European Polymer Journal 70 (2015) 286–305

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

# Structural analysis of the curing of epoxy thermosets crosslinked with hyperbranched poly(ethyleneimine)s

Xavier Fernández-Francos [a],*, Xavier Ramis [b]

[a] Department of Analytical and Organic Chemistry, Universitat Rovira i Virgili, c/Marcel·lí Domingo s/n, 43007 Tarragona, Spain
[b] Thermodynamics Laboratory, ETSEIB, Universitat Politècnica de Catalunya, Av. Diagonal 647, 08028 Barcelona, Spain

ARTICLE INFO

*Article history:*
Received 30 April 2015
Received in revised form 9 July 2015
Accepted 17 July 2015
Available online 18 July 2015

*Keywords:*
Epoxy
Crosslinking
Hyperbranched polymer
Gelation
Network structure

ABSTRACT

The network build-up process during curing of an epoxy resin using a hyperbranched poly(ethyleneimine) as crosslinking agent has been studied from a theoretical and experimental point of view. A systematic analysis taking into account the stoichiometry of the curing process has been performed. Conversion at gelation has been studied by thermomechanical analysis (TMA) and differential scanning calorimetry (DSC). Crosslinking density has been studied by dynamomechanical analysis (DMA). Gel fraction after extraction in organic solvents has also been determined. The experimental results have been compared with a theoretical network build-up model based on the random recombination of structural fragments, showing good agreement between theory and experimental results, but deviations from the ideal epoxy-amine polycondensation appear as a consequence of the dilution of the hyperbranched crosslinker in off-stoichiometric formulations.

## 1. Introduction

Hyperbranched polymers (HBPs) are multi-functional polymers that have unique attractive features [1], such as their high degree of branching, which makes them less viscous than their linear counterparts with a similar molecular weight, and their high reactivity, given their elevated concentration of surface groups that can be modified in order to fine-tune their physical/chemical compatibility with other polymers, substrates or resins. In addition, they can be synthesized with relative ease, in batch or semi-batch processes. For that reason, they have a more disperse, less perfect structure than perfect dendrimers, but they have the advantage that no intermediate purification steps are required in their synthesis, leading to a good compromise between affordable cost and properties. In the field of thermosetting polymers, one of their most relevant applications is as toughening agents that phase-separate during curing [2–10], but it is also of interest their role as reagents that get incorporated into the network structure [11–17].

The use of hyperbranched poly(ethyleneimine)s produced by BASF under the tradename of Lupasol™ as crosslinking agents in diglycidyl ether of bisphenol A (DGEBA) formulations was recently studied with certain detail, focusing on their effect on the curing kinetics [16] and thermomechanical properties [17] The curing process is an epoxy-amine polycondensation between the epoxy groups and the primary and secondary amine groups in the polymer structure, leading to similar materials to those obtained in the crosslinking process with smaller aliphatic amine curing agents [16]. Off-stoichiometric formulations with excess of epoxy groups can be fully cured in the presence of a suitable anionic initiator such as

---

* Corresponding author.
*E-mail address:* xavier.fernandez@urv.cat (X. Fernández-Francos).

http://dx.doi.org/10.1016/j.eurpolymj.2015.07.031
0014-3057/

1-methylimidazole, leading to highly crosslinked materials [17]. However, a rigorous treatment on the effect of hyperbranched poly(ethyleneimine)s in terms of network build-up process is missing.

Random statistical procedures are commonly used to study the structure of hyperbranched polymers, but a series of deviations from the ideal situation are expected due to substitution effects during polymerization, the occurrence of side reactions and intramolecular cyclization [18–25]. The high mass-average molecular weight and polymer dispersity of the resulting polymers can be controlled by means of the addition of small core molecules [18,19,26], a feature that can be easily incorporated into statistical models. The use of highly branched precursors in polymer networks, including hyperbranched polymers, has been rigorously studied from a theoretical point of view by Dušek and co-workers [27–30]. Hyperbranched polymers may be obtained by semi-batch, slow monomer addition procedures, leading to narrower polymer dispersities [31,32], but in this case the hypothesis of the random polymerization may not apply, therefore a different methodology should be used. Hyperbranched poly(ethyleneimine)s are obtained from the polymerization of aziridine. The process is complex [33–35], involving the participation of a number of nucleophilic and electrophilic species. Chain-transfer events are frequent, leading to an approximate ratio of primary, secondary and tertiary amines of 1:2:1 [34]. This amine ratio coincides with the expected distribution of terminal, linear and branching units for a random polymerization of $AB_2$ monomers. An analogy between $AB_2$ polycondensation and ring-opening multi-branching polymerizations can be established [31], and therefore it is hypothesized that the methodologies applicable to HBPs obtained by random polycondensation processes can be also used for poly(ethyleneimine) polymers. The batch synthesis of hyperbranched polyethyleneimines in aqueous solution has been reported [36], leading to polymers with an amine ratio of approximately 1:2:1 determined by NMR. However, commercial polymers may have different amine ratios, about 1:1:1 [36], and with very narrow polymer distribution [37], indicating that the synthetic procedure may be different such as slow monomer addition [31] or else have been synthesized with the addition of a core molecule to control the polymer distribution, as reported in the patent literature [38].

In the present work, a probable structure and polymer distribution of the hyperbranched poly(ethyleneimine)s is generated on the basis of the available structural information provided by the supplier, such as the mass-average molecular weight, $M_w$, and the distribution of primary, secondary and tertiary amine groups, and taking into consideration the presence of a core molecule in the polymer structure. This likely polymer structure is then used as an input for a crosslinking process with DGEBA, following an epoxy-amine polycondensation mechanism. For the derivation of representative statistical averages corresponding to the polymer structure and the crosslinking stage, a recursive method based on the expectation probability described by Miller and Macosko [39–41] is used, making use of the definition and random combination of structural fragments [42–44]. The global approach is similar to that of multi-stage processing, and to that used in other theoretical treatments on the use of hyperbranched polymeric precursors [27–30,43]. The crosslinking process is simulated assuming ideal polycondensation behaviour [27]. Nonideal features such as reduced secondary amine reactivity, high dilution of the amine crosslinking agent or intramolecular loop formation, are also considered and discussed from a qualitative point of view. The crosslinking process of epoxy-amine systems has been studied extensively in the literature from a theoretical point of view [42,45] but the use of hyperbranched crosslinkers in epoxy-amine systems has not been studied yet. The theoretical model developed in this work is compared with the experimental analysis of DGEBA formulations containing a hyperbranched poly(ethyleneimine), Lupasol™ FG, with different epoxy-amine stoichiometric ratios. Diethylene triamine (DETA) is also studied as a means of comparison and for validation purposes. Conversion at gelation, crosslinking density and gel fraction are the key structural parameters that are analyzed. Gel point conversion is determined using a combination of thermo-mechanical analysis (TMA) and dynamic scanning calorimetry (DSC). The crosslinking density of cured samples is determined by dynamomechanical analysis (DMA). Gel fraction is determined after reflux extraction with suitable solvents.

## 2. Experimental

### 2.1. Materials

Diglycidyl ether of Bisphenol A (DGEBA) (Aldrich) with an epoxy equivalent weight of ca. 174 g/mol was used as base epoxy resin. Hyperbranched poly(ethyleneimine) LP800 (Lupasol™ FG, $M_w = 800$ g/mol, BASF) was used without further purification. Diethylenetriamine (DETA) was purchased from Aldrich and used as received. Anhidrous methylene chloride was purchased from Aldrich.

Different stoichiometric and off-stoichiometric epoxy-amine formulations were prepared and analyzed in order to validate the HBP structural model and the network build-up model used in this work. The formulations have been coded as *LP800-X* or *DETA-X*, where X represents the ratio between reactive amine hydrogens and epoxy groups in the formulation, *r*. For the LP800 formulations, the mass per reactive hydrogen calculated and shown in Table 1 was used. The samples were prepared by adding the corresponding amounts to a glass vial and homogenization by mechanical stirring. The samples were analyzed immediately after preparation or were cured in an open mould for 2 h a 100 °C and subsequently postcured at 180 °C for 1 h (postcuring was not performed in formulations with $r < 1$ to prevent the occurrence of epoxy anionic homopolymerization catalized by the tertiary amines). Details and composition of the formulations are shown in Table 2.

**Table 1**
Structural parameters of the crosslinking agents under study (see the theoretical section and Supporting Information for details on the specific expressions used).

| | LP800 | DETA |
|---|---|---|
| $M_w$ (g/mol) | 800[a] | 103[b] |
| $n1{:}n2{:}n3$[c] | 1:0.82:0.53[a] | 1:0.5:0[b] |
| $\lambda$ (Eq. (5)) | 0.125 | – |
| $M_n$ (g/mol) (Eq. (6)) | 404 | 103[b] |
| $M_w/M_n$ | 1.98 | 1 |
| g/eqH (Eq. (7)) | 33.67 | 20.6 |
| g/eqN (Eq. (8)) | 40.40 | 34.33 |
| $f_w$ (Eq. (9)) | 18.60 | 5[b] |
| $a1{:}a2{:}a3$[c] | 0.979:0.704:0.432 | 1:0:0 |
| $c1{:}c2{:}c3$[c] | 0.021:0.116:0.098 | 0:0.5:0 |

[a] Obtained from the material data sheet.
[b] Determined from the monomer structure.
[c] Expressed with respect the total amount of primary amine groups $n1$.

**Table 2**
Composition of the formulations studied in this work.

| Formulation | $r$ | $m_{epoxy}$ (g/g$_{\text{total}}$) | $m_{amine}$ (g/g$_{\text{total}}$) |
|---|---|---|---|
| LP800-0.2 | 0.2 | 0.9627 | 0.0373 |
| LP800-0.4 | 0.4 | 0.9282 | 0.0718 |
| LP800-0.6 | 0.6 | 0.8960 | 0.1040 |
| LP800-0.8 | 0.8 | 0.8659 | 0.1341 |
| LP800-1 | 1 | 0.8379 | 0.1621 |
| LP800-1.2 | 1.2 | 0.8115 | 0.1885 |
| LP800-1.4 | 1.4 | 0.7868 | 0.2132 |
| LP800-1.6 | 1.6 | 0.7636 | 0.2364 |
| DETA-0.4 | 0.4 | 0.9548 | 0.0452 |
| DETA-1 | 1 | 0.8941 | 0.1059 |

### 2.2. Characterization techniques

A differential scanning calorimeter Mettler DSC821e calibrated with indium standards has been used to study the curing of the different formulations. Samples of ca 10 mg were placed inside an aluminum pan with a pierced lid and cured at 2 °C/min, from −50 to 200 °C, under nitrogen atmosphere. Assuming that the reaction heat evolved is proportional to the reaction of epoxy groups, the degree of conversion of epoxy groups $x$ can be determined using the following expression

$$x = \frac{\Delta h}{\Delta h_{total}} \cdot x_{theor}, \tag{1}$$

where $\Delta h$ and $\Delta h_{total}$ are the reaction heat released up to a temperature $T$ and the total reaction heat evolved during the dynamic experiment, corrected by the maximum degree of conversion achieved, $x_{theor}$, determined from the expected heat released per epoxy group for complete conversion $\Delta h_{theor}$ as

$$x_{theor} = \frac{\Delta h_{total}}{\Delta h_{theor}} \tag{2}$$

The glass transition temperature ($T_g$) of the samples cured following the schedule defined in the preceding section was determined by a scan at 10 °C/min, as the half-way point in the jump in the heat capacity step, following the DIN 51007 method in the STARe software by Mettler. The heat capacity step $\Delta C_p$ during the glass transition was also determined likewise.

Cured samples were analyzed with a FTIR spectrometer Bruker Vertex 70 with an attenuated total reflection accessory with thermal control and a diamond crystal (Golden Gate Heated Single Reflection Diamond ATR, Specac-Teknokroma) and equipped with a mid-band liquid nitrogen-cooled mercury-cadmium-telluride (MCT) detector. Spectra were collected at room temperature in the absorbance mode at a resolution of 4 $\text{cm}^{-1}$ in the wavelength range of 600–4000 $\text{cm}^{-1}$ and 20 scans were averaged for each spectrum. The spectra were corrected for the wavelength dependence of the absorbance in ATR devices. The disappearance of the absorbance peaks at 915 $\text{cm}^{-1}$ (epoxy bending) was used to determine the epoxy group conversion. The peak at 1508 $\text{cm}^{-1}$ (carbon–carbon ring stretch of $p$-disubstituted benzene ring of DGEBA) was used as an internal standard. The epoxy group conversion was calculated as:

$$A'_{epoxy,t} = \frac{A_{915,t}}{A_{1508,t}} \quad (3)$$

$$x = 1 - \frac{A'_{epoxy,t}}{A'_{epoxy,0}} \quad (4)$$

A thermo-mechanical analyzer Mettler TMA SDTA840 was used to determine the conversion at the gel point following a procedure previously discussed [46]. A silanized glass fiber disc ca. 5 mm in diameter was impregnated with the liquid formulation and sandwiched between two thin aluminum discs. The sample was heated up from 30 to 150 °C at 2 °C/min, and subject to an oscillatory force of 0.005–0.01 N with an oscillation frequency of 0.083 Hz (dynamic load thermo-mechanical analysis mode, DLTMA). The gel point temperature was taken as the onset in the decrease of the oscillation amplitude measured by the probe. The conversion at the gel point has been determined from the gel point temperature and a dynamic curing experiment in the DSC at the same heating rate. The sample temperatures measured by the thermocouple below the sample in the TMA analyzer, and that measured by the cell in the DSC, have been used to ensure accuracy of the measurement. This direct comparison between DSC and TMA was validated by measuring by DSC, at 2 °C/min, the residual heat of a sample partially cured up to the gel point in the TMA.

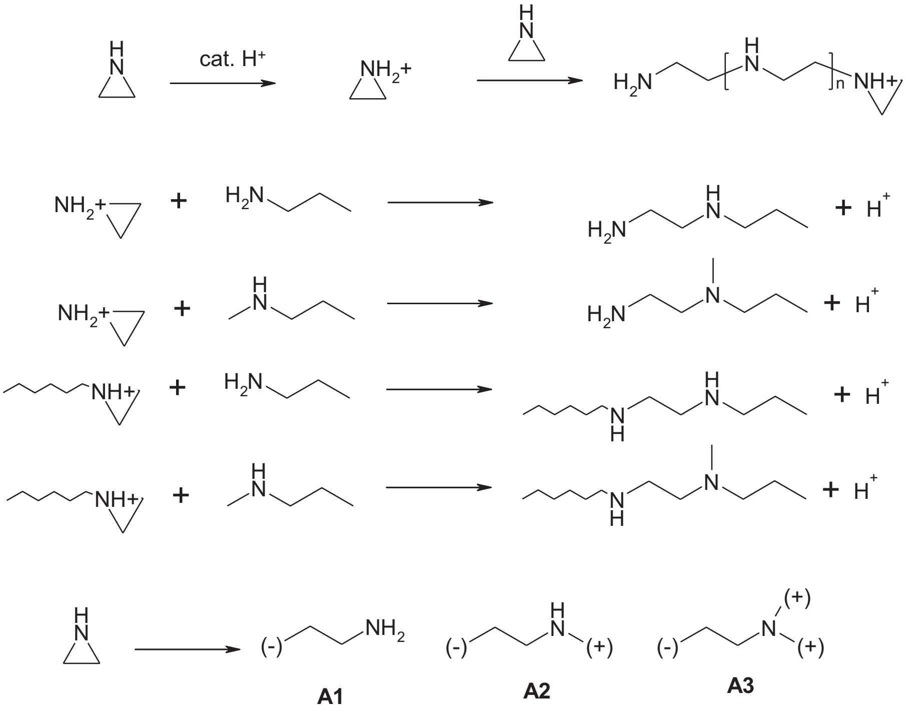
A TA Instruments DMA Q800 was used to study the dynamic-mechanical properties of the materials. Prismatic rectangular samples (ca $10 \times 12 \times 1.3$ mm$^3$) were analyzed in single-cantilever mode at 1 Hz and 10 μm strain amplitude at 3 °C/min from 30 to 200 °C.

The gel fraction of the cured samples was determined by reflux extraction in methylene chloride overnight and drying of the filtered solid residue under vacuum and a temperature of 80 °C until constant weight.

## 3. Theoretical

### 3.1. HBP structure

In spite of the complexity of the polymerization of aziridine [33–35] it is assumed that, essentially, it leads to a number of primary, secondary and tertiary amine structures coming from the ring-opening of the aziridine units and chain-transfer processes between the different species. In Scheme 1 we show a simplified reaction scheme along with the possible structural fragments resulting from the aziridine polymerization, neglecting the existence of remaining cyclic aziridine or aziridinium structures or internal loop formation.



**Scheme 1.** Simplified aziridine polymerization scheme and structural fragments resulting from the polymerization of aziridine.

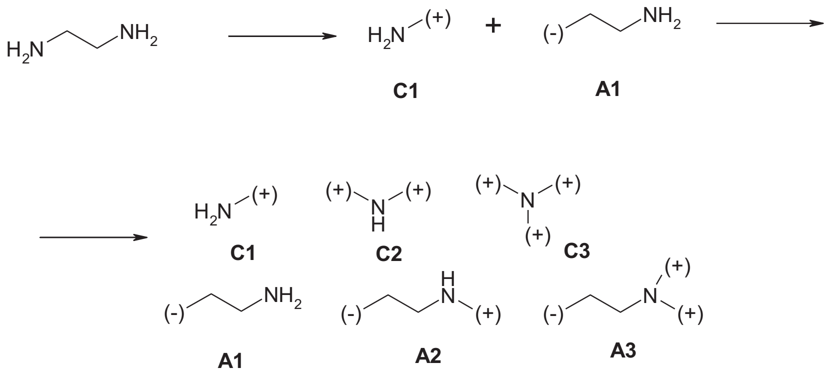
The different fragments resulting from the aziridine polymerization are also shown in Scheme 1. According to the material specifications provided by the supplier of Lupasol, no unreacted aziridine rings should be present in the polymer structure, and therefore the corresponding fragments are not considered. Note that the different fragments, coded as A1, A2 and A3, issue (−) and (+) virtual bonds representing their connection to the other fragments, leading to the polymer structure. These bonds result from both the aziridine ring-opening and chain-transfer between the ethylenimminium cations and the different nucleophiles taking place during the aziridine polymerization [34]. The (+) and (−) bonds indicate the direction towards the chain start and the chain end, respectively. Because a (−) bond indicates that there is a connection with a (+) bond, the number of (−) and (+) bonds must be equal throughout the polymerization process and in the final structure of the polymer. This is equivalent to say that, in analogy with a polycondensation processes, the number of reacted B groups must be equal to the number of reacted A groups, providing there are not other unidentified species or structures in the system.

Assuming that all the primary, secondary and tertiary amines from Lupasol (see $n1$:$n2$:$n3$ ratio in Table 1) come from the polymerization of aziridine alone, that would give a number of (−) bonds greater than the number of (+) bonds. Therefore, the description of the polymer structure based only on the aziridine fragments is incomplete. It is hypothesized that there must be a number of fragments resulting from the presence of a core molecule during the aziridine polymerization process such as ethylenediamine [38]. It can be assumed that it participates by a chain-transfer process in a very similar to that of the primary and secondary amines generated during the polymerization of aziridine and produces, in fact, very similar structures. As can be seen in Scheme 2, ethylenediamine can be splitted into two structural fragments, one of them, A1, identical to the one resulting from the aziridine polymerization and a new one coded C1. From the participation of C1 fragments in the aziridine polymerization process following Scheme 1, C1, C2 and C3 fragments might also be present in the polymer structure. Part of the primary, secondary and tertiary amino groups in the structure might come from this added ethylenediamine core, and this would help to equilibrate the number of (−) and (+) bonds. The resulting polymer distribution, resulting from the combination of the different fragments, is shown in Scheme 3.

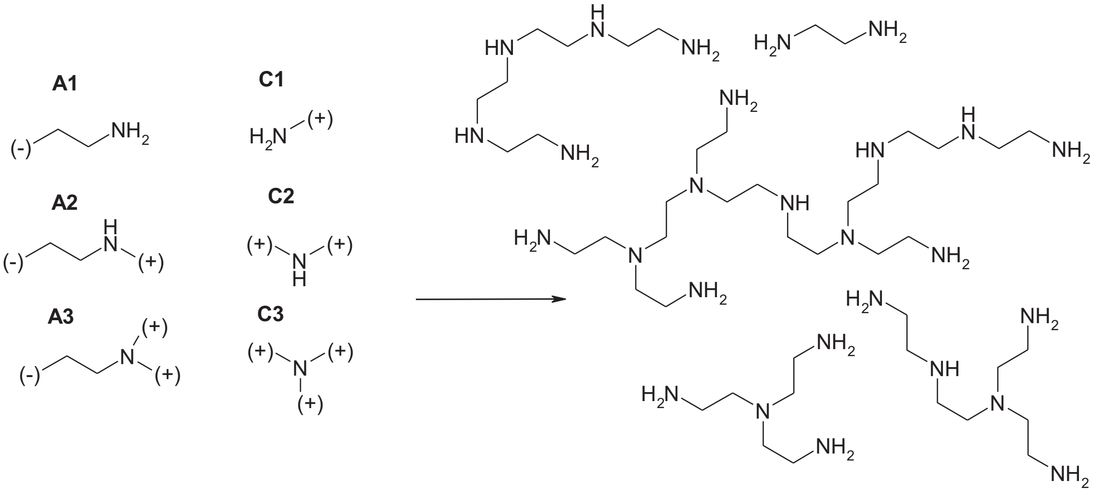
It is usually shown that $^1$H NMR analysis of commercially available hyperbranched poly(ethyleneimine)s shows only signals characteristic of the amine protons and the methylene groups neighbouring amine groups.[47,48] The $^{13}$C NMR analysis of commercial poly(ethyleneimine)s also shown only signals corresponding to methylene carbons neighbouring amine groups [47]. The $^1$H NMR and $^{13}$C NMR spectra of LP800 (see Supporting Information) show identical features. No signals corresponding to other methylene groups [49], N-substituted ethyleneimine rings, aziridine or other moieties could be observed, so it is assumed that the proposed structural model is valid, and that ethylenediamine has been effectively used as core molecule in these polymers.

An additional advantage of this modelling is that it can be applied to model more simple systems, small amine crosslinkers such as diethylenetriamine (DETA) (Scheme 4). As can be seen, there is only one possible combination of fragments leading to the monomer structure.

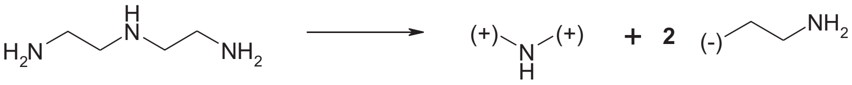
By analogy with $AB_2$ polycondensation processes [31], it can be considered that a likely polymer structure can be determined from the random recombination of structural fragments, such as those shown in Scheme 3, corresponding to the primary, secondary and tertiary amines produced in the aziridine polymerization in the presence of ethylenediamine. A recursive method making use of the concept of expectation probability described by Miller and Macosko [39–41] and the statistical combination of structural fragments that are present in the polymer structure or during the crosslinking process has been used. Detailed explanation of the fragment methodology can be found in the literature [42]. The concentration of the different structural fragments ($a1$, $a2$, $a3$ and $c1$, $c2$, $c3$, note that lowercase labels are used for the normalized concentration of each species) is fitted taking into account the overall concentration of primary, secondary and tertiary amines ($n1$, $n2$, $n3$, determined experimentally by the supplier) and the mass-average molecular weight of the polymer (determined experimentally by the supplier), $M_w$.



**Scheme 2.** Structural fragments resulting from the participation of ethylenediamine as chain-transfer agent and core in the polymerization of aziridine.



**Scheme 3.** Formation of a polymer distribution by random combination of structural fragments.



**Scheme 4.** Decomposition into structural fragments of diethylene triamine (DETA).

Other relevant parameters can be obtained such the relation between core and aziridine units in the hyperbranched structure $\lambda$ (Eq. (5)), the number-average molecular weight $M_n$ (Eq. (6)), the mass per reactive amine hydrogen $M_{eqH}$ (Eq. (7)) or the mass per amine group $M_{eqN}$ (Eq. (8)). Noticeably, all these parameters can be calculated on the basis of the overall concentration of primary, secondary and tertiary amines ($n1$, $n2$, $n3$) and the mass of the structural fragments. In the expressions used, and according to the fragment structure in Schemes 1 and 2, $M_a$ is equal to the mass of aziridine plus one hydrogen, 44 g/mol, and $M_{core}$ has a value of 16 g/mol (see the Supporting Information for the detail on the mass of each structural fragment).

$$\lambda = \frac{n1 - n3}{2 \cdot (n2 + 2 \cdot n3)} \tag{5}$$

$$M_n = \frac{(n2 + 2 \cdot n3) \cdot (M_a - 1) + \left(\frac{n1-n3}{2}\right) \cdot (M_a + M_{core})}{(n1 - n3)/2} \tag{6}$$

$$M_{eqH} = \frac{(n2 + 2 \cdot n3) \cdot (M_a - 1) + \left(\frac{n1-n3}{2}\right) \cdot (M_a + M_{core})}{2 \cdot n1 + n2} \tag{7}$$

$$M_{eqN} = \frac{(n2 + 2 \cdot n3) \cdot (M_a - 1) + \left(\frac{n1-n3}{2}\right) \cdot (M_a + M_{core})}{n1 + n2 + n3} \tag{8}$$

The second moment of the number of reactive groups in the HBP or mass-average polymer functionality, $f_w$, can be approximately estimated from the following expression:

$$f_w \cong \frac{M_w}{M_a - 1} \tag{9}$$

where $M_a - 1$ is the mass of the aziridine repeating unit in the HBP. In spite of the presence of core ethylenediamine fragments in the polymer structure, there are a number of reasons supporting this expression: (1) each polymerized aziridine monomer contributes, on average, to one reactive group in the HBP, (2) in the calculation of the second moment (or mass-average) more weight is given to polymer molecules with higher molecular mass and therefore higher amount of polymerized aziridine, therefore minimizing the effect of the presence of core molecules in the structure, and (3) the structure of the ethylenediamine core is, in any case, very similar to that of the polymerized aziridine repeating units. A verification has been made using the polymer distributions reported by Yan and Zhou [26]. The values of $f_w$ and $M_w/(M_a - 1)$ have been calculated for a random polymer with the same $\lambda$, showing an error of less than 1%. In order to test the accuracy of this expression, $\lambda$ was changed between 0.05 and 0.2, keeping the error within 5–6%. Taking into account the other sources of uncertainty, this approximation should be valid for the present case.

The details on the recursive procedure and the derivation of all the relevant structural parameters are found in the Supporting Information.

### 3.2. Epoxy-amine crosslinking

During epoxy-amine curing processes, the main reactions taking place are the nucleophilic addition of the primary and secondary amine to the epoxy ring, catalyzed by proton donors, as illustrated in Scheme 5. The real mechanism can be significantly more complex, involving the formation a number of reaction complexes [50–53], but this may have limited influence on the structure development during curing.

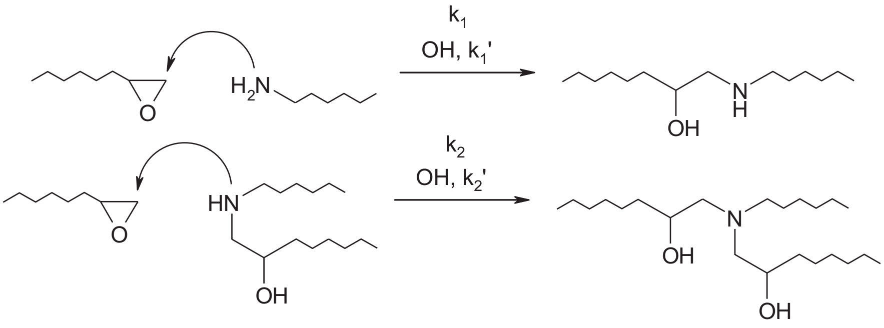
The possible structural fragments present during the epoxy-amine polycondensation process are found in Schemes 6 and 7. According to these schemes, once an amine fragment reacts, it issues a new bond labelled DG+ indicating the connection to a reacted epoxy fragment. Accordingly, once an epoxy fragment reacts, a new bond labelled DG− appears, indicating the connection to a reacted amine fragment. It follows that only connections between DG+ and DG− fragments are possible during the crosslinking process. Individual fragments for the mono- and di-reacted epoxy monomer have been considered (see Scheme 7), a structural fragment definition close to that employed by Dušek and co-workers [27,29]. This fragment definition would allow easy introduction of nonideal features such as negative substitution factor for the reaction amine or epoxy groups. The former possibility is widely acknowledged, while in contrast it is commonly assumed equal and independent reactivity of epoxy groups in an epoxy monomer [42]. The lower reactivity of the remaining epoxy group in a mono-reacted epoxy monomer would produce a reduction in the probability of inter-molecular bonding and have a significant impact on the network build-up. It is envisioned that this effect may can take place in highly off-stoichiometric systems with large excess of epoxy groups, in a similar way to the slow monomer addition synthesis of hyperbranched polymers [31]. Other possibilities such as steric effects on reactivity or intra-molecular loop formation might be operative, but these need a more rigorous treatment that falls out of the scope of this work [29,54–58]. In addition, reaction of all the epoxy or amine groups might not be possible due to topological restrictions towards the end of the process [23]. Therefore, for simplicity purposes, the network build-up process will be described and analyzed in detail only in the ideal case and deviations from this ideal behaviour will be discussed in the subsequent comparison of the experimental results with the theoretical predictions.

Taking into account the initial concentration of the different structural fragments of the hyperbranched polymer, one can define $r$ as the stoichiometric ratio between amine and epoxy groups,

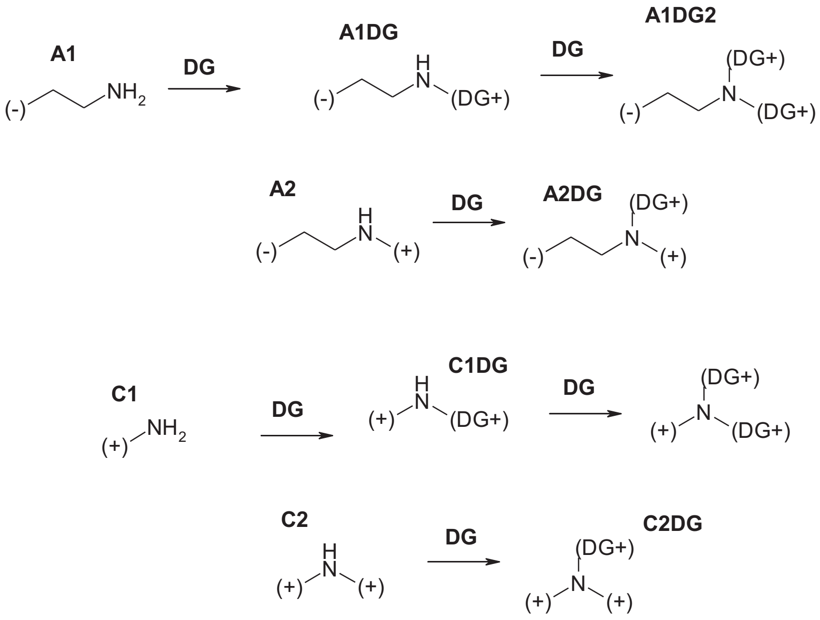
$$r = \frac{2 \cdot a1_0 + a2_0 + 2 \cdot c1_0 + c2_0}{dg_0} \tag{10}$$

where the different terms in lowercase indicate a normalized concentration of the corresponding structural fragments, with respect to the initial number of amine groups, and the subscript 0 indicates beginning of cure. If one calls $x$ as the epoxy conversion, the global conversion of amine hydrogens is $x/r$. In aliphatic amines, it is usually considered that the reactivity of primary and secondary amine hydrogens is similar [42,59]. Therefore, in the case of an ideal polycondensation process, the concentration of the different fragments is statistical, depending only on $r$ and $x$. Assuming no epoxy homopolymerization takes place, in the case of excess of epoxy groups ($r < 1$) the maximum epoxy conversion is $r$ while, in the case of excess amine groups ($r > 1$) epoxy conversion can be complete but the maximum conversion of amine groups is $1/r$.

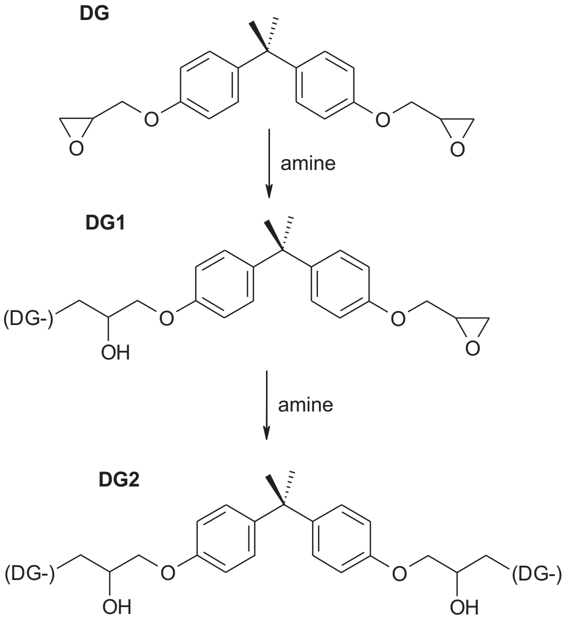
The inputs for the crosslinking stage are the concentration of the different structural fragments ($a1$, $a2$, $a3$ and $c1$, $c2$, $c3$) coming from the structural modelling of the hyperbranched polymer and the concentration of diepoxy monomers ($dg$). The connectivity between the different fragments is respected taking into account the labelling of the different virtual bonds issued by each fragment and their complementarity. Relevant structural parameters can be determined, including (but not limited to): epoxy conversion at the gel point ($x_{gel}$), the mass-average molecular weight before gelation ($M_w$), soluble and gel fraction ($w_{sol}$ and $w_{gel}$ respectively) and crosslinking density ($n_{cross}$) after gelation. The statistical averages are



**Scheme 5.** Simplified reaction mechanism during epoxy-amine curing.



**Scheme 6.** Structure of amine fragments appearing during epoxy-amine curing.



**Scheme 7.** Structure of epoxy fragments appearing during epoxy-amine curing.

determined recursively using the concept of expected molecular weight before the gel point, and the concept of extinction probability after the gel point. The methodology is described in detail in the literature [39–42].

Following Dušek and Dušková-Smrčková [27], conversion at gelation between a hyperbranched crosslinker and a bifunctional monomer can also be determined from the Stockmayer relationship, Eq. (11), using the second moment of the polymer functionality, $f_w$, instead of the functionality $f$ in the case of simple monomers or well-defined dendrimers.

$$x_{gel} = \sqrt{\frac{r}{f-1}} \tag{11}$$

Taking into account that the functionality of the HBP is only estimated using Eq. (9), the error in the determination of the gel point conversion $\Delta x_{gel}$ can be calculated as

$$\Delta x_{gel} \cong r^{-1/2} \cdot (f_w - 1)^{-3/2} \cdot \Delta f_w = x_{gel} \cdot (f_w - 1)^{-1} \cdot \Delta f_w, \tag{12}$$

where $\Delta f_w$ is the difference between the real and estimated functionality of the HBP. Given that $f_w$ is high for a multi-functional crosslinker (resulting in low values of $x_{gel}$), and assuming $\Delta f_w$ is small, this error should be negligible from a practical point of view.

Gelation can only take place for stoichiometric ratios $r$ within a certain range, given by the following expression, depending on the crosslinker functionality [42]:

$$\frac{1}{f-1} < r < f - 1 \tag{13}$$

The critical gelation ratios are defined as the lower and upper bounds. The error in their determination, using $f_w$, depend also on the accuracy on the estimation of $f_w$ using Eq. (9).

The details on the determination of the fragment distribution, the recursive procedure and the relevant statistical parameters during the crosslinking process are found in the Supporting Information.

## 4. Results and discussion

### 4.1. Analysis of the HBP structural model and crosslinking process

Table 1 shows the structural parameters of hyperbranched poly(ethyleneimine)s LP800 obtained from the product datasheet, the mass-average molecular weight $M_w$ (determined by light scattering) and the ratio of primary, secondary and tertiary amines $n1{:}n2{:}n3$ (determined by NMR, procedure and assignments can be found elsewhere [47] and references therein), as well as the calculated structural parameters following the model in this work.

Noticeably, the proportion $n1{:}n2{:}n3$ is somewhat different from that reported for other hyperbranched poly(ethyleneimine)s [36,47], and far from what can be expected from a random $AB_2$ polymerization, but this can be consequence of the use of a core molecule. According to Scheme 1, the presence of a diamine with two primary amine groups may lead to a final greater amount of primary amines because of its participation in the chain-transfer events with the different ethyleneimmonium cations and the restarting of new chains.

As shown in the previous section, the number-average molecular weight $M_n$, the equivalent weight per reactive hydrogen and the ratio ethylenediamine:aziridine in the polymer structure, $\lambda$, can be determined from the overall distribution of primary, secondary and tertiary amines $n1{:}n2{:}n3$ only. A $M_n$ of 404 g/mol has been calculated, yielding a polymer dispersity about 2. The value of polymer dispersity is a bit high for slow monomer addition polymerization processes [32], suggesting that a batch polymerization synthetic process has been used, with the use of a core molecule to control the polymer distribution [26]. This also indicates that the proposed procedure, based on the random recombination of structural fragments, may be valid. Indeed, the parameter $\lambda$ is rather high, an indication of the significant amount of ethylenediamine needed to control the mass-average molecular weight $M_w$ to such a low value and the polymer dispersity.

The parameters reflecting the polymer distribution, the ratios of aziridine/ethylenediamine fragments $a1{:}a2{:}a3$ and ethylenediamine fragments $c1{:}c2{:}c3$ have been calculated using the recursive methodology assuming an objective $M_w$ of 800 g/mol for LP800, subject to all the constraints, in terms of core and aziridine composition, as described in the Supporting Information. It should be noted that different ratios having the same molecular weight could be calculated, because there is an extra degree of freedom that is not covered by any expression. The ratios shown in Table 1 correspond only to one of the possible solutions. However, it can be advanced that, when the apparently different structures were used as input for the subsequent crosslinking process, they produce almost identical results, indicating that the crosslinking process is not very sensitive to the exact amine distribution. This can be rationalized by the fact that the role of the hyperbranched poly(ethyleneimine)s as crosslinkers depends on their reactive equivalent, depending on $n1{:}n2{:}n3$, and the experimental determination of $M_w$ and polymer dispersity $M_w/M_n$. This implies that all the distributions represented by the $a1{:}a2{:}a3$ and $c1{:}c2{:}c3$ ratios, having the same reactive equivalent and values of $M_w$ and $M_w/M_n$, are statistically equivalent and almost identical from a practical point of view.

The proposed structural model is capable of simulating a range of polymer distributions with different $M_w$ and equal $M_n$, by changing the distribution of the core and aziridine fragments, given by the $a1{:}a2{:}a3$ and $c1{:}c2{:}c3$ ratios. Using the current approach, the model is capable of simulating, for LP800, polymers with $M_w$ ranging from 590 g/mol (PD 1.46) to 2406 g/mol (PD 5.95). Due to the random recombination of fragments, the model is limited to high polymer dispersities for higher polymer sizes, and this may prevent its application to polymers obtained by less random, slow monomer addition procedures [31,32]. While this may not be a problem for low molecular weight polymers, such as LP800, as the random recombination can lead to relatively narrow polymer distributions, the structural model should be modified to be able to simulate larger molecules with less random structure and narrow distribution.

Although it is claimed that poly(ethyleneimine)s are composed manly of ethyleneimine homopolymer and should have a H equivalent mass (the mass per reactive amine hydrogen, in g/eqH) of 43 g/mol, an equivalent weight of 33.67 g/mol can be calculated in the present case. This value coincides with the one reported previously, in spite of the different structure definition [17]. This can also be explained by the use of ethylenediamine core. It has to be taken into account that each aziridine molecule polymerized introduces one reactive hydrogen in the polymer structure, but the reaction of ethylenediamine introduces four, resulting in an increase in the amount of reactive hydrogens in the final polymer structure and a subsequent lowering of the reactive amine hydrogen equivalent weight.

The model calculates exactly the gel point conversion for the ideal polycondensation using small amine crosslinkers such as DETA, which can also be calculated using the well-known Stockmayer or Flory equation (Eq. (11)) ($f = 5$ for DETA). This was to be expected, since these simple expressions can be derived from the application of the fragment methodology [42]. For LP800, the predictions of the model and those obtained by the application of the theoretical Eq. (11) and $f_w$ calculated using Eq. (9), also show very good agreement, as seen in Fig. 1. The little discrepancies arise because the estimation of $f_w$ takes into account only $M_w$ and the mass of the repeating unit of polymerized aziridine but, as discussed in the theoretical section and the Supplementary Information, it was verified that the error could be negligible. The model also predicts, for the ideal polycondensation with LP800, that gelation takes place within a range of $r$ between 0.055 and 18.21, indicating that very little amount of LP800 would result in a gelled material and preventing the storage of formulations containing LP800 for a long period of time. The results also agree well with those calculated using Eq. (13).

Fig. 2 compares some relevant statistical averages corresponding to the network build-up process of stoichometric DETA and LP800 formulations assuming ideal polycondensation behaviour and complete conversion of epoxy and amine groups. In the pregel state, it can be observed that $M_w$ increases more rapidly in the case of LP800, resulting in much earlier gelation, when $M_w$ diverges to infinity, at an epoxy conversion of 0.23, in contrast with the value of 0.50 for DETA. Given that the curing kinetics of hyperbranched poly(ethyleneimine)s and DETA are similar [16] and that the conversion at gelation is much lower for LP800, one should expect a shorter pot life for formulations containing LP800 than DETA, as was put into evidence in a previous experimental work using a higher molecular weight hyperbranched poly(ethyleneimine) [16]. After gelation, the soluble fraction $w_{sol}$ decreases also earlier in the case of LP800, from 1 at the gel point down to 0 in the fully crosslinked material, and the resulting material should have a higher crosslinking density $n_{cross}$ than DETA.

The above results coming from the application of the structural model can be easily explained by the multi-functionality of LP800, with an average functionality $f_w$ of 18.60 (in comparison of 5 for DETA, see Table 1), leading to earlier gelation as expected, and by the activation of internal branching points, the tertiary amine groups in the LP800 structure, leading to a more densely crosslinked network than DETA. Dušek and Dušková-Smrčková showed that, for dendrimer crosslinkers, the inner branching points of the dendrimer structure are activated before the outer branching points [27]. Likewise, it can be shown that the preexisting branching points coming from the tertiary amines in the HBP structure are activated before, followed by the ones coming from the reaction of the secondary amines, and last of them all the ones coming from the reaction of primary amines. This is due to the fact that a primary or secondary amine crosslink may not be activated unless it has completely reacted and all three paths issuing from the crosslink have an infinite continuation, while in the case of the tertiary amine crosslink it is only necessary that all the three paths have an infinite continuation.

### 4.2. Comparison of theory with experiments

A number of formulations with different epoxy-amine stoichiometric ratios were prepared. In the case of LP800 formulations, the reactive hydrogen equivalent weight calculated according to the model was used (see Table 1). The composition of the different formulations is shown in Table 2.

Fig. 3 compares the dynamic curing at 2 °C/min of different formulations containing LP800 and DETA. It can be observed that the curing process takes approximately within the same temperature range for all the formulations with LP800,

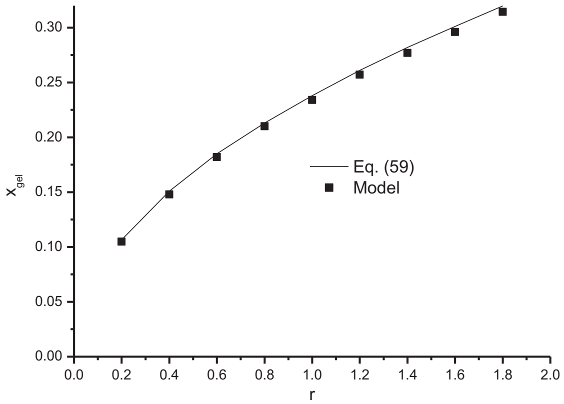


**Fig. 1.** Epoxy gel point conversion calculated using the theoretical expression Eq. (11) and the model, corresponding to the curing of diepoxy monomers with LP800 with different amine:epoxy ratios $r$.

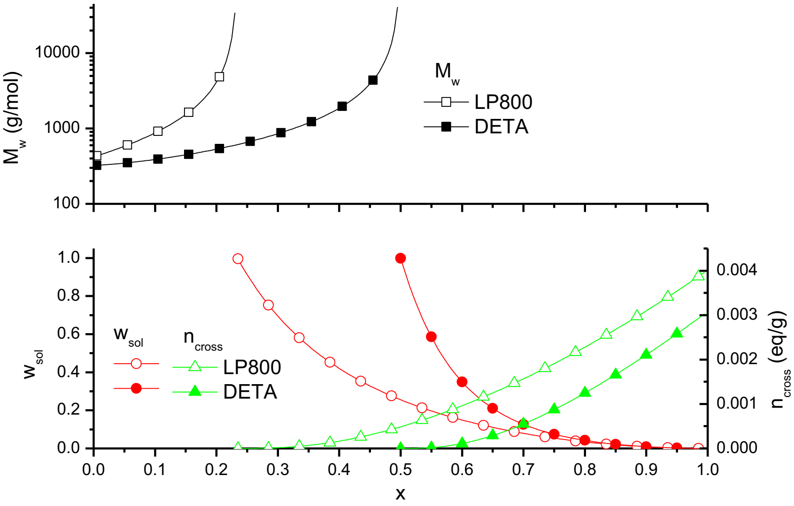


**Fig. 2.** Comparison of the main statistical averages during crosslinking of stoichiometric formulations of LP800 (open symbols) and DETA (close symbols).

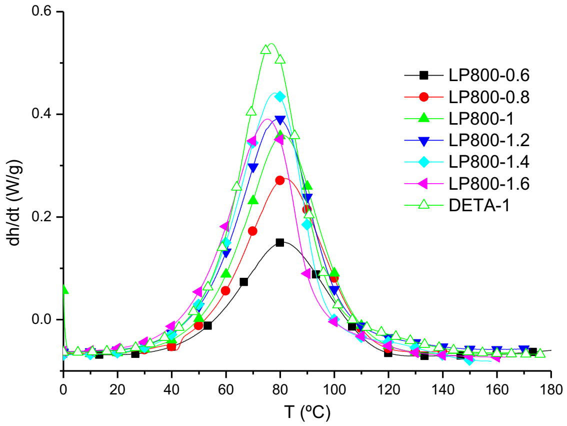


**Fig. 3.** Dynamic curing at 2 °C/min of different formulations with LP800 and DETA.

regardless of the stoichiometric ratio. However, it is observed that a deficit of LP800 in the formulation has a more dramatic effect in terms of kinetics and exothermicity than an excess, because of the much lower reactive hydrogen equivalent weight of LP800 (33.67 g/eq, see Table 1) in comparison with that of DGEBA (174 g/eq). The curing of formulations LP800-0.4 and LP800-0.2 (not shown in the figure) proceeds at a remarkably slower rate due to the lower amine concentration but within the same temperature range.

Table 3 shows the results of the calorimetric analysis during curing, showing that for the formulations containing LP800 the degree of cure achieved, $x_{DSC}$, is lower than that expected, $x_{max}$, taking into account the proportion of the crosslinking agent. In the case of DETA, conversion of epoxy groups was quantitative (the reaction heat was only slightly lower than expected for DETA-0.4). A reaction heat of 117 kJ/mol of epoxy group has been assumed for the calculations, corresponding to the curing of the LP800-1.4 formulation, a value that is in agreement with commonly reported values [60]. The degree of cure was measured by FTIR/ATR on cured samples of formulations with stoichiometric ratios $r$ of 0.2–1. In spite of the uncertainty in the determination of the conversion due to the partial overlapping of signals in the region of the reference and epoxy signals (see Fig. 4), the calculation of conversion by FTIR, $x_{FTIR}$, agrees well with those obtained by DSC, $x_{DSC}$, thus validating the calculation of the final conversion on the basis of this reference heat of 117. A fraction of unreacted amines ($f_{amine}$) around 0.2 has been calculated for all formulations between LP800-0.2 and LP800-1.2, indicating that there are amine groups that are not available for reaction. It might be claimed that the proposed hyperbranched structure and the calculation of the reactive amine equivalent weight are wrong but, as discussed in the theoretical section, the model should be appropriate taking into account the experimental evidence. In addition, modification of the amine groups in hyperbranched poly(ethyleneimine)s is commonly reported to be incomplete [47], to a similar extent to that reported in the present work. It is

**Table 3**
Results of the calorimetric analysis of the curing of the different formulations and of the cured samples. The symbol "–" indicates that the measurement was not performed.

| Formulation | $\Delta h\left(\frac{\mathrm{J}}{\mathrm{g}}\right)$ | $\Delta h\left(\frac{\mathrm{kJ}}{\mathrm{ee}}\right)$ | $x_{\max}$ | $x_{DSC}$ | $x_{FTIR}$ | $f_{amine}$ | $T_g$ (°C) | $\Delta C_p$(J/g K) |
|---|---|---|---|---|---|---|---|---|
| LP800-0.2 | 106.9 | 19.32 | 0.2 | 0.165 | 0.18 | 0.17 | −8.8 | 0.596 |
| LP800-0.4 | 195.7 | 36.69 | 0.4 | 0.314 | 0.35 | 0.22 | 12.0 | 0.698 |
| LP800-0.6 | 269.4 | 52.3 | 0.6 | 0.448 | 0.45 | 0.25 | 34.7 | 0.585 |
| LP800-0.8 | 379.4 | 76.2 | 0.8 | 0.652 | 0.62 | 0.19 | 82.9 | 0.455 |
| LP800-1 | 478.9 | 99.5 | 1 | 0.850 | 0.90 | 0.15 | 116.7 | 0.344 |
| LP800-1.2 | 510.3 | 109.4 | 1 | 0.935 | – | 0.22 | 140.3 | 0.324 |
| LP800-1.4 | 527.5 | 116.7 | 1 | ~1 | – | 0.29 | 137.7 | 0.324 |
| LP800-1.6 | 491.2 | 111.9 | 1 | ~1 | – | 0.40 | 122.8 | 0.388 |
| DETA-0.4 | 242.5 | 44.2 | 0.4 | 0.378 | – | 0.05 | 19.3 | 0.669 |
| DETA-1 | 591.4 | 115.1 | 1 | ~1 | – | ~0 | 134.1 | 0.288 |

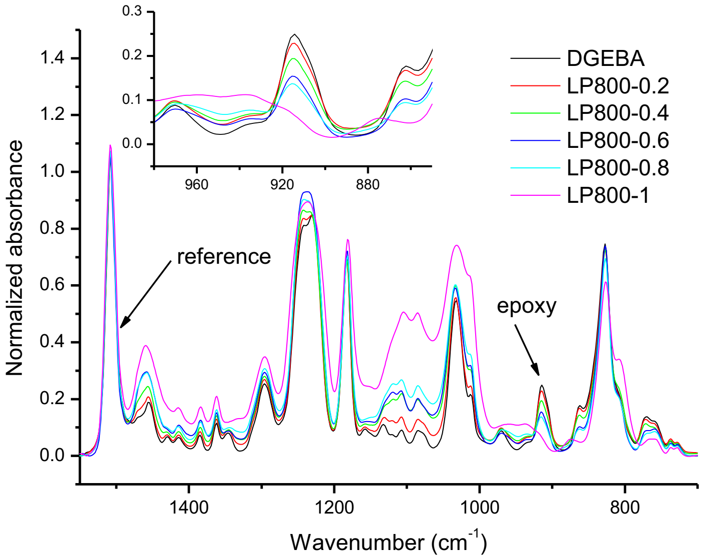


**Fig. 4.** FTIR-ATR spectra of the epoxy resin DGEBA and cured samples of LP800 formulations from 1:0.2 to 1:1. The inset expands the region corresponding to the epoxy band around 915 cm$^{-1}$.

acknowledged a number groups in the hyperbranched structure are less accessible [23] and may be eventually prevented from reacting at all during the crosslinking process due to topological limitations.

Table 3 also shows other relevant parameters determined from the calorimetric analysis of the cured samples. It can be seen that, on increasing the amount of hyperbranched crosslinker in the modifier, the $T_g$ of the cured material increases and the $\Delta C_p$ decrease, in agreement with the expected increase in the crosslinking density. An optimum is reached for formulations LP800-1.2 and LP800-1.4, after which the $T_g$ decreases and $\Delta C_p$ increases as well. In previous works, it was seen that the properties of materials with LP800 did not reach those with DETA [17], but it was not paid attention to the fact that reaction of the amine groups of LP800 was not complete. In fact, an optimized formulation with LP800 has higher $T_g$ than the stoichiometric DETA formulation, in spite of the presence of unreacted amine groups. The optimized formulations result from a compromise between having unreacted epoxy groups or having complete epoxy conversion but with a certain amount of unreacted amine groups, resulting in a more densely crosslinked and constrained network structure. Given the data reported in Table 3, it is deduced that the presence of unreacted epoxy groups has a more detrimental effect on the thermal–mechanical properties than an excess of unreacted amine groups. Several factors should contribute to this, namely: (1) the presence and size of pendant mono-reacted epoxy chain-ends carrying an excess of free volume, (2) a significant decrease in crosslinking density and (3) the plasticizing effect of the soluble fraction. The effect of the epoxy excess on soluble fraction and on crosslinking density is discussed later on when the network structure is analyzed in more detail. The effect of excess epoxy groups in DETA formulations is similar to that in LP800 formulations.

The gel point conversion during curing of the various formulations was measured using a procedure already described in the literature, based on the combination of TMA and DSC [46,61]. Fig. 5 illustrates a typical determination of gel point conversion by combination of TMA and DSC data, of formulation LP800-1. Note that, in the figure, the DSC conversion curve is already corrected taking into account the maximum conversion achieved, yielding the value of $x_{gel}$ of 0.23 reported in

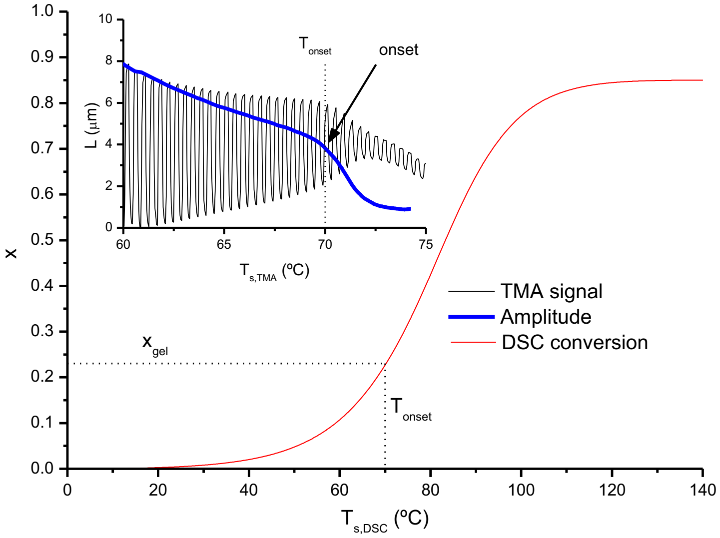


**Fig. 5.** Determination of gel point conversion by combination of TMA oscillatory and DSC measurements, corresponding to formulation LP800-1.

Table 4. The validity of this procedure has been checked by comparison of the experimental gel point conversion of two formulations with DETA with those predicted by theory. The agreement between theory and experiment (see Table 4, last two entries) is excellent and within experimental error, taking into account the uncertainty in the determination, given by the sensitivity $dx/dT_{gel}$, for the comparison of TMA and DSC experiments.

If one examines the results for the LP800 formulations, there is an excellent agreement between the calculated values and the experimental ones from LP800-1 up to LP800-1.6, with excess amine. However, from LP800-1 down to LP800-0.2, with excess epoxy, there is a systematic deviation of the theoretical values with respect to the experimental ones and, in fact, formulation LP800-0.2 does not gel (TMA did not show traces of gelation and complete solubility of cured samples in dichloromethane was verified). Surprisingly, the critical gelation ratio for LP800 formulations with excess epoxy ($r < 1$) would be similar to the one for DETA, 0.25.This contrasts with the theoretical critical gelation ratio $r$ of ca. 0.055 that would be predicted in the case of ideal polycondensation. Some practical consequences of this are the possibility of preparing of intermediate ungelled materials using off-stoichiometric formulations containing LP800 in dual-curing processes, providing a suitable initiator is used for the excess epoxy groups [17]. In the case of DETA such deviations in the gel point conversion are not observed, following ideal polycondensation behaviour.

Intramolecular loop formation is one major deviation from the ideal polycondensation behaviour, leading to higher gel point conversion than expected, higher soluble fraction of the crosslinked material and lower crosslinking density due to the formation of elastically inactive loops or wasted network junctions [55,62]. This is also of importance for hyperbranched polymers [23], due to the high density of neighbouring reactive groups. It is acknowledged dilution increases the likelihood of intramolecular loop formation due to the reduced probability inter-molecular reaction between diluted molecules [55,57,63]. Following Dušková-Smrčková et al. [57], we have observed that, in the formulations with a lower LP800 content, the ratio $x_{gel}/x_{gel,ideal}$ scales well with the stoichiometric ratio, $r$, that is approximately equivalent to the inverse of the amine concentration in the formulation. This suggests that the dilution of the amine crosslinking agent results in an increase in intramolecular loop formation but this interpretation may not be accurate, because in the present case the dilution takes place within the same diepoxy monomer. Moreover, the observed departures from the ideal situation are not observed in

**Table 4**

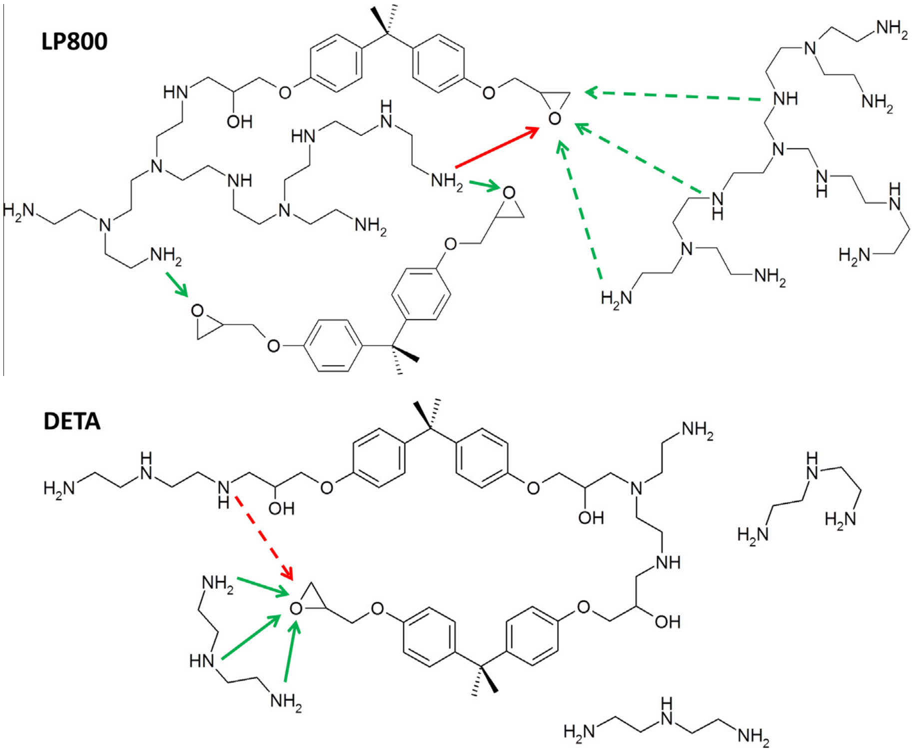
Conversion at gelation determined experimentally ($x_{gel,exp}$), and calculated using the model assuming ideal polycondensation behaviour ($x_{gel,ideal}$).

| Formulation | $r$ | $x_{gel,exp}$ | $dx/dT_{gel}$ (1/K) | $x_{gel,ideal}$ |
|---|---|---|---|---|
| LP800-0.2 | 0.2 | not gelled | | 0.105 |
| LP800-0.4 | 0.4 | 0.21 | 0.007 | 0.148 |
| LP800-0.6 | 0.6 | 0.21 | 0.011 | 0.182 |
| LP800-0.8 | 0.8 | 0.23 | 0.015 | 0.210 |
| LP800-1 | 1 | 0.23 | 0.016 | 0.234 |
| LP800-1.2 | 1.2 | 0.26 | 0.018 | 0.257 |
| LP800-1.4 | 1.4 | 0.28 | 0.020 | 0.277 |
| LP800-1.6 | 1.6 | 0.32 | 0.019 | 0.296 |
| DETA-0.4 | 0.4 | 0.33 | 0.008 | 0.316 |
| DETA-1 | 1 | 0.48 | 0.030 | 0.5 |

the formulations with DETA, only in those with a deficit in LP800, in which the hyperbranched crosslinker is progressively diluted within the epoxy medium.

The specific behaviour of LP800 may be explained by its densely branched, multi-functional structure. The situation is illustrated in Scheme 8. It can be observed that the reactive amine groups are not distributed homogeneously in the reaction medium when LP800 is used, but concentrated in the LP800 molecules. A consequence of this is that LP800 may promote intra-molecular cyclization more easily due to the presence of neighbouring amine groups. However, intra-molecular cyclization may not take place extensively due to the abundance of available epoxy groups surrounding the hyperbranched molecules. The dilution of LP800 in the reaction medium enhances the heterogeneity of the distribution of reactive amine groups further. The consequence is that the likelihood that a monoreacted epoxy monomer, attached to a LP800 molecule, reacts with another LP800 molecule is greatly reduced. In an inert solvent, the reaction between LP800 and unreacted diepoxy monomer would decrease and the probability of intramolecular loop formation would no doubt increase but, in the present case, the solvent is the diepoxy monomer itself, which means that the reaction between LP800 and the unreacted diepoxy is not negatively affected and even enhanced in comparison. This results in an apparent negative substitution effect for the mono-reacted epoxy monomer, becoming more relevant as the dilution of LP800 increases. In consequence, the probability of inter-molecular bonding is significantly decreased, slowing down the increase in $M_w$ during the curing process and delaying gelation. This invalidates, for this particular case, the common hypothesis of independent reactivity of epoxy groups in a diepoxy monomer [42]. This is similar to what happens in the synthesis of hyperbranched polymers by slow addition techniques, in which extreme dilution of one of the components that is slowly added results in preferential reaction pathways in comparison with bulk polymerization techniques in which reaction takes place randomly [32]. In contrast, the use of DETA as crosslinking agent leads to a more homogeneously distributed amine groups within the reaction medium. In Scheme 8 it is shown that inter-molecular reactions are in principle more favoured in the presence of DETA than with LP800. Dilution of DETA would not show any of these effects because of its small structure, more homogeneous distribution in the system and the fact that the degree of dilution is relatively small.

In the light of these experimental results, one can better interpret the previous results obtained for a hyperbranched poly(ethyleneimine) with a $M_w$ of 2000 g/mol [16]. For a stoichiometric formulation, it was determined experimentally a conversion at gelation of ca. 0.25, but the application of the current model to such a hyperbranched polymer would predict a conversion at gelation of 0.15, assuming ideal polycondensation. In that previous work, incomplete conversion of epoxy groups was not considered so that the corrected conversion at gelation would be lower, around 0.21, still higher than expected. Taking into account the higher molecular weight, one can argue that the distribution of amine groups in the



**Scheme 8.** Schematic representation of the possible inter- and intra-molecular reaction taking place during curing of DGEBA formulations with LP800 or DETA as crosslinking agent. The green lines indicate inter-molecular reaction and the red lines intra-molecular reaction. Dashed lines indicates lower likelihood of taking place. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 5**
Experimental gel fraction ($w_{gel,exp}$), and theoretical gel fraction calculated assuming ideal polycondensation ($w_{gel,ideal}$). In all cases, the final conversion $x_{DSC}$ reported in Table 3 has been used for the calculations.

| Formulation | $w_{gel,exp}$ | $w_{gel,ideal}$ |
|---|---|---|
| LP800-0.2 | 0 | 0.24 |
| LP800-0.4 | 0.55 | 0.52 |
| LP800-0.6 | 0.81 | 0.71 |
| LP800-0.8 | ~1 | 0.89 |
| DETA-0.4 | 0.44 | 0.45 |

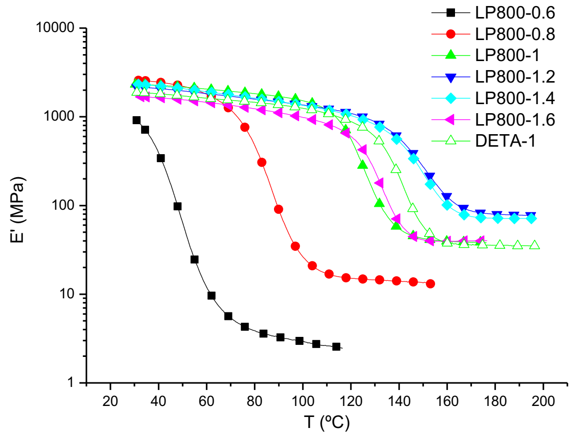


**Fig. 6.** $E'$ traces obtained during DMA analysis of the cured samples.

reaction medium would be less homogeneous, and this might result in similar substitution effects or intramolecular loop formation as observed in LP800 formulations with $r < 1$, thus increasing the gel point conversion further.

The gel fraction of the cured LP800 thermosets was determined by reflux extraction in dichloromethane and subsequent drying of the filtered solid. Table 5 shows the results of the experimental determination of the gel fraction in comparison with the values predicted by the theory, assuming ideal polycondensation. Note that formulations with excess LP800 are not shown in the table, as the calculated theoretical soluble fraction is negligible given the densely branched structure and high functionality of LP800. In all cases the achieved epoxy conversion, $x_{DSC}$ in Table 3, has been considered. The experimental values follow the predicted trends but the ideal polycondensation model predicts a certain gel fraction for LP800-0.2 formulation while this sample is fully soluble. This is explained by the delay in gelation due to dilution of the hyperbranched crosslinker, as discussed above, which is not taken into account by the ideal polycondensation model. The experimental values are in general higher than those predicted in any of the cases, except the formulation DETA-0.4, for which the measured value, taking into account experimental error, is very similar to the theoretical one. The differences between experimental and theoretical predictions for LP800 may be a consequence, first, of the inaccuracy of the structural model and the presence of nonidealities not accounted properly by the model. It can also be hypothesized that dichloromethane is not able to remove all the soluble material when LP800 is used due to the high polarity of LP800. Similar results were obtained using chloroform as solvent. Methanol is a good solvent for poly(ethyleneimine)s but, in spite of its better compatibility with LP800, methanol was not suitable for soluble fraction extraction of the DGEBA-LP800 materials. Neither was a chloroform and methanol mixture (50/50 v/v). One can also consider that there might be an alkylation reaction between the amine groups and the employed solvent, dichloromethane. It is acknowledged that the alkylation rate is very slow [64], but it can be accelerated in the case of macrocyclic amines that stabilize a reaction intermediate [65] by hydrogen bonding with neighbouring groups, which may be the situation in LP800 formulations with unreacted amine groups.

The results of the DMA analysis of the cured samples are shown in Figs. 6 and 7, and the main parameters are summarized in Table 6. From the figures it can be observed a clear increase in the network relaxation temperature indicated by the drop in storage modulus $E'$ and the tan $\delta$ peak, as the content in LP800 increases, up to a maximum around the formulations LP800-1.2 and LP800-1.4. Further increase in the LP800 content reduces the relaxation temperature. These trends are in full agreement with the data obtained with DSC reported in Table 3, since the mechanical relaxation of the network is connected with the glass transition temperature, $T_g$. There are not systematic trends in relaxation breadth, as seen from the *FWHM* (full width at half-maximum) values of the tan $\delta$ peak reported in Table 6. The area below the tan $\delta$ peak, however, decreases significantly with increasing LP800 content down to a minimum for formulation LP800-1.4. The trend is identical to that of the $\Delta C_p$ determined from the DSC analysis. This is not surprising because the area below the tan $\delta$ peak is connected with the

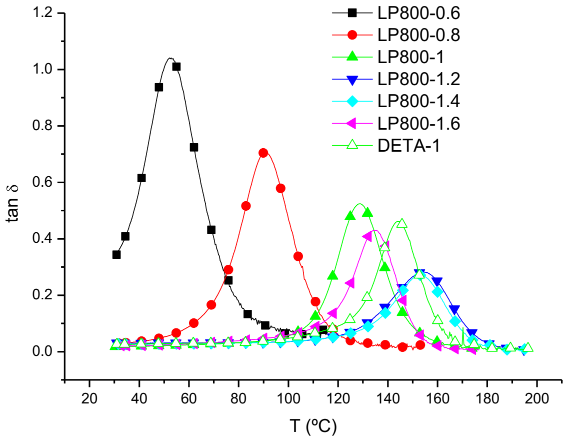


**Fig. 7.** Tan $\delta$ traces obtained during DMA analysis of the cured samples.

**Table 6**
Results of the DMA analysis of the cured samples. *FWHM* stands for full width at half-maximum. The symbol "–" indicates that the value was not or could not be determined.

| Formulation | tan $\delta$ | | | | $E'_r$ (MPa) |
|---|---|---|---|---|---|
| | Peak $T$ (°C) | Height | *FWHM* (°C) | Area (°C) | |
| LP800-0.6 | 52.7 | 1.040 | ~27 | – | ~3 |
| LP800-0.8 | 90.5 | 0.706 | 24.6 | 20.0 | 14.4 |
| LP800-1 | 128.8 | 0.524 | 22.0 | 13.7 | 38.3 |
| LP800-1.2 | 154.9 | 0.282 | 29.1 | 8.6 | 77.3 |
| LP800-1.4 | 153.1 | 0.271 | 25.1 | 7.7 | 71.4 |
| LP800-1.6 | 134.9 | 0.430 | 20.5 | 11.1 | 39.9 |
| DETA-1 | 144.3 | 0.461 | 20.0 | 11.1 | 35.1 |

increase in mobility at $T_g$ and the ability of the material to participate in the relaxation process, and $\Delta C_p$ with the increase in mobility of the network at $T_g$ as well. Concerning the relaxed storage modulus $E'_r$, it increases significantly with LP800 content up to an optimum around the formulations LP800 1:1.2 and LP800 1:1.4 and then decreases again, following a parallel trend to $T_g$ and the relaxation temperature. According to the rubber elasticity theory, $E'_r$ is related with the crosslinking density of the cured materials, and is a clear indication that LP800 increases crosslinking, especially in off-stoichiometric with $r < 1$, as expected from its densely branched structure. Indeed, the values of network strand density $\nu_e$ shown in Table 7, calculated using the model and taking into account the achieved epoxy conversion $x_{DSC}$ (see Table 3), confirm this. The increase in crosslinking results in a progressive decrease in the mobility of the network, which can only relax at higher temperatures. The constraint imposed by the increasing number of crosslinks also reduces the degree of participation of the material in the relaxation process, thus reducing the intensity of the relaxation peak. Noticeably, the network strand density $\nu_e$ is less sensitive to an excess of amine groups than to an excess of epoxy groups, because the high functionality and densely branched architecture of LP800 should lead to a high crosslinking density in spite of the presence of unreacted amine groups leading to incomplete activation of all the possible branching points.

In Fig. 8 the network strand density $\nu_e$ (see Table 7) is compared with the tan $\delta$ peak temperature and the relaxed modulus $E'_r$ (see Table 6). It can be observed that the glass transition temperature, given by the tan $\delta$ peak, has an excellent correlation with the calculated network strand density, making the crosslinking density the most relevant factor affecting the value of $T_g$. This is also observed for the relaxed modulus $E'_r$, but there are significant departures in formulations LP800-1.2 and LP800-1.4. The calculated crosslinking density in formulations LP800-1, LP800-1.6 and DETA-1 are within the same range, but the apparent modulus in formulations LP800-1.2 and LP800-1.4 is about twice. In a recent work we could see that, in formulations combining epoxy-amine polycondensation and epoxy homopolymerization, the apparent relaxed modulus was also much higher than expected because of mobility constraints imposed by the densely crosslinked network structure [17]. This was also observed recently in shape-memory thermosets based on epoxy-amine polycondensation using hyperbranched poly(ethyleneimine)s [66]. One can argue that, in formulations LP800-1.2 and LP800-1.4, the combination of highest epoxy conversion with moderate amount of unreacted amine groups leads to the most constrained network structure, with the highest $T_g$, and lowest network mobility and stretchability.

Departures from the ideal affine network and other models are expected in crosslinked thermosets due to a variety of reasons [42,67–69]. This may be of relevance in the present case, taking into account the highly branched structure of

**Table 7**
Calculation of the network strand density $\nu_e$ using the ideal polycondensation model and the achieved epoxy conversion $x_{DSC}$ (see Table 3). The factor $\phi$ from the rubber elasticity equation, Eq. (14), is also calculated taking into account the experimental values reported in Table 6, a temperature equal to the tan $\delta$ peak temperature +40 °C, and assuming a density of ca. 1100 kg/m$^3$.

| Formulation | $\nu_e$ (mol/kg) | $\phi$ |
|---|---|---|
| LP800-0.6 | 0.81 | 0.49 |
| LP800-0.8 | 2.19 | 0.59 |
| LP800-1 | 4.02 | 0.79 |
| LP800-1.2 | 4.73 | 1.27 |
| LP800-1.4 | 5.21 | 1.07 |
| LP800-1.6 | 4.83 | 0.67 |
| DETA-1 | 4.62 | 0.61 |

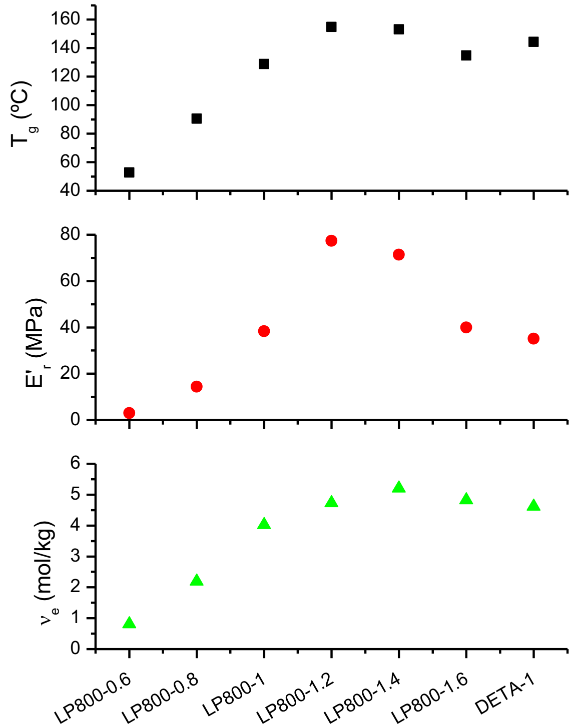


**Fig. 8.** Correlation of network structure parameters obtained from DMA (Table 6) and theoretical network strand density (Table 7), assuming ideal polycondensation behaviour.

LP800 and the presence, in the crosslinked material, of very short strands corresponding to short ethylene segments in LP800 between neighbouring amine crosslinks. A factor $\phi$ representing the deviation from the affine network model can be calculated [42], according to Eq. (14). It is argued in many cases that a correction to the affine network model should be already made taking into account the fluctuation of the crosslinks [42,68–70]. Assuming that all the crosslinks are trifunctional, the so-called phantom networks, with crosslink fluctuation, should have a correction factor $\phi$ of 1/3 with respect to the affine model [42]. The correction factor $\phi$ was calculated, taking into account the experimental data and the network strand density $\nu_e$ determined for this model. It can be seen in Table 7 that, except for formulations LP800-1.2 and LP800-1.4, the values of $\phi$ are around 0.7. These calculated values are between the phantom and affine network models, as commonly observed for epoxy-amine systems [45]. In a previous work, values of $\phi$ around 0.7 could also be calculated for epoxy-amine networks with DETA or hyperbranched poly(ethyleneimine)s [71], but in that case incomplete conversion of epoxy groups, as demonstrated in this work, was not taken into consideration. Whatever the sources of nonideal behaviour [68], it is clear is that the LP800-1.2 and LP800-1.4 materials have higher $\phi$factors resulting from their more constrained network structure, leading to a less ideal behaviour in comparison. DETA-1 formulation, in spite of having complete epoxy/amine groups conversion, has not the same behaviour as the optimum LP800 formulations because of the absence of a hyperbranched structure constraining the network structure, and resembles more the one of the less crosslinked off-stoichiometric LP800 formulations, with $\phi$ around 0.7.

$$E'_r = \phi \cdot 3 \cdot R \cdot T \cdot \nu_e \cdot \rho \tag{14}$$

To sum up, the curing of DGEBA with hyperbranched poly(ethyleneimine)s has some particular features that are not present using other curing agents, because of their densely branched architecture and the concentration of reactive amine groups in the polymer molecules. Some amine groups may remain unreacted in the hyperbranched structure due to topological hindrance, resulting in incomplete activation of the crosslinks and internal branching points of the crosslinking agent. The curing process may deviate from the ideal polycondensation mechanism in off-stoichiometric systems with excess epoxy due to the inhomogeneous distribution of amine groups in the reaction medium. Optimum materials may be obtained in formulations with excess of hyperbranched modifier, with a higher crosslinking density and higher glass transition temperature than those that are obtained using smaller amine crosslinking agents with similar structures. The proposed structural model is capable of reproducing the experimental behaviour, but it is recognized that its validity rests upon the reliability of the experimental characterization of LP800 and some relevant assumptions on its structure. The model should also be modified to account for the non-ideal behaviour in LP800 formulations with excess of epoxy groups.

## 5. Conclusions

The network build-up during curing of diepoxy monomers with hyperbranched poly(ethyleneimine)s has been studied from a theoretical point of view. A network build-up model has been elaborated based on the random recombination of structural fragments representing the hyperbranched polymer structure and the species appearing in the subsequent crosslinking process with a diepoxy monomer. A probable hyperbranched structure has been generated on the basis of the available experimental data, the ratio of primary, secondary and tertiary amines and the mass-average molecular weight. This has been used as an input for the subsequent crosslinking stage with variable amine:epoxy rations. The crosslinking process has ben modelled assuming ideal polycondensation behaviour. The results of this network build-up model have been compared with experimental results obtained using a commercial hyperbranched poly(ethyleneimine) coded as LP800 and diethylenetriamine (DETA) as crosslinking agents of diglycidyl ether of Bisphenol A (DGEBA). In spite of the model assumptions and simplifications, it is capable of reproducing the experimental behaviour with a fair degree of accuracy.

Based on the network build-up model, LP800 leads to earlier gelation and higher crosslinking density than DETA. However, it has been shown that there is incomplete reaction of amine groups in LP800 due to topological hindrance, leading to incomplete activation of branching points and lower crosslinking density than expected. Conversion at gelation in LP800 formulations is correctly predicted by the model at stoichiometric ratios $r \geqslant 1$ but in the case of off-stoichometric formulations with $r < 1$, systematic deviations leading to higher gel point conversion than that predicted by the model are observed because of the progressive dilution of the hyperbranched crosslinker in the epoxy monomer and the inhomogeneous distribution of amine groups in the reaction medium. In consequence, the critical gelation ratio for epoxy excess ($r < 1$) is much higher than expected, opening the possibility of easy preparation of ungelled prepolymers starting from moderately off-stoichiometric formulations, with a possible application in dual-curing processes. This has been rationalized by the possible occurrence of a negative substitution effect in the reactivity of epoxy monomers and intramolecular loop formation, but the former is deemed to be more likely due to the fact that dilution takes place in a reactive solvent. No such nonidealities were observed in the case of DETA, that showed ideal polycondensation behaviour at the tested conditions.

The thermal and dynamomechanical analysis of the cured materials reveal that optimum materials can be obtained from off-stoichiometric formulations with a moderate excess of LP800, with higher glass transition temperature and crosslinking density than those obtained with DETA. Deviations from the ideal network behaviour were observed in the case of the optimum LP800 formulations due to the mobility constraints imposed by the resulting highly crosslinked network structure.

## Acknowledgements

Xavier F.-F. acknowledges Juan de la Cierva scholarship (JCI-2010-06187). MINECO and Generalitat de Catalunya are also acknowledged (MAT2011-27039-C03-01, MAT2011-27039-C03-02 and 2009-SGR-1512). BASF is kindly acknowledged for donating hyperbranched poly(ethyleneimine) Lupasol™ samples.

## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.eurpolymj.2015.07.031.

## References

[1] B. Voit, New developments in hyperbranched polymers, J. Polym. Sci., Part A: Polym. Chem. 38 (14) (2000) 2505–2525.
[2] L. Boogh, B. Pettersson, J.-A.E. Manson, Dendritic hyperbranched polymers as tougheners for epoxy resins, Polymer 40 (9) (1999) 2249–2261.
[3] R. Mezzenga, J.A.E. Manson, Thermo-mechanical properties of hyperbranched polymer modified epoxies, J. Mater. Sci. 36 (20) (2001) 4883–4891.

[4] D. Ratna, G.P. Simon, Thermomechanical properties and morphology of blends of a hydroxy-functionalized hyperbranched polymer and epoxy resin, Polymer 42 (21) (2001) 8833–8839.
[5] D. Ratna, R. Varley, G.P. Simon, Toughening of trifunctional epoxy using an epoxy-functionalized hyperbranched polymer, J. Appl. Polym. Sci. 89 (9) (2003) 2339–2345.
[6] J. Xu, H. Wu, O.P. Mills, P.A. Heiden, Morphological investigation of thermosets toughened with novel thermoplastics. I. Bismaleimide modified with hyperbranched polyester, J. Appl. Polym. Sci. 72 (8) (1999) 1065–1076.
[7] I. Blanco, G. Cicala, C. Lo Faro, O. Motta, G. Recca, Thermomechanical and morphological properties of epoxy resins modified with functionalized hyperbranched polyester, Polym. Eng. Sci. 46 (11) (2006) 1502–1511.
[8] R. Mezzenga, C.J.G. Plummer, L. Boogh, J.A.E. Manson, Morphology build-up in dendritic hyperbranched polymer modified epoxy resins: modelling and characterization, Polymer 42 (1) (2001) 305–317.
[9] M. Flores, X. Fernández-Francos, F. Ferrando, X. Ramis, A. Serra, Efficient impact resistance improvement of epoxy/anhydride thermosets by adding hyperbranched polyesters partially modified with undecenoyl chains, Polymer 53 (2012) 5232–5241.
[10] M. Flores, M. Morell, X. Fernández-Francos, F. Ferrando, X. Ramis, À. Serra, Enhancement of the impact strength of cationically cured cycloaliphatic diepoxide by adding hyperbranched poly(glycidol) partially modified with 10-undecenoyl chains, Eur. Polym. J. 49 (6) (2013) 1610–1620.
[11] M. Sangermano, G. Malucelli, R. Bongiovanni, A. Priola, A. Harden, Investigation on the effect of the presence of hyperbranched polymers on thermal and mechanical properties of an epoxy UV-cured system, Polym. Int. 54 (6) (2005) 917–921.
[12] M. Morell, X. Fernández-Francos, X. Ramis, A. Serra, Synthesis of a new hyperbranched polyaminoester and its use as a reactive modifier in anionic curing of DGEBA thermosets, Macromol. Chem. Phys. 211 (17) (2010) 1879–1889.
[13] M. Morell, X. Ramis, F. Ferrando, Y. Yu, A. Serra, New improved thermosets obtained from DGEBA and a hyperbranched poly(ester-amide), Polymer 50 (23) (2009) 5374–5383.
[14] X. Fernandez-Francos, A. Rybak, R. Sekula, X. Ramis, À. Serra, Modification of epoxy-anhydride thermosets using a hyperbranched poly(ester-amide). I. Kinetics study, Polym. Int. 61 (12) (2012) 1710–1725.
[15] X. Fernandez-Francos, A. Rybak, R. Sekula, X. Ramis, F. Ferrando, L. Okrasa, et al, Modification of epoxy-anhydride thermosets using a hyperbranched poly(ester-amide). II. Thermal reworkability and material properties, J. Appl. Polym. Sci. 128 (6) (2013) 4001–4013.
[16] D. Santiago, X. Fernàndez-Francos, X. Ramis, J.M. Salla, M. Sangermano, Comparative curing kinetics and thermal-mechanical properties of DGEBA thermosets cured with a hyperbranched poly(ethyleneimine) and an aliphatic triamine, Thermochim. Acta 526 (2011) 9–21.
[17] X. Fernandez-Francos, D. Santiago, F. Ferrando, X. Ramis, J.M. Salla, À. Serra, et al, Network structure and thermomechanical properties of hybrid DGEBA networks cured with 1-methylimidazole and hyperbranched poly(ethyleneimine)s, J. Polym. Sci., Part B: Polym. Phys. 50 (21) (2012) 1489–1503.
[18] E. Zagar, M. Zigon, S. Podzimek, Characterization of commercial aliphatic hyperbranched polyesters, Polymer 47 (1) (2006) 166–175.
[19] E. Zagar, M. Zigon, Aliphatic hyperbranched polyesters based on 2,2-bis(methylol)propionic acid – determination of structure, solution and bulk properties, Prog. Polym. Sci. (Oxford) 36 (1) (2011) 53–88.
[20] K. Dušek, J. Šomvársky, M. Smrčková, W.J. Simonsick Jr., L. Wilczek, Role of cyclization in the degree-of-polymerization distribution of hyperbranched polymers modelling and experiments, Polym. Bull. 42 (4) (1999) 489–496.
[21] R.A.T.M. van Benthem, N. Meijerink, E. Geladé, C.G. de Koster, D. Muscat, P.E. Froehling, et al, Synthesis and characterization of bis(2-hydroxypropyl)amide-based hyperbranched polyesteramides, Macromolecules 34 (11) (2001) 3559–3566.
[22] E.T.F. Geladé, B. Goderis, C.G. de Koster, N. Meijerink, R.A.T.M. van Benthem, R. Fokkens, et al, Molecular structure characterization of hyperbranched polyesteramides, Macromolecules 34 (11) (2001) 3552–3558.
[23] K. Dušek, M. Dušková-Smrčková, Network structure formation during crosslinking of organic coating systems, Prog. Polym. Sci. (Oxford) 25 (9) (2000) 1215–1260.
[24] K.-C. Cheng, L.Y. Wang, Kinetic model of hyperbranched polymers formed in copolymerization of AB2 monomers and multifunctional core molecules with various reactivities, Macromolecules 35 (14) (2002) 5657–5664.
[25] H. Galina, J.B. Lechowicz, M. Walczak, Kinetic modeling of hyperbranched polymerization involving an AB2 monomer reacting with substitution effect, Macromolecules 35 (8) (2002) 3253–3260.
[26] D. Yan, Z. Zhou, Molecular weight distribution of hyperbranched polymers generated from polycondensation of AB2 type monomers in the presence of multifunctional core moieties, Macromolecules 32 (1999) 819–824.
[27] K. Dušek, M. Dušková-Smrčková, Polymer networks from precursors of defined architecture. Activation of preexisting branch points, Macromolecules 36 (8) (2003) 2915–2925.
[28] K. Dušek, M. Dušková-Smrčková, B. Voit, Highly-branched off-stoichiometric functional polymers as polymer networks precursors, Polymer 46 (12) (2005) 4265–4282.
[29] K. Dušek, M. Dušková-Smrčková, Modeling of polymer network formation from preformed precursors, Macromol. React. Eng. 6 (11) (2012) 426–445.
[30] K. Dušek, M. Dušková-Smrčková, J. Huybrechts, A. Ďuračková, Polymer networks from preformed precursors having molecular weight and group reactivity distributions. Theory and application, Macromolecules 46 (7) (2013) 2767–2784.
[31] A. Sunder, R. Hanselmann, H. Frey, R. Mulhaupt, Controlled synthesis of hyperbranched polyglycerols by ring-opening multibranching polymerization, Macromolecules 32 (13) (1999) 4240–4246.
[32] R. Hanselmann, D. Hölter, H. Frey, Hyperbranched polymers prepared via the core-dilution/slow addition technique: computer simulation of molecular weight distribution and degree of branching, Macromolecules 31 (12) (1998) 3790–3801.
[33] G.G. Odian, Principles of Polymerization, fourth ed., Wiley, 2004.
[34] G.D. Jones, D.C. MacWilliams, N.A. Braxtor, Species in the polymerization of ethylenimine and N-methylethylenimine, J. Org. Chem. 30 (6) (1965) 1994–2003.
[35] P. Kubisa, S. Penczek, Cationic activated monomer polymerization of heterocyclic monomers, Prog. Polym. Sci. (Oxford) 24 (10) (1999) 1409–1437.
[36] A. von Harpe, H. Petersen, Y. Li, T. Kissel, Characterization of commercially available and synthesized polyethylenimines for gene delivery, J. Control. Release 69 (2) (2000) 309–322.
[37] D. Appelhans, H. Komber, M.A. Quadir, S. Richter, S. Schwarz, J. van der Vlist, et al, Hyperbranched PEI with various oligosaccharide architectures: synthesis, characterization, ATP complexation, and cellular uptake properties, Biomacromolecules 10 (5) (2009) 1114–1124.
[38] P. Antoni, P. Begovac, K. Leontein, D. Nyström, K. Pietrzak, Improvements to Immobilised Biological Entities, A61K47/48; A61L27/34; A61L31/10; A61L33/00 ed2012.
[39] D.R. Miller, E.M. Valles, C.W. Macosko, Calculation of molecular parameters for stepwise polyfunctional polymerization, Polym. Eng. Sci. 19 (4) (1979) 272–283.
[40] D.R. Miller, C.W. Macosko, Molecular weight relations for crosslinking of chains with length and site distribution, J. Polym. Sci., Part B: Polym. Phys. 25 (12) (1987) 2441–2469.
[41] D.R. Miller, C.W. Macosko, Network parameters for crosslinking of chains with length and site distribution, J. Polym. Sci., Part B: Polym. Phys. 26 (1) (1988) 1–54.
[42] J.P. Pascault, H. Sautereau, J. Verdu, R.J.J. Williams, Thermosetting Polymers, Marcel Dekker, New York, 2002 (etc.).
[43] R.J.J. Williams, C.C. Riccardi, K. Dušek, Build-up of polymer networks by initiated polyreactions, Polym. Bull. 25 (2) (1991) 231–237.
[44] X. Fernandez-Francos, A. Serra, X. Ramis, Comparative analysis of stochastic network build-up methods for the curing of epoxy-anhydride thermosets, Eur. Polym. J. 53 (2014) 22–36.
[45] L. Matejka, Amine cured epoxide networks: formation, structure, and properties, Macromolecules 33 (10) (2000) 3611–3619.

[46] X. Fernandez-Francos, W.D. Cook, J.M. Salla, A. Serra, X. Ramis, Crosslinking of mixtures of DGEBA with 1,6-dioxaspiro[4,4]nonan-2,7-dione initiated by tertiary amines. III. Effect of hydroxyl groups on network formation, Polym. Int. 58 (2009) 1401–1410.

[47] L. Antonietti, C. Aymonier, U. Schlotterbeck, V.M. Garamus, T. Maksimova, W. Richtering, et al, Core–shell-structured highly branched poly(ethylenimine amide)s: synthesis and structure, Macromolecules 38 (14) (2005) 5914–5920.

[48] H. Liu, Y. Chen, D. Zhu, Z. Shen, S.-E. Stiriba, Hyperbranched polyethylenimines as versatile precursors for the preparation of different type of unimolecular micelles, React. Funct. Polym. (2007) 67.

[49] E.M.M. de Brabander-van den Berg, E.W. Meijer, Poly(propylene imine) dendrimers: large-scale synthesis by heterogeneously catalyzed hydrogenations, Angew. Chem., Int. Ed. Engl. 32 (9) (1993) 1308–1311.

[50] H.J. Flammersheim, Kinetics and mechanism of the epoxide-amine polyaddition, Thermochim. Acta 310 (1) (1998) 153.

[51] S. Swier, G. Van Assche, B. Van Mele, Reaction kinetics modeling and thermal properties of epoxy-amines as measured by modulated-temperature DSC. II. Network-forming DGEBA + MDA, J. Appl. Polym. Sci. 91 (5) (2004) 2814–2833.

[52] S. Swier, G. Van Assche, B. Van Mele, Reaction kinetics modeling and thermal properties of epoxy-amines as measured by modulated-temperature DSC. I. Linear step-growth polymerization of DGEBA + aniline, J. Appl. Polym. Sci. 91 (5) (2004) 2798–2813.

[53] J.-E. Ehlers, N.G. Rondan, L.K. Huynh, H. Pham, M. Marks, T.N. Truong, Theoretical study on mechanisms of the epoxy-amine curing reaction, Macromolecules 40 (12) (2007) 4370–4377.

[54] C. Sarmoria, E.M. Valles, D.R. Miller, Validity of some approximations used to model intramolecular reaction in irreversible polymerization, Macromolecules 23 (2) (1990) 580–589.

[55] C. Sarmoria, D.R. Miller, Spanning-tree models for Af homopolymerizations with intramolecular reactions, Comput. Theor. Polym. Sci. 11 (2) (2001) 113–127.

[56] J. Šomvársky, K. Dušek, M. Smrčková, Kinetic modelling of network formation: size-dependent static effects, Comput. Theor. Polym. Sci. 8 (1–2) (1998) 201–208.

[57] M. Dušková-Smrčková, H. Valentová, A. Ďuračková, K. Dušek, Effect of dilution on structure and properties of polyurethane networks. Pregel and Postgel cyclization and phase separation, Macromolecules 43 (15) (2010) 6450–6462.

[58] Y. Tanaka, J.L. Stanford, R. Stepto, Interpretation of gel points of an epoxy-amine system including ring formation and unequal reactivity: reaction scheme and gel-point prediction, Macromolecules 45 (17) (2012) 7186–7196.

[59] S. Paz-Abuin, A. Lopez-Quintela, M. Varela, M. Pazos-Pellin, P. Prendes, Method for determination of the ratio of rate constants, secondary to primary amine, in epoxy-amine systems, Polymer 38 (12) (1997) 3117–3120.

[60] B.A. Rozenberg, Kinetics, thermodynamics and mechanism of reactions of epoxy oligomers with amines, Adv. Polym. Sci. 75 (1986) 113–165.

[61] X. Fernandez-Francos, X. Ramis, A. Serra, From curing kinetics to network structure: a novel approach to the modeling of the network build-up of epoxy-anhydride thermosets, J. Polym. Sci., Part A: Polym. Chem. 52 (2014) 61–75.

[62] K. Dušek, M. Gordon, S.B. Ross-Murphy, Graphlike state of matter. 10. Cyclization and concentration of elastically active network chains in polymer networks, Macromolecules 11 (1) (1978) 236–245.

[63] P. Polanowski, J.K. Jeszka, W. Li, K. Matyjaszewski, Effect of dilution on branching and gelation in living copolymerization of monomer and divinyl cross-linker: modeling using dynamic lattice liquid model (DLL) and Flory-Stockmayer (FS) model, Polymer 52 (22) (2011) 5092–5101.

[64] G.O. Nevstad, J. Songstad, Solvent properties of dichloromethane. 2. The reactivity of dichloromethane toward amines, Acta Chem. Scand. Ser. B-Org. Chem. Biochem. 38 (6) (1984) 469–477.

[65] J.-J. Lee, K.J. Stanger, B.C. Noll, C. Gonzalez, M. Marquez, B.D. Smith, Rapid fixation of methylene chloride by a macrocyclic amine, J. Am. Chem. Soc. 127 (12) (2005) 4184–4185.

[66] D. Santiago, X. Fernández-Francos, F. Ferrando, S. De la Flor, Shape-memory effect in hyperbranched poly(ethyleneimine)-modified epoxy thermosets, J. Polym. Sci., Part B: Polym. Phys. 53 (13) (2015) 924–933.

[67] J.D. Ferry, Viscoelastic Properties of Polymers, third ed., John Wiley and Sons, New York, 1980 (etc.).

[68] J.M. Charlesworth, Effect of crosslink density on molecular relaxations in diepoxide-diamine network polymers. Part 2. The rubbery plateau region, Polym. Eng. Sci. 28 (4) (1988) 230–236.

[69] D.R. Miller, C.W. Macosko, A new derivation of post gel properties of network polymers, Macromolecules 9 (2) (1976) 206–211.

[70] W.W. Graessley, Statistical mechanics of random coil networks, Macromolecules 8 (2) (1975) 186–190.

[71] X. Fernández-Francos, D. Santiago, F. Ferrando, X. Ramis, J.M. Salla, À. Serra, et al, Corrigendum: network structure and thermomechanical properties of hybrid DGEBA networks cured with 1-methylimidazole and hyperbranched poly(ethyleneimine)s, J. Polym. Sci., Part B: Polym. Phys. 51 (9) (2013) 772–773.