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COMMUNICATION

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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A star-epoxy monomer (TriaEP) has been synthesized by creation of a 1,3,5-triazine core. Its association with an aromatic di-amine reveals an A_4B_3 cross-linked polymer which exhibits a complex mechanism of self-assembly. These architectural aspects, resulting from both fractal polymerization and mesophase growing, will be discussed in regard to its outstanding thermo-mechanical properties.

Three-armed mesogens also called star-shaped mesogens with an idealized C_3 -symmetry are a fascinating platform for the exploration of self-assembly process into complex hierarchical and functional soft materials.¹ Compared with conventional mesogens cores design such as rod-like² or disc-like³ shapes the multiarm-mesogens self-assembly, extends to dendrons, dendrimers^{4,5} or supramolecular mesogens,⁶ are driven by the nanosegregation of building blocks and their proclivity of efficiency fill the space in condensed matter.⁷ In contrast to these assumptions, star-mesogens family can also be self-organized into nematic, lamellar, columnar or cubic phases.^{3,8} This study focus on octopolar 1,3,5-triazine derivatives which are well known for the development of organic light emitting diodes (OLEDs)^{3, 9} and for its various biocide properties.^{10,11} Herein, the design of a star-epoxy monomer has been investigated to explore its proclivity of self-assembly in a tridimensional architecture, from the three-armed oligomer, obtained on the first stage of polymerization in a pre-gel state, to the macromolecule and infinite network at the post-gel state.¹² The epoxide function has been chosen due to its versatility and propensity to design a myriad of elastomers, thermoset architectures and supramolecular polymers.^{13,14,15} This work emphasis on the elaboration of a liquid-crystalline thermoset (LCT)^{16,17} with an A_4B_3 architecture, provided by

polymerization with an aromatic di-amine cross-linker having a rod-like geometry : the 2,7-diaminofluorene (2,7-DAF). The choice of the cross-linker is the key of the self-assembly design. Its functionality and chemical structure such as the length, the aromaticity and the hydrophobic/hydrophilic balance, are to be taken into account for the network conception.^{13,14} The construction of an anisotropic network may depends on both π - π stacking and hydrogen bonds of secondary groups induced by either polymerization reactions or by considered cross-linker.^{18,19} Some studies also highlight the important contribution of alkyl moieties as entropic reservoir for mesophase design.²⁰ The synthesis of star-epoxy monomer

1,3,5-triazine,2,4,6-tris[4-(2-oxiranylmethoxy)phenyl] called TriaEP is summarized on Figure 1 (a). The central 1,3,5-triazine core is synthesized from an acid catalyzed cyclotrimerization using 4-cyanophenol as precursor. The resulting compound is 4,4',4''-(1,3,5-triazine-2,4,6-triyl)triphenol (1).^{21,22} Then, the tri-epoxydation of (1) to get (2) has been done by adapting Mikroyannidis²³ protocol. The synthesis details, and the physico-chemical characterizations are presented in Supporting Information.

The DSC thermogram of TriaEP monomer exhibits two endothermic peaks as shown in Figure 2 (a). These phenomena could be respectively associated to the succession of transitions from a solid crystal to a liquid-crystalline phase and eventually to an isotropic liquid phase.²⁴ In agreement with polarized optical microscopy (POM), the liquid-crystalline phase is stable in the temperature range from 130 to 152°C. The TriaEP birefringence at 140°C (Figure 2 (a)) reveals a dense texture, characteristic of an ordered organization¹⁷, such as nematic discotic (N_D) or nematic columnar (N_C) mesophase. This kind of self-assembly can be observed in the case of mesogens built from 1,3,5-triazine core.³

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Electronic Supplementary Information (ESI) available: contain details on apparatus, monomer synthesis and characterization, FT-IR and SAXS of resulting polymer. See DOI: 10.1039/x0xx00000x

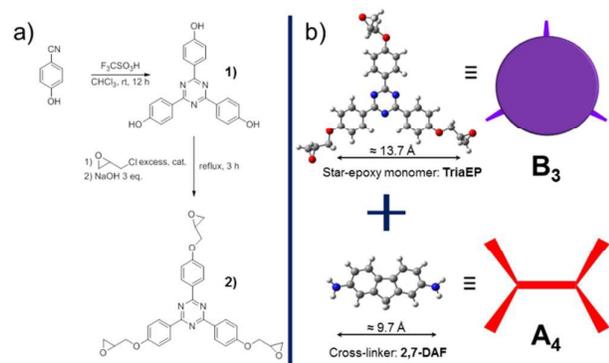


Fig. 1 Star-epoxy monomer synthesis: yields: (1) 91%, (2) 95% (a); monomer and cross-linker to design A_4B_3 TriEP/2,7-DAF polymer. Distances were calculated with Gaussian03 software²⁵ with DFT method at the B3LYP/6-311G+ level of theory (b).

TriEP/2,7-DAF polymer exhibits an A_4B_3 structure (Figure 1 (b)) with a stoichiometric ratio of monomer and cross-linker.¹³ These components in powder form have been finely crushed together and put in the DSC pan to measure the heat flow evolution in dynamic scanning temperature mode. An endothermic peak around 123°C is observed and it could be associated with the TriEP and 2,7-DAF mixture melting (Figure 2 (b)). This phenomenon is immediately followed by an exothermic event corresponding to the epoxy-amine reaction.¹³ The polymerization reaction starts as soon as a part of the components became more reactive by transition to a liquid phase. This related exothermic event occurs around 150°C. The very steep slope of the curve is characteristic of epoxy-amine cross-linking in a liquid-crystal media because the ordered state favours the crosslinking reaction.¹⁶ In the present study, the occurrence of epoxy/amine cross-linking has been checked by infrared spectroscopy as depicted in the Supporting Information (Figure S4). The network anisotropy was confirmed by the birefringence of Schlieren texture observed by POM (Figure 2 (b)). As described for their calamitic mesogen homologues, the nematic mesophases issued from discotic mesogen (N_D , N_C) exhibit the same symmetry and thus exhibit also a Schlieren texture.³

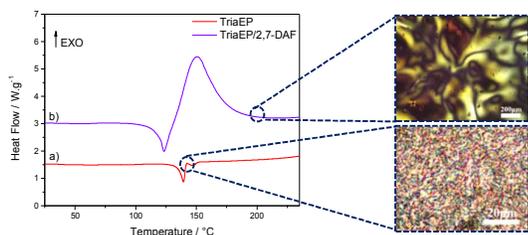


Fig. 2 Corroboration between DSC thermogram of TriEP monomer at 5 K/min⁻¹ a); TriEP/2,7-DAF at 20 K/min⁻¹ b) and the textures of mesophases obtained by POM.

In Figure 3 (a) WAXS profile shows a diffraction peak at 4.4 Å for TriEP molecule at 140°C in liquid-crystalline state. This distance typically corresponds to the π - π stacking space

between two conjugated aromatic plane rings that are two TriEP discs. Furthermore, it could be associated to the lateral average distance between two discs.^{3,26} Meanwhile, TriEP/2,7-DAF polymer cured during 1h at 160°C exhibits a major diffraction peak at 5.0 Å, provided by the cross-linking. This can be associated to the polymer nematic organization, and more precisely related to the distance between two π -delocalized systems, possibly including the 2,7-DAF cross-linker. The weak intensity of WAXS peaks is characteristic of this kind of anisotropic thermoset as it was reported in the literature.²⁷ Because of the amorphous character of epoxy/amine network, the generated anisotropy is not comparable to a well definite classical mesophase. However, some molecules issued from this network are able to self-organise into preferential directions. Without the intervention of an external stress such as magnetic field, these self-organised regions are structured at the micro-scale on polydomains, each domain possessing a specific preferential orientation.²⁸

The presence of a diffraction peak at 55.2 Å could be associated to a long range order induced by the presence of columnar structure composed by TriEP discs and/or due to the diameter of dendritic-like shape as fractal hyper-branched polymer colloids.²⁹ Indeed, this result is unexpected considering the abundant literature on Liquid Crystalline Epoxy Resin (LCER), where the longer measured order for a smectic frozen mesophase (calamitic monomer) was found in the range from 15 to 30 Å. The lamellar length of such smectic mesophase is generally conditioned by its constitutive building blocks dimensions.^{19,30,27} Herein, if we compare WAXS results with the computed distances of TriEP and 2,7-DAF (seen on Figure 1 (b)), the occurrence of a smectic mesophase could not be envisaged. This last hypothesis of the polymer colloid presence could be related to the cryo-fracture morphology of the fully cured polymer observed by SEM (Figure 3 (b)). The observed nodular surface structure is characteristic of fractal polymers (FPs), commonly derived from three-arms connectors with a rod-like spacer, as for TriEP/2,7-DAF polymer.¹⁷ Furthermore, Aharoni et al.²⁹ explained that primary structural unit of a FPs is formed by dense colloidal particles of diameter of around 50 Å. To support this assumption of a cross-linking model based on fractal growing, the dependence of scattering intensity $I(q)$ versus the momentum transfer vector q (available on Supporting Information) has been measured by SAXS. The intensity of SAXS analysis of fractal objects can be described by the Equation (1). An exponent power between 3 and 4 is an indication of the fractal nature of the thermoset network (Equation (1))^{31,32,33} with a mass fractal dimension (D_f) between 3 and 4 and a surface fractal dimension (D_s) between 2 and 3 (Equation (2)).

$$I(q) \propto q^{-D_f}; 3 < D_f \leq 4 \quad (1)$$

With

$$6 - D_s = D_f; 2 \leq D_s < 3 \quad (2)$$

The results summarized in Table 1 corroborate the supposition of a fractal growing nature of this A_4B_3 anisotropic epoxy-amine network with a D_s value of 2.5. Since $D_s = 2$ corresponds to a smooth surface and increases toward 3 for a corrugated one,³⁴ this intermediate value of 2.5 could be explained by a balance contributions of two antagonist factors: i) the tri-dimensional hyper-branched cross-linking of amorphous thermoset (toward to $D_s = 3$); ii) the propensity of matter organization through the creation of the mesophase (toward to $D_s = 2$). This hypothesis, illustrated in Figure 4, could be related to the unusual reactivity of epoxy/amine crosslinking in liquid-crystalline media described in the literature.^{35,36} Thus, the first stage of polymerization could promote the 3D branching (due to the secondary amine attack) vs the 2D linear growing (reaction with primary amine) due to a proximity of the electrophile site.

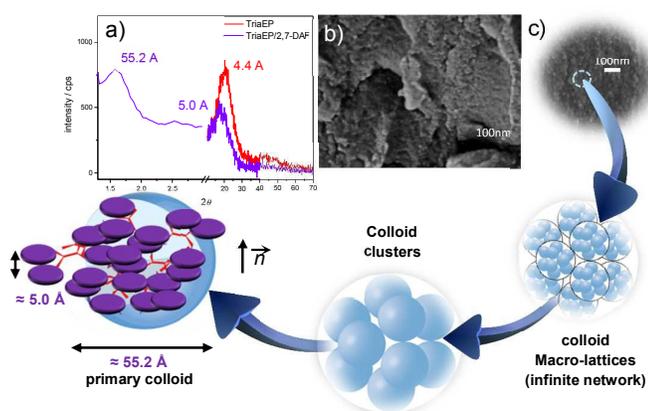


Fig. 3 WAXS pattern for TriEP monomer at 140°C and TriEP/2,7-DAF polymer cured at 170°C for 1h (a); SEM fracture surface of fully cured network (b); model of TriEP/2,7-DAF network self-assembly inspired by the Genealogically Directed Synthesis (GDS) which mimic the fractal abiotic molecular self-assembly of biological system (c).³⁷

From a geometrical point of view, a model of fractal growing based on the Voronoi tessellation concept³⁸ has been already proposed for two-dimensional networks building, and may be extended for the description of three-dimensional systems.²⁹ Another approach to model the development of such architecture could be associated to the Genealogically Directed Synthesis (GDS) concept. This strategy, inspired by the biological self-assembly of protein aggregation³⁹ or nucleotide pairing⁴⁰ for instance, can be assimilated to a general scheme to design hyper-branched covalent assemblies.³⁷ Thus, as depicted in Figure 3 (c), a model of self-assembly have been proposed, combining the mesophase occurrence with the fractal aggregation development: from primary colloids to an infinite covalent bonded network.^{41,42} This model is also in a good accordance with the classical network morphology described by Dusek⁴³ who considers a microgel agglomeration into clusters and their coalescence.

As specified by Baer et al.,⁴⁴ information concerning the self-organization of hierarchical structures can be useful to have an overview of the nanoscopic complexity and to be able to envision the desired spectrum of functional properties. Thus, this biomimetic model could be a good approximation in regard to the fractal development which is a recurrent scheme to describe the great variety of natural structures.⁴⁵ The $\tan \delta$ curves of Figure 5 (a) make the distinction between three relaxations, commonly called γ , β , α , in an ascending temperature range order, and associated to the mobile chains of the polymer.⁴⁶ TriEP/2,7-DAF polymer is characterized by a main cooperative α transition at 220°C for a curing temperature of 170°C for 3h. This very high transition temperature is usually found for aromatic cross-linked networks.^{16,47} The weak amplitude of α relaxation peak could be explained by a very dense network due to a high functionality of its building block as well as to its mesogenic character. Indeed, Ortiz et al.²⁸ explained this molecular constraint by a restriction of the cross-link motions from all directions, imposed by the supramolecular self-assembly associated to the randomly oriented mesophases in poly-domains. The residual segmental mobilities in an interval temperature below T_{α} , such as β transitions at 85°C, could be correlated to the crankshaft motion of the $-N-CH_2-CH(OH)-CH_2-$ segment in the epoxy-amine network. This high temperature for a β relaxation indicates the toughness properties of the material.⁴⁶ The γ relaxation is generally associated to the rotational contributions (e.g. the hydroxyl groups generated during the epoxy-amine reaction). This relaxation which occurs at -62°C could be also associated to the sub-motions of methylene groups from epoxy-amine segments.⁴⁸

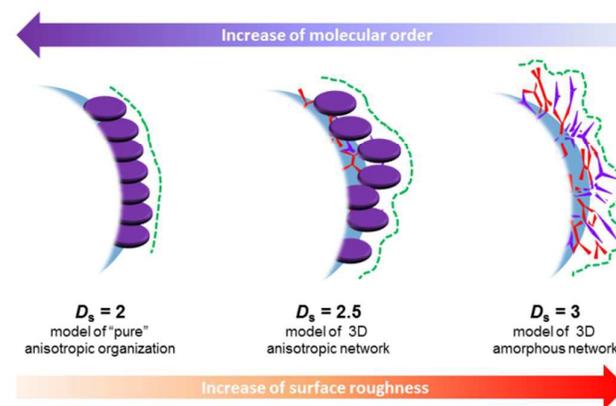


Fig. 4 Models of colloid surfaces depending on the D_s value in regard to amorphous polymer architecture and anisotropic organization factors.

The polymer exhibits a modulus of $E' = 2.41$ GPa at room temperature. However the most notable result concerns the extremely high value of $E' = 690$ MPa in the rubbery region, above T_{α} , even for a liquid-crystalline epoxy networks. For the sake of comparison, Ortiz et al.²⁸ measured a modulus of $E' = 115$ MPa for a very ordered smectic epoxy thermoset network on the rubbery plateau. This unusual high value of modulus

plateau is a characteristic of mesogenic tri-dimensional networks. Indeed, in the case of anisotropic networks, secondary interactions such as π -stacking can become preponderant at the glass transition. These interactions can be strong enough to permit to the network to conserve certain integrity. Indeed, the deformation is mostly dominated by the entropic response and the mobility of the aliphatic part from epoxy ring-opened group.²⁸

Table 1 X-ray d-spacing and scattering exponents

TriaEP/2,7-DAF polymer	X-ray d-spacing (\AA)		mass fractal dimensions D_f	surface fractal dimensions D_s
	short range	long range		
WAXS	5.0	55.2	-	-
SAXS	-	-	3.5	2.5

This particularity allows to the polymer architecture to conserve its organized structure integrity above T_α until thermal degradation (around 270 °C as seen on Figure 5 (b)). Noticed that the DSC curve (Figure 5 (b)) of the resulting polymer do not present any thermal event before degradation. That suggests two facts: we reach a maximum extend of cure and the LC phase is well frozen on the tridimensional network. Then concerning the material thermo-degradation profile, a two steps thermal decomposition mechanism could be observed within 25-800°C temperature range. A first thermo-degradation reaction, the cleavage of the network, occurs around 350°C highlighting the good thermal resistance of such LCER.⁴⁹

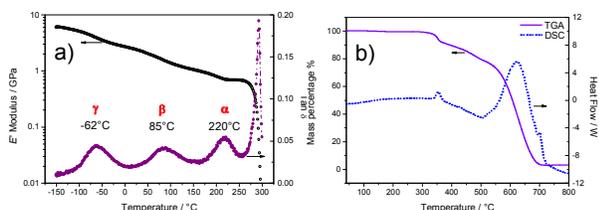


Fig. 5 tan δ and E' modulus curves from DMA experiments in traction mode for TriaEP/2,7-DAF polymer at 1Hz and 1K.min⁻¹ (a); mass percentage and heat flow curves from TGA/DSC measurement at 10K.min⁻¹ under air (b).

The material loses 10% of its initial mass at 393°C. As observed in Figure 5 (b), the slope of the TG curve, which is proportional to the degradation rate, is very slow in this temperature domain. This is a proof of the material stability against temperature, being degraded only in proportion of 30% at 500°C. This peculiar behavior underlines the high thermo-stability of this material.⁵⁰ The starting temperature domain of degradation of the polymeric network is well correlated with the DSC results. According to the literature,⁵¹ the first degradation step can be mostly associated to two reactions: the elimination of water accompanied by the formation of an alkene group⁵² and the nucleophilic chain scission with the formation of N-methyldiamines.⁵⁰ Considering the water evaporation as an endothermal event, the small exotherm in

DSC curve at 354°C could be mainly associated to the nucleophilic scission reaction.⁵³ However a deeper investigation on this complex phenomenon is necessary to confirm and complete this hypothesis. Another exothermic peak observed in DSC at 621 °C should be correlated with the photo/thermo-oxidation and carbonization of the aromatic moieties. This second degradation mechanism occurs very fast, with a complete degradation of the material without any residual products for a temperature higher to 700°C.

Conclusions

In this work we report, at our present knowledge, the first study of a star-shaped epoxy mesogen molecule, called TriaEP, synthesized with a very good yield. This new molecule presents a liquid-crystalline behaviour. Although its important potential as precursor of C₃-symetric supramolecule, the present investigation was focused on its reactivity as monomer. In association with an aromatic di-amine having a rod-like geometry (2,7-DAF), the unusual A₄B₃ polymer structure reveals a hierarchical self-organization. A proposition of polymer growth mechanism has been supported as a balance contribution between the tri-dimensional fractal amorphous cross-linking and of the propensity of matter organization through the creation of mesophase. The resulting network possesses high thermo-mechanical properties. This study offers many exciting perspectives on the study of three-armed epoxy mesogen monomers and on their process of self-assembly in a polymer network. In term of applications, these kinds of materials could cover a large panel of fields: materials for non-linear optics (NLO), medicine and superamphiphobic films for instance. Another interesting application could be the design of microporous materials by the creation of an A₂B₃ network.

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