Supporting Information

Star-epoxy mesogen with 1,3,5-triazine core: a model of $A_4B_3$ fractal polymerization in a liquid-crystalline thermoset media

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I. Materials and general methods

Materials:

Products were purchased from Sigma Aldrich: 4-Cyanophenol 95%, Trifluoromethanesulfonic acid ≥99%, (+)-Epichlorohydrin ≥99%, benzyltrimethylammonium bromide 97%, 2,7-diaminofluorene >97%.

Polymer processing and sample elaboration:

Firstly, TriaEP and 2,7-DAF, in form of powder at RT, have been finely crushed together with two series of 30 min. Then, the polymerization has been done by simple heating of the resulting reactants powder mixture. Concerning the curing protocol, for WAXS/SAXS experiments and POM pattern of the obtained thermoset, it consisted in an isothermal step at 170°C for 1h (It was checked that there is no more evolution of the diffractogram/birefringence after this period). For the DMA, SEM and TGA/DSC the curing protocol was an isothermal step at 170°C for 3h. Concerning the elaboration of DMA
samples, the powder has been pressed under 10 bars in a mold and then cured. The resulting sample was homogeneous without bubbles after this conditioning step.

**Differential Scanning Calorimetry (DSC):**

DSC measurements were carried out on a Mettler-Toledo DSC 1 equipped with STARe© software. This apparatus has a very high sensitivity due to its heat-flux ceramic sensor FRS5 (with 56 thermocouples Au-Au/Pd). Temperature and enthalpy calibrations were performed by using indium and zinc standards. Cross-linking reactions were directly performed in DSC pans, by simple heating. Samples of about 15 mg were placed in 40 µL aluminum crucibles.

**Thermogravimetric Analysis (TGA):**

Thermogravimetric measurements (TGA) were carried out on a TGA/DSC 1 from Mettler-Toledo. The microbalance has a precision of ± 1 µg. Samples of about 15 mg were placed into 70 µL alumina pans. To characterize thermal stability of the thermosets the samples were heated at 10 K.min⁻¹ from 25°C to 900°C under air gas flow of 50 mL.min⁻¹.

**Infrared (FT-IR)**

An infrared Perkin Elmer Spectrum BX II spectrophotometer was used in Attenuated Total Reflectance (ATR) mode, with a diamond crystal. The spectrum of air was recorded as background. A total of 120 scans with a resolution of 1cm⁻¹ have been done by experiment.

**X-Ray diffraction:**

**WAXS:** The Wide Angle X-ray Scattering (WAXS) measurements has been realized with the PANalytical X'PERT Pro diffractometer using a standard copper anode source (λ = 1,54 Å).

**SAXS:** The small-angle X-ray scattering experiments (SAXS) were performed on a Nanostar U-Bruker system equipped with a Vantec 2000 detector (diameter of 200 mm) and an x-ray I µS microsource. The wavelength of the incident x-ray beam was λ = 1.54 Å (Cu Kα) and the beam was collimated by three pinholes.

**Dynamic Mechanical Analysis (DMA):**
The DMA measurements were conducted using a TT DMA Triton Technology, in tension mode. The DMA specimens were prepared in order to have free dimensions of 20x4x1.5 mm$^3$. The tests were carried out by heating the samples from -150 to 300°C at 1K.min$^{-1}$ with a 1Hz oscillating stress. The loss ($E''$), storage ($E'$) Young moduli and damping factor ($\tan \delta = E''/E'$) were determined.

**Nuclear Magnetic Resonance (NMR):**

$^1$H NMR and $^{13}$C NMR characterizations of star-monomer and precursor were recorded in DMSO-$d_6$ with a Bruker AVANCE I instrument with direct probe working at 500.23 MHz for $^1$H and 125.75 MHz for $^{13}$C. The residual solvent signal at 2.50 ppm has been used as a standard reference.

### II. Monomer characterization

**Star-epoxy monomer synthesis:**

*Synthesis of 2,4,6-Tris(p-hydroxyphenyl) triazine.* 500 mg of 4-Cyanophenol (4.197 mmol) was dissolved in 10mL of dry chloroform. The cyclotrimerization proceed in triflic acid (CF$_3$SO$_3$H) media with the addition of 1.9 mL (20.98 mmol) at 0°C. The mixture was stirred at 0°C for 10 min and then keeps under nitrogen and at room temperature for 12 h. The reaction mixture was quenched with a dilute solution of ammonia until neutralization. The reaction mixture was filtered and washed with water. Then, the product was recrystallized from acetone to obtain 455 mg of pure compound as a colorless solid, yield 91%. Melting point: greater than 250°C. $^1$H NMR (500 MHz, DMSO-d6) $\delta$ 10.30 (s, 3H, OH), 8.56 (d, $J = 8.8$ Hz, 6H, Ar-H), 6.98 (d, $J = 8.8$ Hz, 6H, Ar-H). $^{13}$C NMR (125 MHz, DMSO-d6) $\delta$ 170.0 (C=N), 161.7 (Ar-C), 130.6 (Ar-C), 126.5 (Ar-C), 115.5 (Ar-C). NMR analysis of this precursor is in good agreement with the literature$^1$ confirming the synthesized structure.
Synthesis of 1,3,5-Triazine,2,4,6-tris[4-(2-oxiranylmethoxy)phenyl] (TriaEP). 1g on 2,4,6-tris(p-hydroxyphenyl) triazine (2.798 mmol), 20mL of epichlorohidrin and 0.05g of benzyltrimethylammonium bromide as catalyst was charged in a two-necked flask. The mixture was stirred and refluxed for 120 min. Then 0.370g of sodium hydroxide (9.250 mmol) (stoichiometric more 10 wt.-%) were added as 15 wt.-% aqueous solution. After refluxing for another 60 min, the mixture was allowed to cool at room temperature. Then epichlorohydrin was removed under vacuum at 80°C and the residue was thoroughly washed several times with distillated water and dried again under vacuum. Finally the product was purified by recrystallization from toluene, and then dried under vacuum at 80°C during 2h to give 1.34g of a white powder. Noticed that the product is stable and can be stored at RT for weeks. Yield 95%, ^1^H NMR (500 MHz, DMSO-d6) δ 8.65 (d, J = 8.9 Hz, 6H, Ar-H), 7.19 (d, J = 8.9 Hz, 6H, Ar-H), 4.49 (dd, J = 11.4, 2.5 Hz, 3H, CH$_2$ of glycidyl), 3.97 (dd, J = 11.4, 6.6 Hz, 3H, CH$_2$ of glycidyl), 3.39 (m, 3H, CH of epoxy), 2.89 (dd, 3H, CH$_2$ of epoxy), 2.78

Figure S1. H-NMR spectra of TriaOH synthesized molecule.
(dd, $J = 5.0, 2.6$ Hz, 3H, CH$_2$ of epoxy). $^{13}$C NMR (125 MHz, DMSO-d$_6$) $\delta$ 170.1 (C=N), 162.1 (Ar-C), 130.5 (Ar-C), 128.2 (Ar-C), 114.7 (Ar-C), 69.2 (CH$_2$ of glycidyl), 49.5 (CH of epoxy), 43.7 (CH$_2$ of epoxy). The classical glycidyl NMR shifts are in good agreement with the literature.$^2$

![Figure S2. H-NMR spectra of TriaEP synthesized molecule.](image)

Molecular Weight: 525.5 g.mol$^{-1}$
**Figure S3.** a) TriaEP spectrum of ESI-MS: [M + H]$^+$ = 526.3 g mol$^{-1}$ quasi molecular mass; enhanced resolution experiment (zoom scan) confirms isotropy; b) MS/MS experiment under CID condition (isolation width: 1.5 m/z; NCE: 40%).

Structure of TriaEP was confirmed through fragmentation with:

m/z 482: [M + H − 44]: loss of C$_2$H$_4$O: $\text{Δ}$

m/z 470: [M + H − 56]: loss of C$_3$H$_4$O: $\text{Δ}$

m/z 176: correspond to the following substructure C$_{10}$H$_{10}$NO$_2^+$:

III. Polymer characterization

1) FT-IR investigation:

Epoxy/amine cross-linking has been confirmed by FT-IR investigations, as observed in Figure S4, with the decrease of the peak at 916 cm$^{-1}$ sign of oxiran ring consumption and the
peak apparition at 1217 cm\(^{-1}\) which could be attributed to the aromatic C-N stretching of tertiary amine groups. The shift at 1360 cm\(^{-1}\) could also be correlated with C-N stretching of the secondary amine groups.

\[ q = 4\pi \sin\left(\frac{\theta}{2}\right)\lambda \]

characterized by the scattering angle \( \theta \) and the wavelength \( \lambda \) of the scattered beam.\(^3\)

Figure S4. FT-IR spectra of TriaEP monomer and 2,7 DAF cross-linker in regard to the resulting cross-linked polymer.

2) X-ray investigation:

The momentum transfer \( q \), also called the scattering vector, is defined as:

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characterized by the scattering angle \( \theta \) and the wavelength \( \lambda \) of the scattered beam.\(^3\)
Figure S5. Intensity of SAXS versus $q$ of highly cross-linked TriaEP/2,7-DAF thermoset plotted on log-log scale.

Reference: