase then washed with 200 mL brine. After drying of the organic phase over $MgSO_4$ and evaporation of the solvent on the rotavap, 2.5-furan-dicarboxyaldehyde (**FDC**) was obtained as a yellow powder (4.2 g, 81 %). ^{1}H NMR (ppm): 9.85 (2H, s) 7.85 (2H, s). ^{13}C NMR (ppm): 179 (CHO), 154, 119. IR (ν, cm^{-1}): 3127, 3102, 1663.

Synthesis of vitrimer 1. FDC (200 mg, 1.6 mmol, functionality 2) was added to Priamine 1071 (1091 mg, 1.76 mmol, functionality 2.2) in 20mL THF. The reaction was stirred for 1h and solvent casted in a Teflon mold overnight. The film obtained was cut into small pieces (< 10 mm) and pressed at 120°C under 20 tons for 1h (with 10 venting cycles of 60s).

Reprocessability of vitrimer 1. The polymer was broken into small pieces (< 10 mm) and placed into the dog bone-shaped mold used for tensile test, which was then placed in a hot press at 120 °C for 10 minutes.

Swelling experiments of vitrimer 1 were done in THF, DMF, EtOH, neutral H_2O, 1M solution of NaOH and 1M solution of HCl. Samples were about 5 x 5 x 1 mm and 30 mg for each experiment, and were immersed in 2mL of the corresponding solvent for 48h at 25°C.

$$\text{soluble fraction} = (m_i - m_d)/m_i$$

$$\text{swelling ratio} = (m_s - m_i)/m_i$$

m_i, m_s, and m_d being respectively initial, swollen, and dry mass.

Figure S1. Pictures of dog bone-shaped samples of vitrimer **1**.

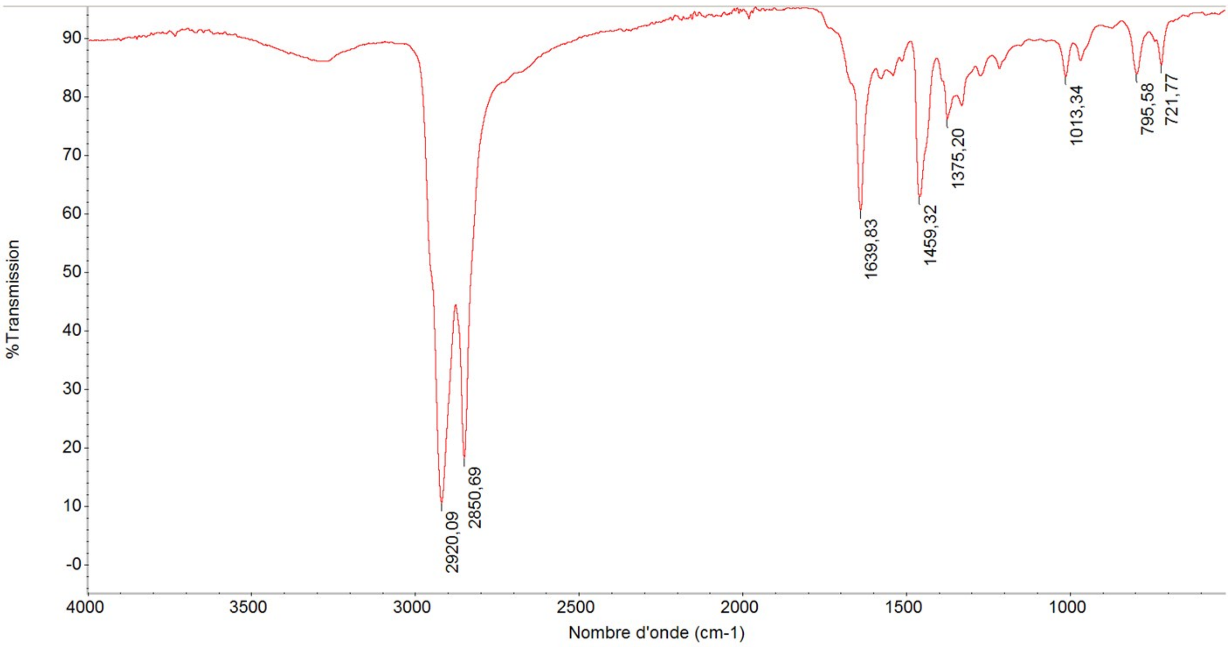

Figure S2. FTIR spectra of vitrimer **1**.

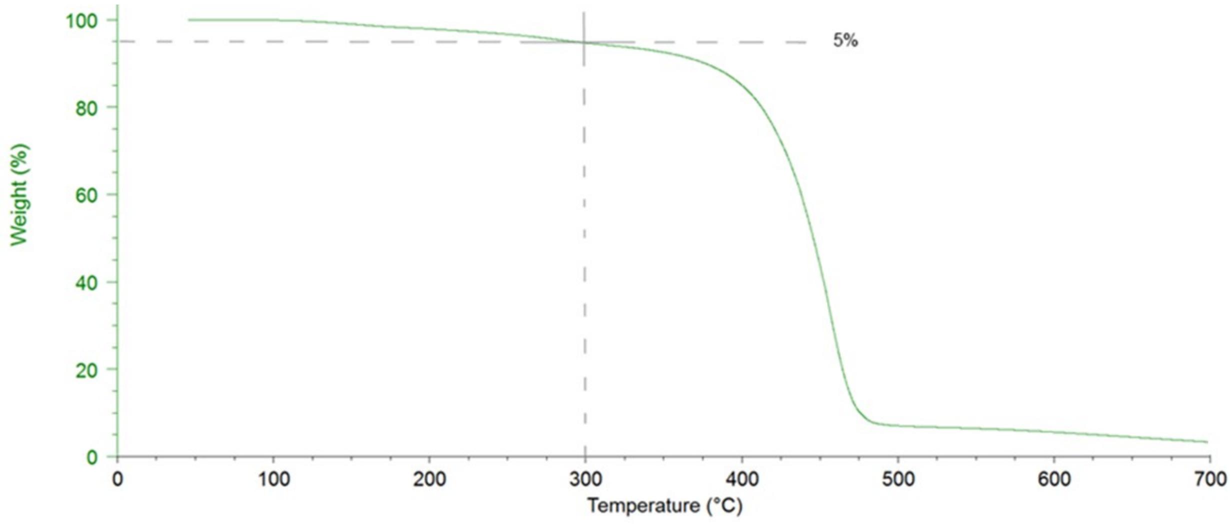

Figure S3. TGA of **vitrimer 1** from 50 to 700°C at 10°C/min.

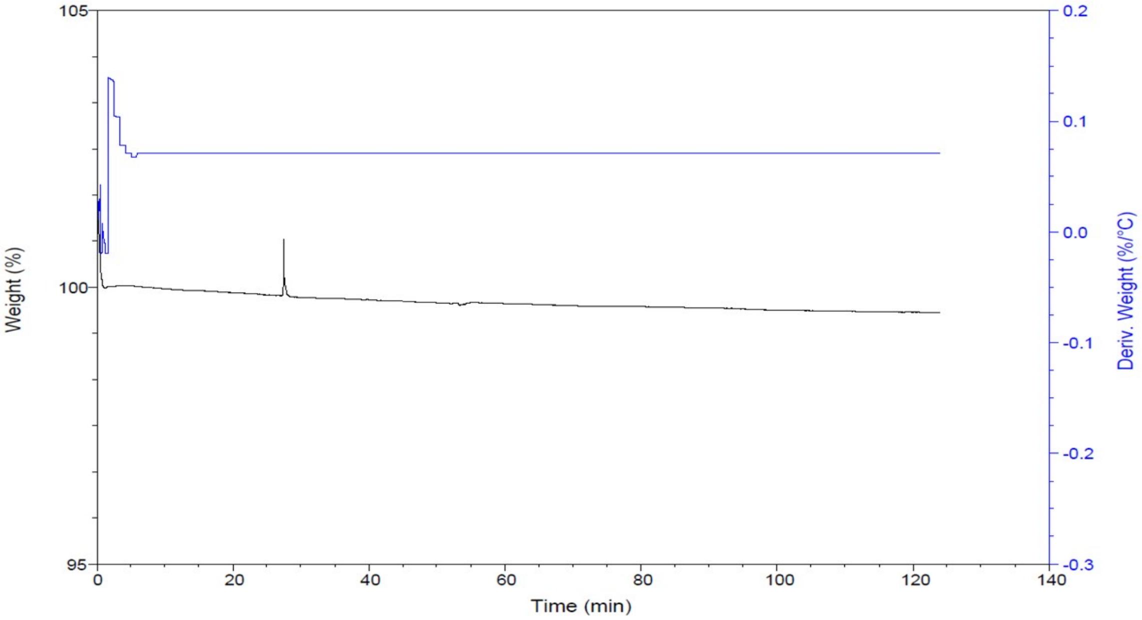

Figure S4. Isothermal TGA analysis of **vitrimer 1** at 120°C for 2h.

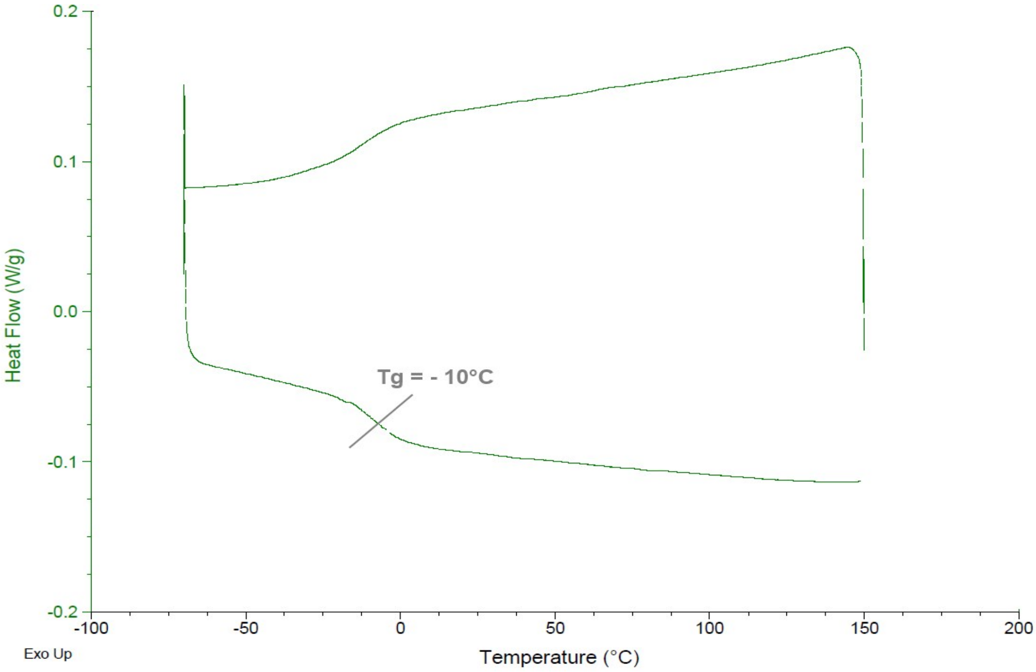

Figure S5. DSC of **vitrimer 1** from -50 to 150°C at 10°C/min.

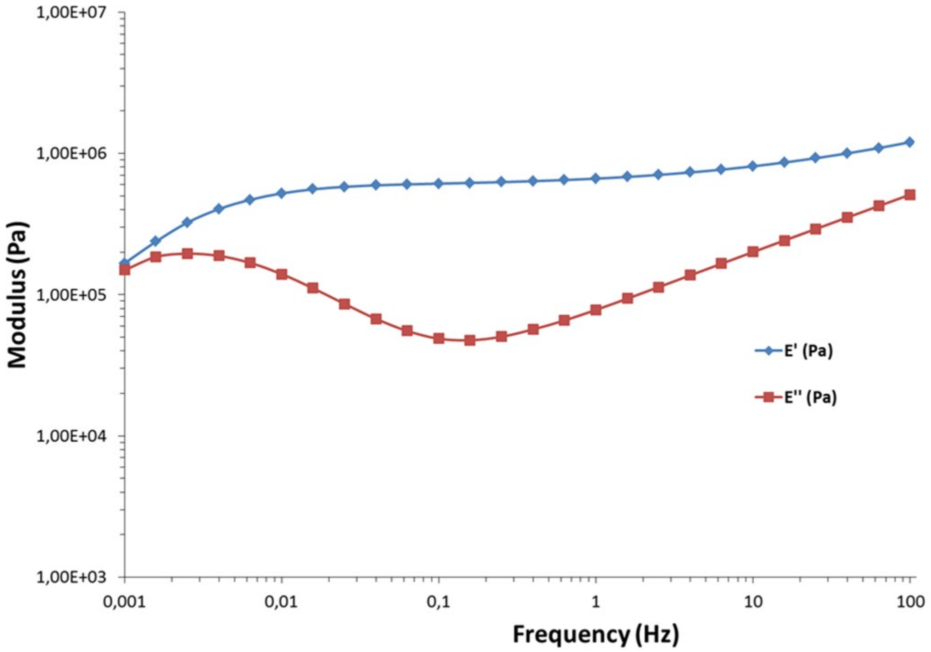

Figure S6. Storage modulus (E') and loss modulus (E'') obtained from DMA experiment performed on vitrimer **1** at room temperature.

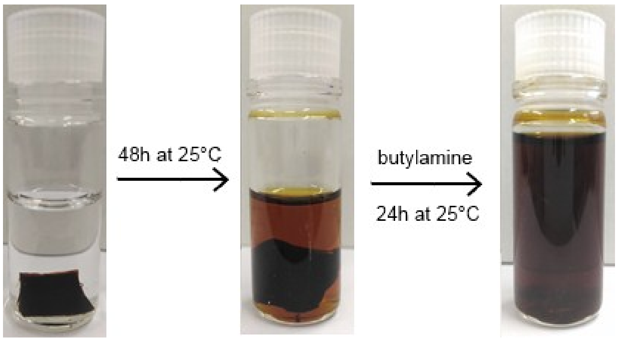

Figure S7. A sample of vitrimer **1** (5 x 5 x 1 mm) after immediate immersion in THF (*left*), after 48h at 25°C in THF (*middle*) and after 24h at 25°C in 1mL 1M butylamine solution in THF (*right*). The sample dissolved after treatment with butylamine.

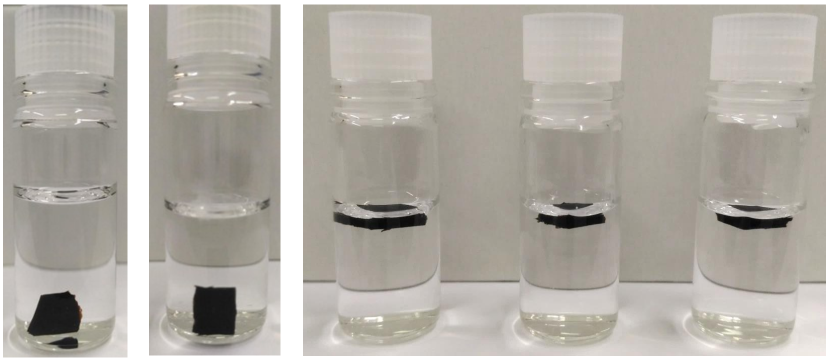

Figure S8. A sample of vitrimer **1** (5 x 5 x 1 mm) after immersion during 48h at 25°C in (*left to right*) DMF, EtOH, 1M NaOH, neutral H_2O and 1M HCl.

Calculations for stress relaxation derived activation energy

Equation obtained from Arrhenius law: $y = 7.7047x - 21.167$ ($R^2 = 0.9989$)

Which corresponds to: $\ln(\tau^*) = 7.7047 * 1000/T - 21{,}167$

The Arrhenius law related to the activation energy is: $\tau^* = \tau_0 \exp(E_a/RT)$ ($R = 8.314$)

Therefore: $\ln(\tau^*) = \ln(\tau_0) + E_a/RT$

Identifying this to the experimental equation: $Ea/R = 7.7047 * 1000$

$E_a = 7.7047 * 1000 * 8.314 = 64$ kJ/mol

Calculations for creep recovery derived activation energy

Equation obtained from Arrhenius law: $y = 7.1957x - 17.989$ ($R^2 = 0.9967$)

Which corresponds to: $-\ln(\acute{\varepsilon}) = 7.1957 * 1000/T - 17.989$

Similar to above, the Arrhenius law related to the activation energy is: $\acute{\varepsilon} = \acute{\varepsilon}_0 \exp(E_a/RT)$

Identifying this to the experimental equation: $Ea/R = 7.1957 * 1000$

$E_a = 7.1957 * 1000 * 8.314 = 60$ kJ/mol

Calculations for vitrimer temperature (T_v) using Arrhenius equation from stress relaxation

Arrhenius equation: $y = 7.7047x - 21.167$

The Maxwell equation below is used to calculate Tv, using a viscosity value taken arbitrary as: $\eta=10^{12}$

$$\eta = G \times \tau^*$$

$$G^2 = G'^2 + G''^2$$

The value G' = 0.6 MPa and G" = 0.08 MPa are extracted from DMA experiments at room temperature and at 1Hz (Figure S6, rubbery plateau).

Consequently: $G = \sqrt{G'^2 + G''^2} = 0.605$

$\tau^* = \eta/G = (10^{12})/(0.605\times10^6) = 1.65\times10^6$

$\ln(\tau^*) = \ln(1.65\times10^6) = 14.31$

using the equation from stress relaxation: $x = 1000/T = (\ln(\tau^*) + 21.167) / 7.7047 = 4.61$

$T_v = 1000/x = 1000/4.75 = 216.8$ K

$T_v = -58.3$ °C