

Supporting Information

Formation of Cross-linked Films from Immiscible Precursors through Sintering of Vitrimer Nanoparticles.

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1. Materials

Reagents: The hydrogenated dimer fatty acid (COOH eq. 282.3 mol g⁻¹), 2,4,6,8-tetramethyl-2,4,6,8-tetrakis (propyl glycidyl ether) cyclotetra siloxane (**CS697**, *contains also other epoxy-functional cyclosiloxane compounds*, epoxy eq. 169.3 g mol⁻¹), poly dimethyl siloxane diglycidyl ether terminated (**PDMS-diepoxy**, epoxy eq. 477.5 g mol⁻¹), xylene and anhydrous Mg(SO₄) were purchased from Aldrich and used as received. Deionized (DI) water (Purelab Classic UV, ElgaLabWater) was used for all experiments. CDCl₃ was purchased from Eurisotop.

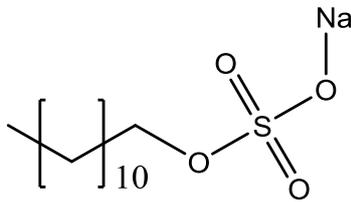
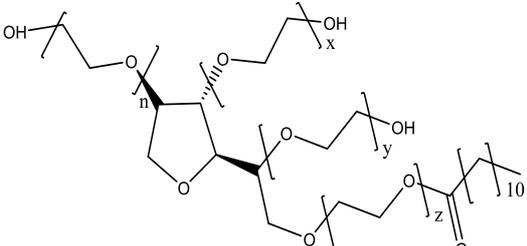
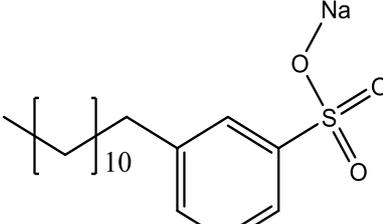
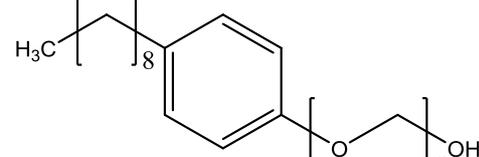
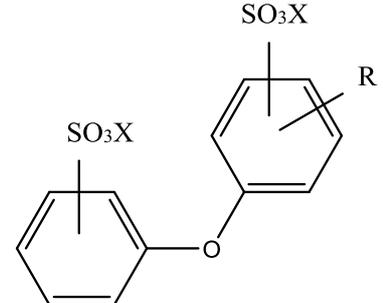
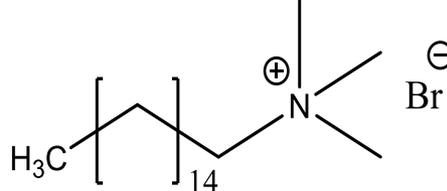
The molar equivalents were measured by ¹H NMR from solutions with known concentrations of reagents and ethylene carbonate as reference compound.

Surfactants: Sodium dodecyl sulfate (SDS), cetyltrimethyl ammonium bromide (CTAB) and Tergitol NP35 were purchased from Aldrich and used as received. Sodium dodecyl benzene sulfonate (SDBS), tween 20 and zinc diacetate dihydrate (purity 98%) were purchased from Acros. Lutensol® AT50 (C16 – C18 fatty alcohol and 50 ethylene oxide units), Dowfax 2A1 and Disponil A3065 were kindly provided by BASF, DOW and Cognis, respectively. The chemical structures of the surfactants and their main properties are shown in Table S1a and S1b.

Table S1a. Main properties of surfactants used

N°	Name	Type	HLB index	M_w (g mol⁻¹)	CMC (mM)	Cloud Point (°C)
I	Sodium dodecyl sulfate (SDS)	Anionic	40	288	8.2	
II	Sodium dodecyl benzene sulfonate (SDBS)	Anionic	40	348	1.6	
III	Dowfax® 2A1	Anionic	16.7	576	0.2 (with 0.1 wt% NaCl)	
IV	Lutensol® AT50	Non-ionic	18	2460	2	80-95
V	Tween 20	Non-ionic	16.7	1228	0.06	
VI	Tergitol NP35	Non-ionic	14.7		0.096	
VII	CTAB	Cationic	10	346	0.83	

Table S1b. Chemical structures of surfactants used

I		V	
II		VI	
III		VII	
IV	<p>RO(CH₂CH₂O)_xH R = Linear, saturated C₁₆ C₁₈ fatty alcohol, x = 50</p>		

2. Instrumentation

DLS analysis was carried out using a Malvern Zetasizer Nano ZS instrument, using the back-scattered signal at 173° angle from highly diluted samples (1 drop latex in 2 mL DI-water). The cumulant analysis method was used to compute the average particle size Z_{av} .

^1H NMR characterization was performed on a Bruker Avance Spectrometer operating at 500 MHz.

The curing was monitored with a Gemini HR Nano rheometer from Bohlin using a 40 mm cone and plate geometry. The storage and loss moduli were recorded using 1 Hz Stress-controlled oscillations. At the initial stage, the oscillation stress was set at 0.1 Pa, and was successively raised to 5, 300 and 3000 Pa during the sintering of the particles, as the oscillation strain became too weak. The oscillation strain always remained below 25%, within the linear regime.

For cryo-transmission electron microscopy (cryo-TEM) analyses, a thin liquid film of a 5 wt% vitrimer latex suspension was formed onto a commercial holey carbon membrane (Quantifoil R2.1 -Germany) and vitrified by quench freezing into liquefied ethane. The grid was then mounted in a Gatan 626 specimen holder, precooled with liquid nitrogen, and subsequently observed at -180°C , using a Philips CM120 Cryo microscope operating at 120 kV.

Creep experiments were performed on fully cured films (15h@ 150°C , under vacuum). Ca. 1.5 mm thick and 20 mm diameter disks were punched out from the films and tested with a MARS60 rheometer from Thermo Fischer Scientific using a 20 mm plate geometry. For each temperature, the sample was equilibrated while applying a 30N normal force. Rotational creep tests were performed by applying 2 kPa stress for 20-60 min.

Thermogravimetric analysis (TGA) was performed under Argon (50 mL min^{-1}) on a TGA/DSC 1 from Mettler Toledo with the following temperature profile: 1. Heating from

25°C to 150°C at 10 K min⁻¹, 2. Isotherm 3h at 150°C, and 3. Heating from 150°C to 500°C at 10 K min⁻¹.

3. Synthesis of vitrimer particles by miniemulsion polymerization

1. A batch of fatty dimer acid containing pre-dissolved $\text{Zn}(\text{ac})_2$ catalyst at a concentration of 5 mol% /COOH was prepared by adding 5.6 g $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ in 146.2 g fatty dimer acid. The mixture was heated to 130°C under dynamic vacuum for 1h, then the temperature was raised up to 180°C until no evolution of gas could be detected and the catalyst was completely dissolved.

2. Straightforward mixing of the different components and xylene only provides a clear oil phase after extended duration of mixing/sonicating. The following method ensures better reproducibility and minimal addition of xylene to compatibilize the precursors.

i) Dimer fatty acid containing 5 mol% Zn (35.0 g) is predissolved with xylene (24.7 g) to yield the **DA5XYL** solution

ii) In a 150 mL vial are added: 6.91 g of **DA5XYL**, 4.15 g of **PDMS-diepoxy** and 3 mL of xylene (2.6 g). The mixture is stirred and degassed in an ultrasonic bath for a few minutes to yield a clear solution.

iii) In this solution are added 1.14 g of **CS697** and 4.4 mL of xylene (3 g). The mixture is again stirred and degassed to yield a slightly turbid oil phase (17.8 g). Optionally the oil phase can be filtered through 0.4 μm PTFE filters to yield a very clear solution.

3. The miniemulsion was prepared by adding to the oil phase 71 g of aqueous solution containing the surfactant pre-dissolved in deionized water. The mixture is then sonicated using a 750 W VibraCell 75043 apparatus (Bioblock Scientific) equipped with a 13 mm probe. The optimized sonication profile consists in 10 sec ON / 10 sec OFF periods for an overall sonication duration of 10 min, at 66% amplitude.

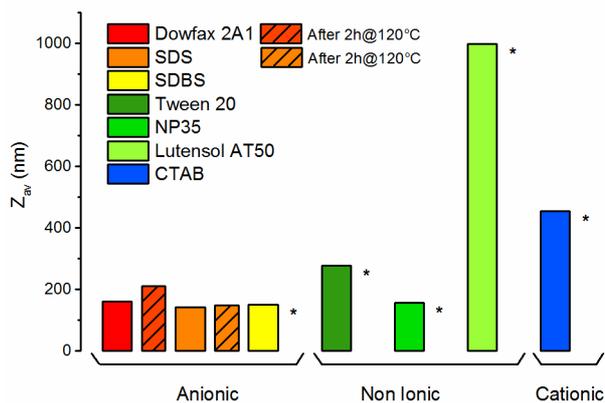


Figure S1. Droplet diameters immediately after 10 min sonication of the miniemulsions with 20 wt% oil content and 10 mM various surfactant solutions. * Indicates that the emulsion was unstable after a few minutes at 120°C.

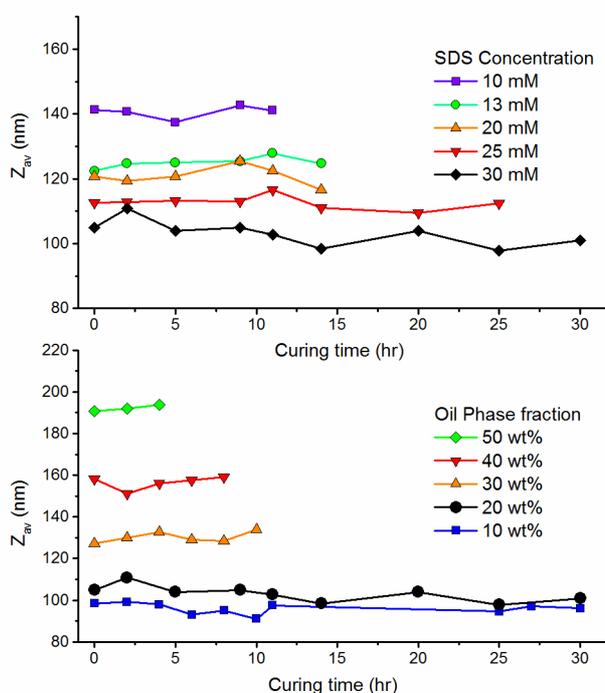


Figure S2. Droplet diameters of the latexes (top: different concentrations of SDS and 20 wt% oil phase, bottom: different oil phase contents and 30 mM SDS) after various curing times at 120°C. For all curves, the last data point immediately precedes destabilization as evidenced by phase separation of the miniemulsion.

4. After sonication, the miniemulsion was transferred in a low pressure, double jacketed 160 mL glass reactor (Series 5100, Paar). It was then stirred at 350 rpm, initially pressurized with 4 bar of N₂ at room temperature, and heated to 120°C with a heating circulator.

4. Analysis of gel fraction of the particles after polymerization.

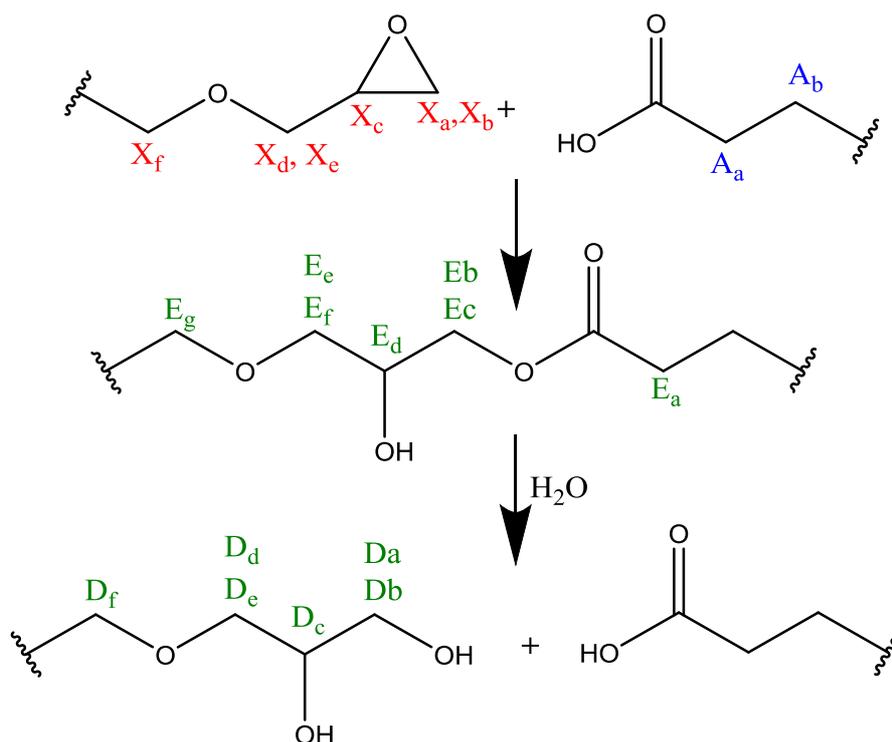
After polymerization, the solids content of the latexes was determined by gravimetry, after drying aliquots at 100°C until constant weight was reached.

In order to measure the gel fraction, THF was added into a known weight of latex until the solution turned clear. The initial weight of epoxy-acid particles in the latex suspension was calculated from the solids content, after subtraction of the corresponding amount of SDS.

Next the THF-latex solutions were dialyzed using semi-permeable cellulose membranes (MWCO 12kD from Roth) and THF as the dialysis solvent. After complete dialysis exchange (48h with frequent changes of dialysis solvent) the content of the dialysis tubes were collected and dried. The gel fraction is the weight ratio after/before dialysis.

5. Analysis of latex composition using ^1H NMR

The latexes were thoroughly dried with high vacuum at room temperature to yield slightly turbid, viscous oils. After dissolution in CDCl_3 , traces of water were further removed by addition of anhydrous $\text{Mg}(\text{SO}_4)$ and filtration.



Scheme S1 – Successive reactions between epoxides and carboxylic acids (catalyzed by Zn(II)), followed by hydrolysis of the β -hydroxyl ester into mono-glycerol.

The mol% fraction of epoxy, β -hydroxyl ester and mono-glycerol were calculated by integration of the corresponding peaks in the ^1H NMR spectra using the following equations:

$$\%epoxy = \frac{I(X_a) + I(X_b)}{I(A_a + E_a)}$$

$$\%ester = \frac{2 * I(E_d)}{I(A_a + E_a)}$$

$$\%m - glycerol = 100 - \%epoxy - \%ester$$

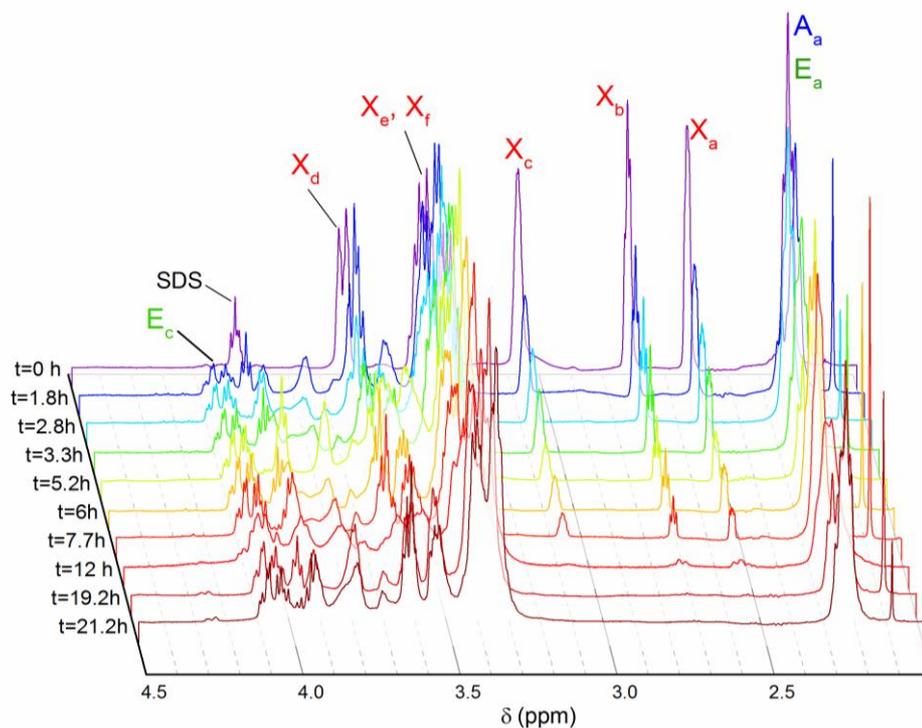


Figure S3a – ^1H NMR spectra (See scheme S1 for attributions) of miniemulsions (30 mM SDS, 20 wt% Oil Phase) cured after various durations at 120°C .

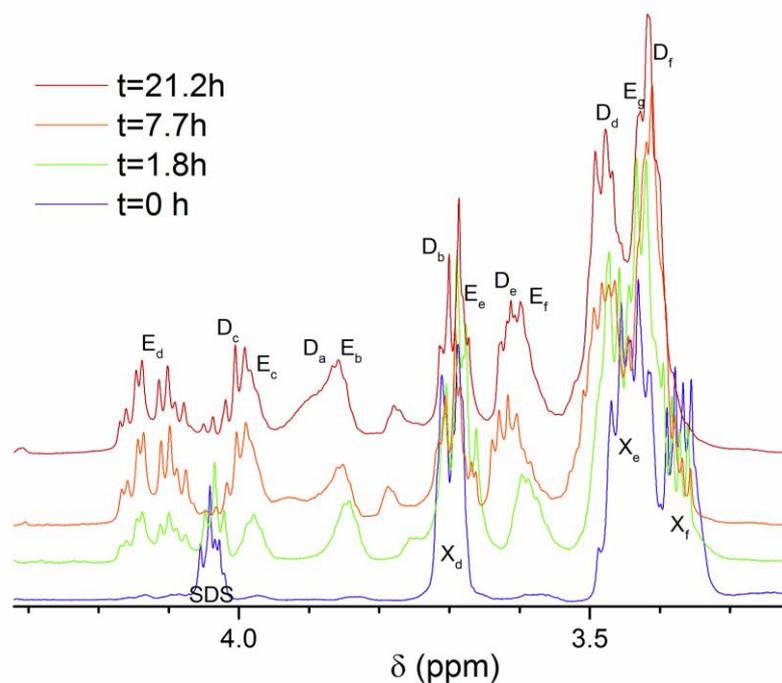


Figure S3b – Close-up of ^1H NMR spectra in the 3-4.5 ppm range.

a. Analysis of gel and sol fractions using ^1H NMR

The gel and sol fractions of sample VP12 were separated by dialysis in THF as described above, and analyzed with ^1H NMR.

In comparison to the VP12 raw sample, the sol fraction shows an increased amount of hydrolyzed species (signal D_c at 4.02 ppm diagnostic of mono-glycerols) whereas the gel fraction shows almost no hydrolyzed species.

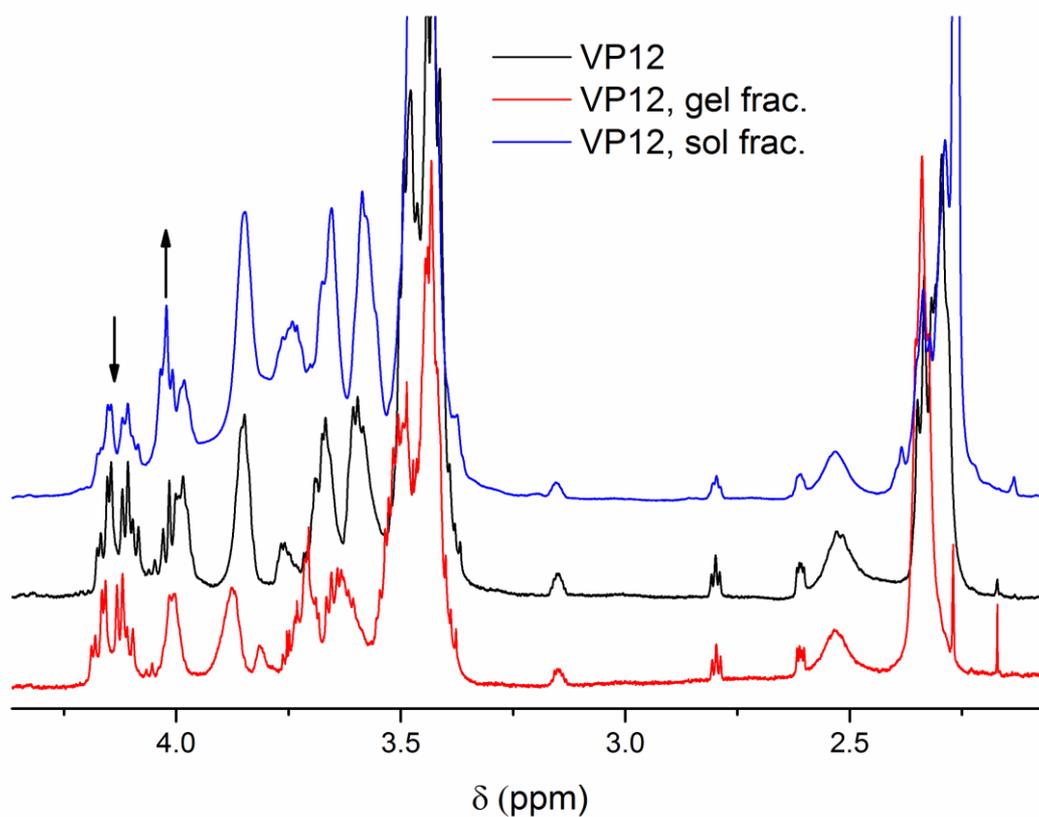


Figure S4 – Enlarged views of ^1H NMR spectra in the 3-4.5 ppm range of sample VP12 as well as its gel and sol fractions separated by dialysis.

6. Rheological analysis of dried latex

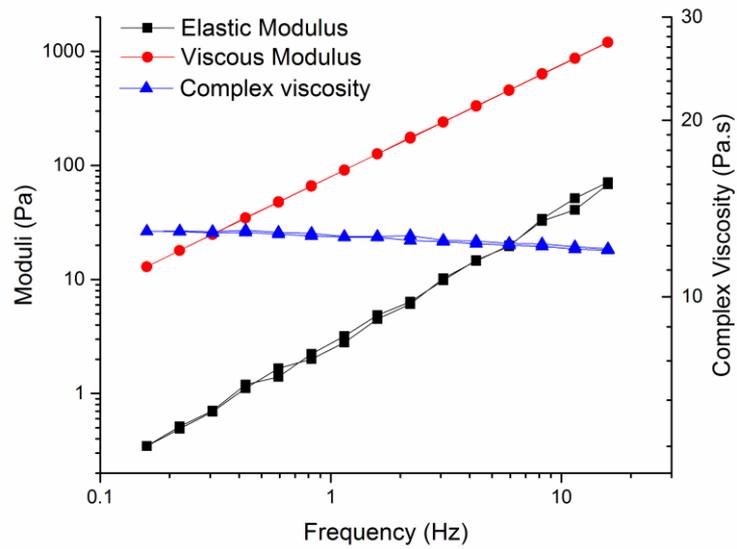


Figure S5a – Frequency-dependent small amplitude oscillations (1% strain) at 25°C on sample VP8, before sintering.

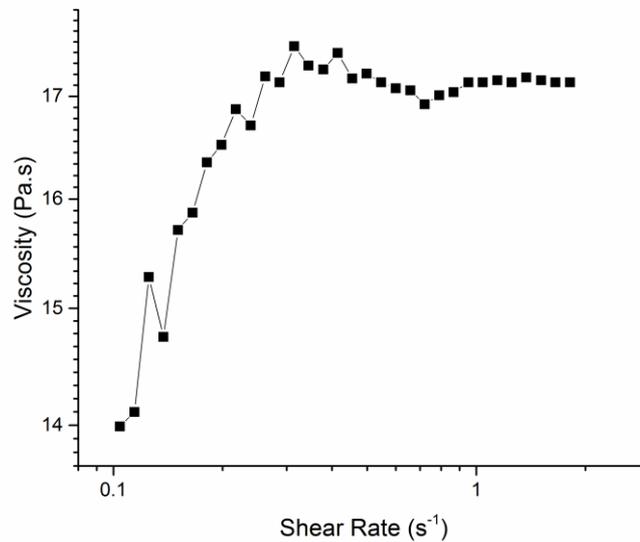


Figure S5b – Rotational flow at 25°C on sample VP8, before sintering.

7. Creep characterization of the cured films.

While performing isothermal steps from 110°C to 200°C, a constant stress of $\sigma = 2$ kPa was applied to the samples and the deformation ϵ monitored. The viscosity as a function of temperature was measured as $\eta = \sigma \left(\frac{d\epsilon}{dt} \right)^{-1}$ after sufficient creep equilibration time. The viscosities were plotted as a function of the reciprocal temperature $1/T$ in order to verify that they obey an Arrhenius law: $\eta = \eta_0 \exp \frac{E_a}{RT}$

8. TGA characterization of VP12.

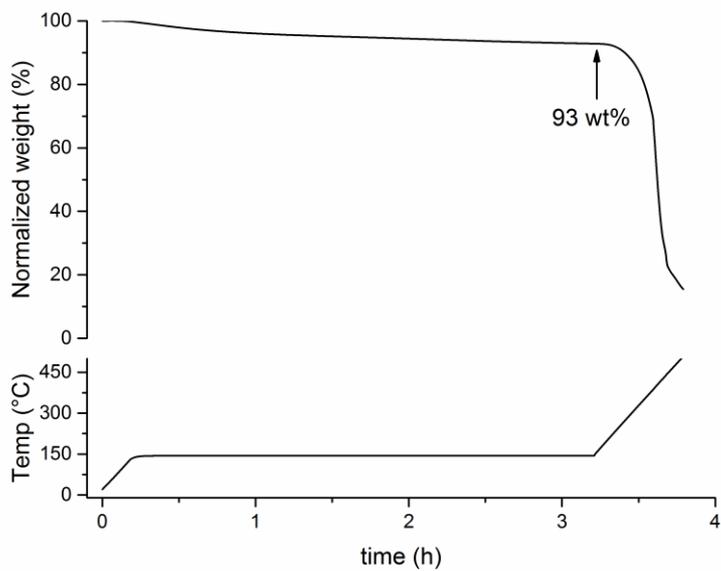


Figure S6– Normalized weight during the TGA characterization of sample VP12.