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Theoretical modeling of the effect of proton donors and regeneration reactions in the network build-up of epoxy thermosets using tertiary amines as initiators

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ABSTRACT

A kinetic-structural model for the curing of epoxy resins with tertiary amines as initiators has been proposed. This model is based on a likely reaction mechanism, which includes the effect of tertiary amine regeneration and the effect of proton donors on the initiation and chain-transfer, and a statistical network build-up methodology based on the independent reactivity of epoxy groups and the random recombination of primary chains. A significant effect of proton donors or impurities is predicted by the model, which can be explained by their likely participation as chain-transfer agents and initiating sites. The occurrence of tertiary amine regeneration has also a profound effect on the curing, but the different regeneration mechanisms have opposite effects and may be counter-balanced. This flexible model is able to explain the curing behavior of different epoxy formulations with tertiary amines as initiator.

1. Introduction

The homopolymerization of epoxides with tertiary amines as anionic initiators has been studied in the past [1–12]. The process is highly complex due to the concurrence of multiple reactions, namely: (1) initiation leading to the formation of an epoxy-tertiary amine adduct alkoxide anion, (2) anionic polyetherification through an alkoxide anion, (3) regeneration of the tertiary amine, which may then restart the homopolymerization sequence and (4) chain-transfer between the alkoxide anions and existing proton donors such as hydroxyl compounds. The complexity of the curing process increases even more if one takes into account the network build-up process. This involves the formation of a variety of n-meric species, macromolecules with an increasing mass and degree of branching as the curing advances. The reactivity of the groups in a chain may depend on the chain size, its topology, the surrounding environment or different levels of substitution effects, among other factors. The occurrence of gelation and vitrification, leads to further topological or mobility restrictions that can have a significant effect on the curing kinetics [13].

Although the epoxy homopolymerization with tertiary amines has been extensively studied [7,9,10,14,15], apparently contradictory results have been reported in the literature concerning the network build-up [10,16]. In some cases, wrong assumptions on the network build-up process have been made [7]. A network build-up method based on the expectation probability, as described by Miller and Macosko [17–19], is used in the present work to model the curing of diglycidyl ether of bisphenol A (DGEBA) thermosetting formulations with tertiary amines as initiators. This method is based on the generation of primary chains or clusters that are later on on randomly recombined in different ways to conform the network structure. Primary chain methods have been used in the past to study

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relatively simple chainwise polymerizations [20–22] but can be applied to rather complex copolymerization processes involving substitution effects, chain coupling and chain scission, among other features [23–25]. This method was recently applied, in combination with a relatively simple kinetic model, to the study of the curing of epoxy-anhydride formulations [26]. The effect of proton donors on the curing kinetics and network build-up is taken into account by means of the addition of mono hydroxylic compounds or the increasing hydroxylic oligomer content of DGEBA. Pregel and postgel statistical averages of the primary chain and fragment network build-up methods are calculated and compared with a reference living polymerization kinetic models. The validity and potential applicability of the proposed kinetic and structural model are discussed.

2. Theoretical

2.1. Reaction mechanism

Different initiation mechanisms for the polymerization of epoxy monomers with tertiary amines can be found in the literature [3,4,9]. Although it is commonly assumed that initiation occurs by nucleophilic addition of the tertiary amine to the epoxy ring resulting in a zwitter-ion [1,3,7,9], Scheme 1a, Rozenberg [4] showed that a likely mechanism involved the participation of a proton donor such as a hydroxylic compound, that weakens the oxirane ring strength, resulting eventually in (1) the formation of an alkoxide anion coming from the hydroxylic compound and (2) a tertiary-ammonium counter-cation be with an end hydroxyl group coming from the amine-epoxy addition. According to this mechanism, proton donors become the propagating sites, rather than the epoxy-amine adduct. However, it is also commonly reported that epoxides and imidazoles form adducts [1,7,8], therefore the real initiation mechanism may depend on the type of tertiary amine used for the curing.

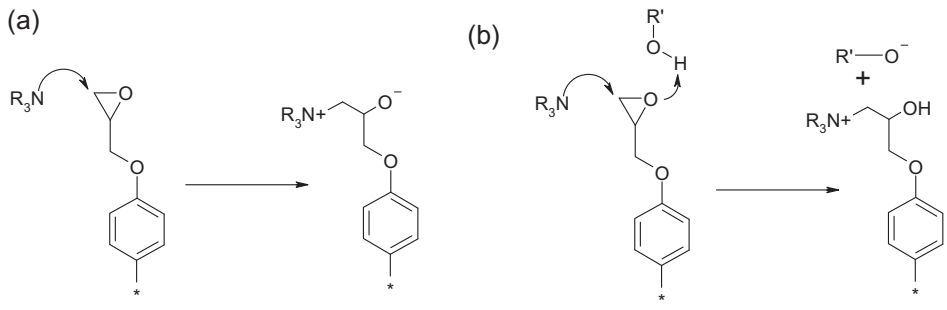
The propagation mechanism, shown in Scheme 2, consists in the ring-opening of an epoxy group by an alkoxide anion.

The regeneration of tertiary amines has been frequently reported in the literature [3,4,9,11,27]. Regeneration may take place by means of two different mechanisms: a β-elimination based on a hydrogen abstraction by an alkoxide anion (Scheme 3a) and a substitution mechanism (Scheme 3b). An important difference between the different tertiary amine regeneration mechanisms is their different effect on the network structure during curing. While elimination simply stops chain growth, thus reducing primary chain length and reducing crosslinking, substitution leads to chain coupling, resulting in an increase in chain length and an increase in crosslinking. In some reports regeneration reactions are considered to be intra-molecular [9], but in the present work it has been assumed that cyclization reactions are negligible and so regeneration is modeled as inter-molecular instead. Matejka et al. [5] reported that initiator regeneration could account for the low molecular weight of the oligomers obtained in the polymerization of N-methylglycidylaniline with tertiary amines or amino alcohols. Short oligomers have also been obtained in the polymerization of phenyl glycidyl ether with different tertiary amines [9]. Although it is acknowledged that the substitution elimination mechanism is a major regeneration mechanism [3,27], evidence of the occurrence of the elimination mechanism is more frequently found [9–11,27]. The formation of hydroxyl groups and vinyl groups during curing has been reported [9,11]. The formation of carbonyl groups has also been reported [11,27] in the literature. Although a rather elaborate mechanism for the presence of carbonyl groups has been recently proposed [11], a more simple mechanism may take place, as illustrated by Scheme 4, if one considers the initiation mechanism proposed by Rozenberg [4] or the occurrence of chain-transfer reactions. However, given the slow intensity of the appearing carbonyl band, this process is considered to take place to a very small extent. The occurrence of termination reactions without regeneration of the tertiary amine, leading to incomplete curing of epoxy resins [9,11], has also been proposed. Chain-transfer reactions between the alkoxide propagating chain and hydroxylic compounds (see Scheme 5) also take place, which has been claimed to have a significant effect on the network build-up during curing [10].

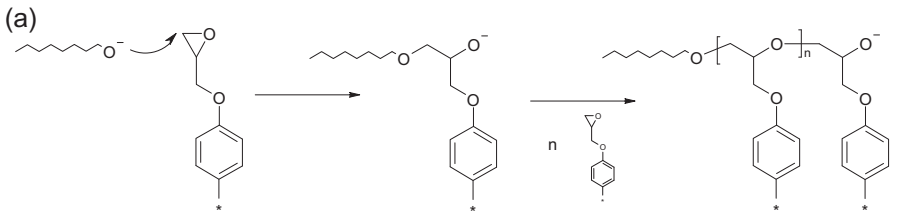
2.2. Kinetic model definition

The above description of the curing mechanisms suggests that, at least, one should consider the following reactions:

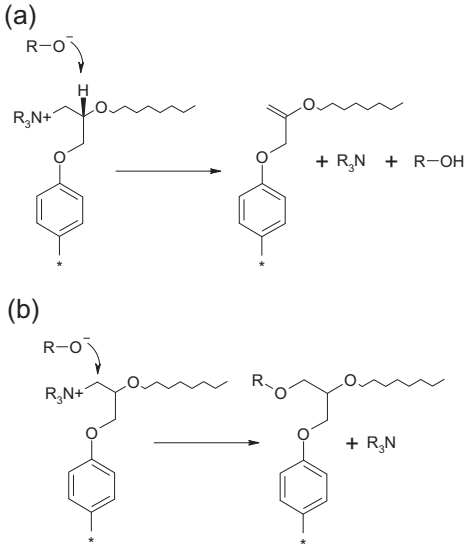
– Initiation by zwitter-ion formation without and with the catalysis of hydroxyl groups.



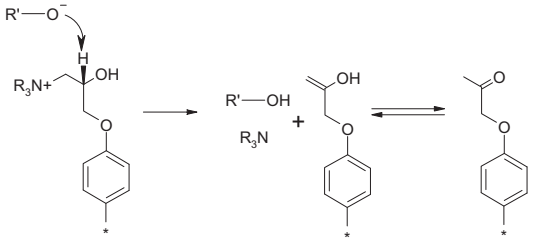
Scheme 1. Initiation mechanisms for the homopolymerization of epoxides with tertiary amines.



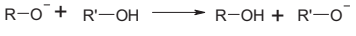
Scheme 2. Propagation mechanism for the homopolymerization of epoxides with tertiary amines.



Scheme 3. Proposed mechanisms for the regeneration of tertiary amines, by (a) elimination and (b) substitution.



Scheme 4. Proposed mechanism for the formation of carbonyl groups.



Scheme 5. Chain-transfer between alkoxide anions and hydroxylic compounds.

- Initiation by adduct formation with transfer to hydroxyl compound.
- Propagation by any alkoxide anion present in the system.
- Chain transfer between any alkoxide anion and hydroxylic species.
- Initiation regeneration by elimination or substitution.

However, if one considers a general reaction mechanism, both initiation reactions lead to the formation of an alkoxide anion and an ammonium cation. In addition, chain transfer does not alter the overall concentration of hydroxylic and alkoxide species. Therefore, the mechanism can be summarized as follows:

$$I + E \xrightarrow{k_{ini}, k_{iniOH}, k_{inicat}} I^+ + E^-$$

$$E^- + E \xrightarrow{k_p} E^-$$

$$I^+E^- \xrightarrow{k_{reg}} I + OH + RG$$

$$I^+E^- \xrightarrow{k_{reg2}} I + chain$$

$$E^- + OH \xrightarrow{k_{trans}} OH + E^-$$

Table 1 shows the generic reactive species that are considered in this work and their expression in terms of normalized concentration with respect to the initial amount of a reference species, in this case the epoxy groups. The use of normalized concentration allows one to use normalized kinetic constants k', defined in Table 2, which allows one to take into account volume effects, if deemed convenient [26]. On the basis of the normalized concentrations shown in Table 1 one can also define an overall conversion as $x = 1 - e$.

Table 3 shows the set of rate expressions that can describe the concentration of the generic species present in the curing process. It should be noted that regeneration reactions, whether of elimination or substitution, are considered to be first order with respect to the active species, or rather, with respect to the ion pair formed with the corresponding couter-ion, as done in previous works [22,26].

Table 1
Expression of the normalized concentration of the reactive species during curing of epoxy-tertiary amine formulations. n_{xxx} represents the number of moles of each *xxx* species.

Species	Symbol	Normalized concentration
Initiator	I	$i = \frac{n_I}{n_{E,0}}$
Tertiary ammonium cation	I^+	$i^+ = \frac{n_{I^+}}{n_{E,0}}$
Alkoxide anion	E^-	$e^- = \frac{n_{E^-}}{n_{E,0}}$
Reactive epoxy	E	$e = \frac{n_E}{n_{E,0}}$
Hydroxyl group	OH	$oh = \frac{n_{OH}}{n_{E,0}}$
Regeneration double bond	RG	$rg = \frac{n_{RG}}{n_{E,0}}$

Table 2
Expression of the normalized kinetic constants. C_{E0} is the initial concentration of unreacted epoxy groups.

Reaction	Kinetic constant	Normalized kinetic constant (s^{-1})	Normalized kinetic constant, constant volume (s^{-1})
Initiation	k_{ini} ($M^{-1}\,s^{-1}$)	$k'_{ini} = k_{ini} \cdot \frac{n_{E,0}}{V}$	$k'_{ini} = k_{ini} \cdot C_{E,0}$
Catalyzed initiation	k_{inicat} ($M^{-2}\,s^{-1}$)	$k'_{inicat} = k_{inicat} \cdot \left(\frac{n_{E,0}}{V}\right)^2$	$k'_{inicat} = k_{inicat} \cdot C^2_{E,0}$
Catalyzed initiation with transfer to OH	k_{iniOH} ($M^{-2}\,s^{-1}$)	$k'_{iniOH} = k_{iniOH} \cdot \left(\frac{n_{E,0}}{V}\right)^2$	$k'_{iniOH} = k_{iniOH} \cdot C^2_{E,0}$
Propagation	k_p ($M^{-1}\,s^{-1}$)	$k'_p = k_p \cdot \frac{n_{E,0}}{V}$	$k'_p = k_p \cdot C_{E,0}$
Elimination regeneration	k_{reg} (s^{-1})	$k'_{reg} = k_{reg}$	$k'_{reg} = k_{reg}$
Substitution regeneration	k_{reg2} (s^{-1})	$k'_{reg2} = k_{reg2}$	$k'_{reg2} = k_{reg2}$
Chain-transfer	k_{trans} ($M^{-1}\,s^{-1}$)	$k'_{trans} = k_{trans} \cdot \frac{n_{E,0}}{V}$	$k'_{trans} = k_{trans} \cdot C_{E,0}$

Table 3
Proposed kinetic model.

Species	Rate expression
i	$\frac{di}{dt} = -(k'_{ini} + k'_{inicat} \cdot oh + k'_{iniOH} \cdot oh) \cdot i \cdot e + (k'_{reg} + k'_{reg2}) \cdot i^+$
i^+ or e^-	$\frac{di^+}{dt} = \frac{de^-}{dt} = -\frac{di}{dt}$
e	$\frac{de}{dt} = -(k'_{ini} + k'_{inicat} \cdot oh + k'_{iniOH} \cdot oh) \cdot i \cdot e - k'_p \cdot e^- \cdot e$
oh	$\frac{doh}{dt} = k'_{reg} \cdot i^+$

The generation of hydroxyl groups by elimination regeneration and their participation as catalyst in the initiation steps can explain the autocatalytic behavior observed in the curing of DGEBA with imidazoles [1] and imidazole adducts [7]. Note that the formation of reaction complexes has not been taken into account for simplicity purposes, although some researchers have found that such consideration can help to improve significantly the kinetic description of the curing process [28,29]. This general kinetic scheme will have to be slightly modified when the different n-meric species present in the medium are considered. For instance, regeneration may not be possible in a zwitterion with a single epoxy moiety, as considered in previous works [22,26].

2.3. Network build-up

A recursive model based on the expectation theory [17–19] is used in the present work to study the network build-up during homopolymerization of DGEBA initiated by tertiary amines. In this method it is considered that tetrafunctional monomers can be split up into difunctional units with independent reactivity [23,24] and issuing each a virtual bond connecting it with any other difunctional unit. Upon polymerization a set of primary chains is formed, issuing each one a number of virtual bonds, which are then randomly recombined to form a likely network structure [23,24]. This methodology has been recently applied to model the cationic homopolymerization of DGEBA [30] or the curing of epoxy-anhydride formulations [26].

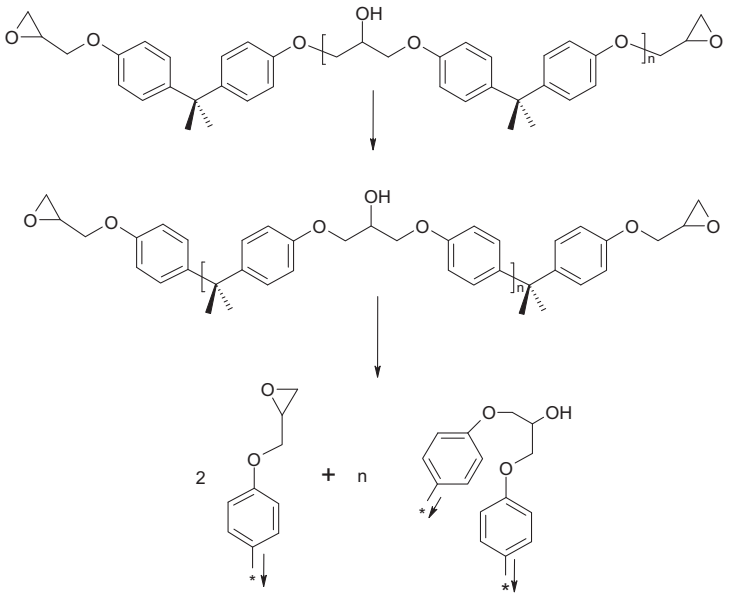
The reaction scheme shown in the preceding section needs to be slightly modified when the network build-up is considered, because of the presence of chains with different lengths. The primary chains present in the system may have different beginning or ending moieties depending on the different possible reactions that may take place during the curing process. The chain length distribution can be quite complex because (1) the regeneration reactions stop chain growth releasing the initiator, which may start another chain, but (2) elimination regeneration reduces average chain length but coupling increases average chain lengh, and (3) hydroxyl groups generated by elimination regeneration and added hydroxyl compounds can participate in chain-transfer reactions during curing.

Moreover, if oligomeric DGEBA resin is considered instead of a pure diepoxy monomer, the scenario is somewhat altered, as diepoxy monomers may not be simply splitted into two monoepoxides. Scheme 6 shows how a DGEBA oligomer can be split into different fragments that include the epoxy ends and the hydroxyl oligomer fraction. These fragments issue virtual bonds symbolized by an arrow that represent the connection with any other fragment issuing a virtual bond. It is assumed a completely random distribution of oligomer in DGEBA resin, although it may not be strictly true.

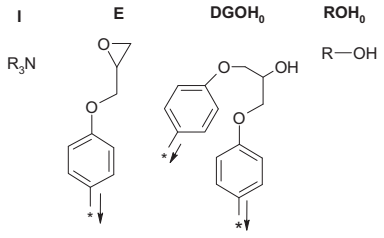
Upon polymerization, a series of primary chains is formed with a degree of polymerization n, where n stands for the number of reacted epoxy groups present in the chain. Each one of these chains will issue a number n of virtual bonds except those starting with the DGEBA oligomer, which in addition have two more virtual bonds coming from the oligomer structure. In the subsequent calculations of the pregel and postgel statistics, it will be assumed that the virtual arrow bonds can be randomly recombined.

In addition to oligomeric DGEBA, one should consider the presence of impurities. The strategy followed in this work is to consider the addition of a known amount of a small molecular weight monoalcohol. Therefore, in a curing formulation, the following species, shown in Scheme 7, should initially be present: tertiary amine initiator (I), epoxy groups (E), hydroxyl-ended DGEBA oligomer ($DGOH_0$) and added monoalcohol (ROH_0).

A complex reaction scheme arises from the first initiation and propagation steps, taking into account possible regeneration and transfer reactions. This leads to a variety of species that needs to be identified properly in order to avoid confusions. The different species present in the system have been coded according to the possible chain starts and chain ends. The following labels have been used: I (initiator), RG (regenerated double bond), R (monoalcohol), DG (oligomeric DGEBA hydroxyl group), C (coupled chain start or chain end), OH (end hydroxyl group), E (end alkoxide anion). Schemes 8 and 9 illustrate the different possible chains. The labeling and notation used to discern the



Scheme 6. Splitting up of a DGEBA oligomer into different structural fragments (hereinafter, the asterisk at the end of each fragment represents a half $C(CH3)_2$ moiety).



Scheme 7. Initial species present in the system.

primary chains are shown in Table 4. Scheme 10 illustrates the different reaction pathways that can take place in the system. According to this reactivity map, any generic species with end alkoxide anions may propagate and regenerate or undergo transfer reactions. Any species with a hydroxyl group may participate in the initiation mechanism. Any generic species beginning with an initiator moiety at the beginning may experience also a number of regeneration reactions. The only exception to this reactivity is the species coded as IE_1 (see Scheme 8), the zwiterionic initiator-epoxy adduct. It is considered that this species cannot undergo regeneration, like in previous works [22,26], because the proximity of the anion to the counter-cation prevents the attack of any other alkoxide anion by electrostatic repulsion and the small number of bonds in between makes an intramolecular attack highly unlikely. In addition, in the curing of epoxides with 1-unsubstituted imidazoles it is often observed that the adduct formation and the polyetherification reactions constitute well-separated reaction steps [1–3]. However, this may not work for other tertiary amines such as 1-substituted imidazoles [1,3] and therefore it is not considered in the present work.

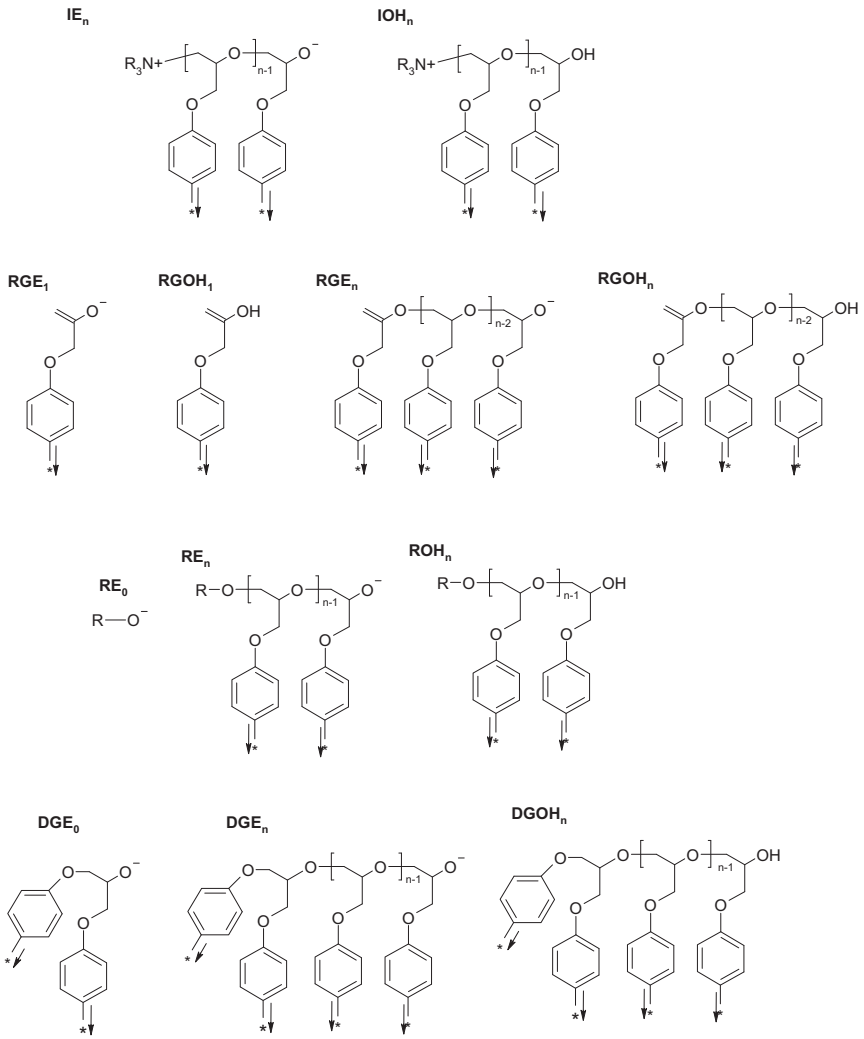
It should be clarified that zwiterr-ion species IE_n may undergo intramolecular regeneration depending on the chain size, leading directly to $RGOH_n$ species by elimination regeneration or to the formation of a macrocycle by substitution regeneration, as stated by Dell'Erba and Williams [9]. Such possibility is not considered explicitly in this work for the sake of simplicity. Dušek and Šomvársky [24] argued that primary chain cyclization may be very weak depending on the monomer structure and therefore were not considered for structure calculations. Cyclization reactions were also excluded by Matejka et al. [23] in their study of the cationic homopolymerization of DGEBA.

Treatment given to the modeling of regeneration by substitution should be commented. A polymeric chain P_n bearing an initiator moiety I^+ at the beginning may undergo a substitution, in the presence of another polymeric chain P_m bearing an alkoxide anion E^- at the end, which would lead to a coupling of chains (or even a cyclization, if an intramolecular reaction is considered):

$$I^+P_n + P_mE^- \xrightarrow{substitution} I + P_{m+n}$$

An obvious effect of this coupling would be a significant broadening of the primary chain distribution towards larger chain lengths and multiply the number of possible species present in the medium. In order to reduce the amount of species and the computational load, the following strategy has been used: a label C has been added to identify a new set of primary chains that have been coupled by the chain start or the chain end:

$$I^+P_n + P_mE^- \xrightarrow{substitution} I + CP_n + P_mC$$

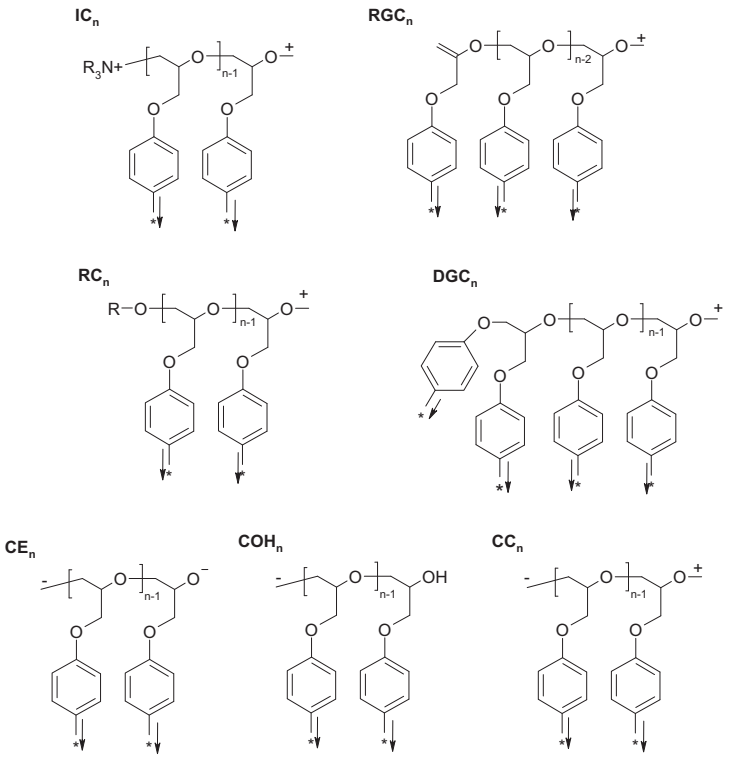


Scheme 8. Representation of the different primary chains defined by the network build-up model taking into account initiation, transfer and elimination regeneration reactions.

Chains with *C* label may be recombined in the calculations following strict direction rules. Therefore, the chain initially bearing the initiator moiety, after the substitution reactions now issues a virtual bond symbolized with *a* −, indicating the direction towards the chain start. The chain initially bearing the alkoxide anion, after this reaction now issues a virtual bond symbolized with *a* +, indicating the direction towards the chain end. This is illustrated in Scheme 9, where the different possible chains resulting from regeneration by substitution are shown. In contrast with arrow virtual bonds, which can be randomly recombined, - bonds can only be recombined with + bonds, and this needs to be taken into account when calculating the pregel and postgel statistics. This approach is different from that of Matejka et al. [23], by which an explicit distribution of recombined chains is obtained. A disadvantage of the strategy employed in this work is that the real distribution of primary chains cannot be exactly determined. Moreover, the accuracy of the statistical method may be somewhat reduced, as has been shown in the extreme case of using statistical fragments instead of primary chains [15,21].

It should be noted that chains starting with *I*, *RG* and *C* can have a degree of polymerization *n* greater or equal than 1, taking the degree of polymerization as the number of repeating reacted epoxy units in the chain. However, chains starting with *R* and *DG* can have a degree of polymerization greater or equal than 0, that is, they can have an active alkoxide or hydroxyl chain end without any polymerized epoxy groups, as shown in Scheme 8.

The detailed set of rate expressions for the different species present in the system is available as Supplementary information. These expressions follow the reactivity map outlined in Scheme 10 and take into account the preceding remarks on reactivity. It should be commented that it is an apparently complex model but there are important simplifications in it. The most relevant one is that intermolecular reactions such as chain-transfer or regeneration



Scheme 9. Representation of the primary chains defined by the network build-up model takint into account substitution regeneration reactions.

Table 4
Identification of primary chains present in the system.

Chain start	Chain end	Symbol	Normalized concentration
I	*OH*	IOH_n	$ioh_n = \frac{n_{IOH_n}}{n_{E,0}}$
	E	IE_n	$ie_n = \frac{n_{IE_n}}{n_{E,0}}$
	C	IC_n	$ic_n = \frac{n_{IC_n}}{n_{E,0}}$
RG	*OH*	$RGOH_n$	$rgoh_n = \frac{n_{RGOH_n}}{n_{E,0}}$
	E	RGE_n	$rge_n = \frac{n_{RGE_n}}{n_{E,0}}$
	C	RGC_n	$rgc_n = \frac{n_{RGC_n}}{n_{E,0}}$
R	*OH*	ROH_n	$roh_n = \frac{n_{ROH_n}}{n_{E,0}}$
	E	RE_n	$re_n = \frac{n_{RE_n}}{n_{E,0}}$
	C	RC_n	$rc_n = \frac{n_{RC_n}}{n_{E,0}}$
DG	*OH*	$DGOH_n$	$dgo_n = \frac{n_{DGOH_n}}{n_{E,0}}$
	E	DGE_n	$dge_n = \frac{n_{DGE_n}}{n_{E,0}}$
C	*OH*	COH_n	$coh_n = \frac{n_{COH_n}}{n_{E,0}}$
	E	CE_n	$ce_n = \frac{n_{CE_n}}{n_{E,0}}$
	C	CC_n	$cc_n = \frac{n_{CC_n}}{n_{E,0}}$

have identical kinetic constants regardless of the size and the structure of the reacting species. Thus, an exchange reaction between a given hydroxyl-ended chain and an alkoxide anion is modeled using a generic active species that includes any active species present in the system. Conversely, an exchange between a given alkoxide-ended chain and a hydroxyl compound uses a generic hydroxyl species that includes all the species in the system with hydroxyl groups. The kinetic constants do not depend on the chain size nor on other parameters such the average cluster size (except maybe for the different reactivity of the zwitter-ion species IE_1), but it could be incorporated in the model, as indicated by Dušek and Šomvársky [24]. Other effects such as mobility restriction due to diffusion or vitrification are not present but could be incorporated as well [13,31].

The kinetic scheme satisfies the following mass balances:

$$oh = \sum_{n\geqslant 0}(roh_n + dgoh_n) + \sum_{n\geqslant 1}(ioh_n + rgoh_n + coh_n) \quad (1)$$

$$e^- = \sum_{n\geqslant 0}(re_n + dge_n) + \sum_{n\geqslant 1}(ie_n + rge_n + ce_n) \quad (2)$$

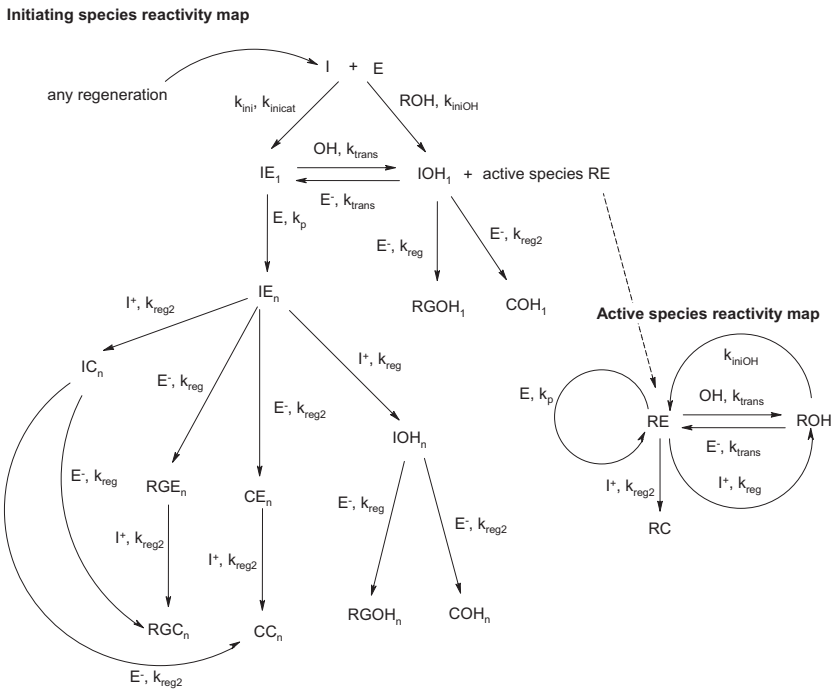
$$i^+ = \sum_{n\geqslant 1}(ie_n + ioh_n + ic_n) \quad (3)$$

Assuming electrical charges equilibrium, it must be fulfilled that $e^- = i^+$.

Taking into account the coupling of chains, it must also be verified that:

$$\sum_{n\geqslant 1}(ce_n + coh_n + cc_n) = \sum_{n\geqslant 0}(rc_n + dgc_n) + \sum_{n\geqslant 1}(ic_n + rgc_n + cc_n) \quad (4)$$

The epoxy group conversion x is equal to the first moment of the degree of polymerization of the different chains with nominal length greater or equal than 1 (that is, they have some reacted epoxy groups):



Scheme 10. Reactivity map of the epoxy homopolymerization using tertiary amines as initiator.

$$x = 1 - e = \sum_{n \geqslant 1} n \cdot (ie_n + ioh_n + ic_n + rge_n + rgoh_n + rgc_n + re_n + roh_n + rc_n + dge_n + dgoh_n + dgc_n + ce_n + coh_n + cc_n) \quad (5)$$

Taking into account that the number of hydroxy groups formed by regeneration is equal to that of double bond chain starts one can also write:

$$oh - oh_{t=0} = \sum_{n \geqslant 1} (rge_n + rgoh_n + rgc_n), \quad (6)$$

where the initial amount of hydroxyl groups $oh_{t=0}$ consists in the oligomeric DGEBA groups and added hydroxyl compounds

$$oh_{t=0} = (dgoh_0 + roh_0)_{t=0} \quad (7)$$

The total mass of the system M_{total} throughout the curing process, which includes the contribution of all primary chains (see Supplementary information for details) must remain constant. Taking into account that, at the beginning, the only available species are e, i, $dgoh_0$ and roh_0:

$$M_{total} = (e \cdot M_e + dgoh_0 \cdot M_{dg} + roh_0 \cdot M_r + i \cdot M_{ini})_{t=0} = constant \quad (8)$$

The statistical recursive methodology [18] defines the average molecular weight W pending from any of the arrows of the unreacted monomer or primary chains. Following the methodology described for statistical fragments [32], one can also define the average molecular weights Y^+ and Y^- pending from + and − bonds of coupled chains, respectively. Since each arrow bond is connected to another arrow bond, W can be determined from the likelihood of randomly capturing an arrow bond of a given primary chain and the molecular weight hanging from this bond, which includes the primary chain mass and the molecular mass W pending from all the remaining arrows, and Y^+ and Y^- if + or − bonds are present. Because Y^+ is the mass pending from a + bond, Y^+ is calculated recursively from the likelihood of capturing a coupled – bond, the cluster mass and the rest of pending average masses, and Y^- is calculated conversely. To summarize it, it is shown that W, Y^+ and Y^- can be calculated from a 3×3 linear system as follows:

$$\begin{aligned} C_{W,W} \cdot W &= K_W + C_{W,+} \cdot Y^+ + C_{W,-} \cdot Y^- \\ C_{+,+} \cdot Y^+ &= K_+ + C_{+,W} \cdot W \\ C_{-,-} \cdot Y^- &= K_- + C_{-,W} \cdot W \end{aligned} \quad (9)$$

Details on the recursive procedure for the determination of these average masses and the constants in the 3×3 system are available as Supplementary information. Before the gel point, the mass-average molecular weight of the system M_w must be finite. Because M_w depends on both the primary chains concentration and mass but also on the average weights W, Y^+ and Y^-, in the pregel state a finite solution for all those statistical averages is found. Gelation is achieved when the mass-average molecular weight of the system M_w diverges to infinity. Because the mass of the primary chains is finite, it is necessary that W, Y^+ and Y^- diverge also to infinity. Solving for W, the gel condition is:

$$C_{W,W} - \left(\frac{C_{-,W} \cdot C_{W,-}}{C_{-,-}}\right) - \left(\frac{C_{+,W} \cdot C_{W,+}}{C_{+,+}}\right) = 0 \quad (10)$$

In order to find the gel conversion one can use the extinction probability, coded as Z in the present work, defined as the probability of finding a finite continuation from each one of the primary chain bonds. The extinction probability is usually coded as v in the literature [23,24,33], or as $P(F_A^{OUT})$ in the work of Miller and Macosko [19], although a variety of symbols may be used [15,32]. Z is determined in a recursive way from the probability of capturing a primary chain and the probability that the rest of the primary chain bonds have a finite continuation. However, in addition to the extinction probability of the arrow bonds Z, one must take into account the presence of extinction probabilities Z^+ and Z^- resulting from the coupling of chains. A series of recursive expressions $Z = f(Z, Z^+, Z^-)$, $Z^+ = f(Z, Z^+)$ and $Z^- = f(Z, Z^-)$ can be defined (see Supplementary information). These functions have the form of probability generating functions that, before the gel point, have only the possible solution $Z = Z^+ = Z^- = 1$, because all chains must have finite continuation. Once gelation takes place, there is always a trivial solution $Z = Z^+ = Z^- = 1$ but there is also a non-trivial solution of the extinction probabilities, each one taking a different value, decreasing with increasing crosslinking down to 0 for a fully crosslinked network (i.e. no probability of finding a finite end to a chain). Gelation takes place then at a conversion at which a non-trivial solution of the extinction probabilities is first found [19].

The soluble fraction w_{sol} after the gel point is determined from the probability that all the virtual bonds in the primary chains have finite continuation, using the extinction probabilities Z, Z^+ and Z^-, and the weight fraction of each primary chain. The gel fraction is automatically defined as $w_{gel} = 1 - w_{sol}$. The number of crosslinks in the network, n_{cross}, is calculated from the probability that a primary chain issues at least three virtual bonds with an infinite continuation. The probability of finding an infinite continuation from a virtual bond is defined from the extinction probability as $1 - Z$, $1 - Z^+$ and $1 - Z^-$. Details on the determination of the extinction probabilities Z, Z^+ and Z^-, w_{sol} and n_{cross} can be found as Supplementary information.

Several reports on the calculation of gel point conversion, pregel and postgel statistical averages using equivalent stochastic network build-up methods can be found in the literature [15,17–21,23,26,32,34–37]. For details on the procedure employed in this work and the derivation of the different statistical averages, the reader should refer to Supplementary information available online.

3. Results and discussion

First, different effects will be studied separately: the role of chain transfer, the initiation mechanism, the reactivity of the propagating species and the occurrence and type of regeneration reactions. The conversion at gelation x_{gel} will be used as a comparing parameter. Next, some practical cases, based on literature data, will be discussed.

To begin with, the effect of chain transfer to hydroxylic compounds has been studied. Fig. 1 compares the effect of chain transfer to oligomeric DGEBA and to an added hydroxylic compound. In general, it is observed an increase in the conversion at gelation due to the increase in chain starts and subsequent shortening of the chain length. However, this effect is only discrete for the hydroxyl groups of DGEBA due to the crosslinking character of the oligomer unit, while it is significant for the added monoalcohol because it results in a net increase in chain starts. When initiation is relatively fast, the effect of adding a monoalcohol is less than additive with respect to the amount of initiator. If the initiation rate was significantly low, the effect of adding a monoalcohol would be more than additive (not shown).

If the initiation mechanism proposed by Rozenberg takes place, then the addition of a proton donor such as a monoalcohol increases the conversion at gelation significantly, as seen in Fig. 2. On the contrary, if one considers only oligomeric DGEBA, the conversion at gelation decreases because of the crosslinking character of the DGEBA oligomer. Possibly the adduct formation given by the first initiation mechanism is also catalyzed by the presence of hydroxyl groups, as shown before [11], in which case the initiation mechanism shown in Scheme 1a would take place but a catalytic constant k'_{inicat} should be used instead of k'_{iniOH}. In this case, and assuming no other reactions take place, conversion at gelation would not be affected by the presence of proton donors (not shown).

The effect of the different regeneration mechanisms is illustrated in Fig. 3. It is seen how the occurrence of elimination regeneration leads to a significant increase in conversion at gelation, as reported previously [26], because the chains are stopped and prevented from growing further, thus lowering the average chain length. In contrast, when substitution regeneration takes place there is a significant decrease in conversion at gelation because chains are recombined, thus leading to an increase in average chain length. The combination of both mechanisms is also shown in Fig. 3. Overall, the substitution mechanism has a stronger effect than the elimination mechanism but its contribution may be lower, leading to an effective shortening of the chain length, as suggested in the literature [9].

In a real formulation, all those effects may be present at the same time. The relative importance of each one should

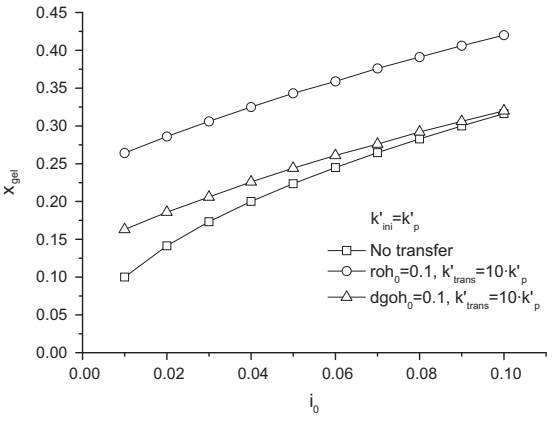


Fig. 1. Effect of the chain transfer in the presence of monoalcohol or oligomeric DGEBA on the conversion at gelation, assuming $k'_i = k'_p$.

depend on the DGEBA oligomer content, the presence of protic impurities, the amount of initiator and its reactivity, and the likelihood of regeneration reactions, among other factors. This complexity is illustrated in Figs. 4 and 5. Fig. 4 shows relevant differences in the network build-up statistics between the living polymerization and the polymerization with chain transfer and regeneration. The conversion at gelation (M_w diverges to infinity) increases, the final crosslinking density is lower and a soluble fraction may be present at the end of the curing process because of the occurrence of regeneration and chain-transfer processes. Fig. 5 shows that, while the living polymerization model results in a Poisson-like distribution of the n-meric species, the regeneration and chain transfer model results in a complex distribution of primary chains which, overall, is closer to a most probable distribution than to a Poisson distribution [38]. Thus, the proposed model is capable of simulating a variety of situations depending on the reactivity of the different species and their initial concentration.

Fernandez-Francos et al. [10] reported that the curing of a DGEBA of ca 190 g/eq with 2 phr of 1-methylimidazole (1MI) led to a conversion at the gel point of 0.48. In that work it was claimed that the occurrence of chain transfer and regeneration had an important effect on the network build-up. Later on, however, Morell et al. [16] reported a conversion at the gel point of 0.30 for the curing of a DGEBA of 182 g/eq and 5 phr of 1MI, a higher amount of initiator than in the previous case. Several reports on the occurrence of imidazole regeneration during curing of DGEBA formulations can be found in the literature [11,39,40]. Given that the initiator employed in both cases is the same, 1MI, initiator regeneration should play a similar role. One can be tempted to explain those differences in terms of the higher hydroxyl content of the DGEBA used in that work. However, it has been shown in the present work that the effect of chain-transfer to DGEBA alone is very limited unless more hydroxyl compounds are present in the mixture either because of regeneration or the presence of impurities.

It is hypothesized that those apparently contradictory results can be explained by the combined effect of regeneration reactions and the presence or absence of impurities,

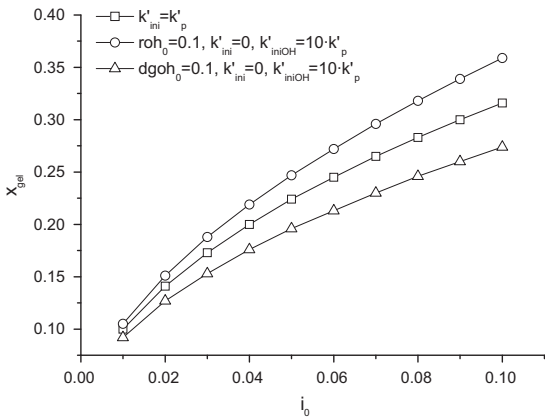


Fig. 2. Effect of the presence of monoalcohol or oligomeric DGEBA on the conversion at gelation, depending on the initiation mechanism.

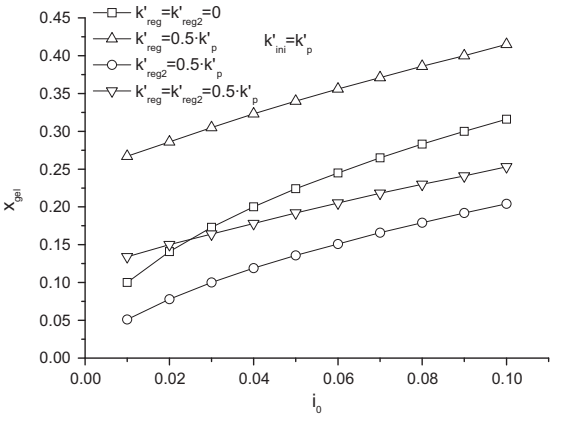


Fig. 3. Effect of elimination and/or substitution regeneration on the conversion at gelation for a DGEBA with no oligomer content and without added protic species.

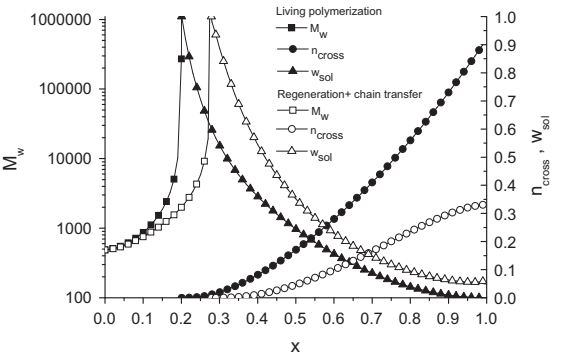


Fig. 4. Relevant statistic averages two different curing situations using DGEBA with an initial oligomer concentration of 0.1 and an initiator concentration of 0.04. The living polymerization has been modeled with $k'_{ini} = k'_p$. The regeneration and transfer polymerization has been modeled with $k'_{ini} = k'_p$, $k'_{inicat} = 10{\cdot}k'_{ini}$, $k'_{gen} = 0.2{\cdot}k'_p$ and $k'_{trans} = 10{\cdot}k'_p$.

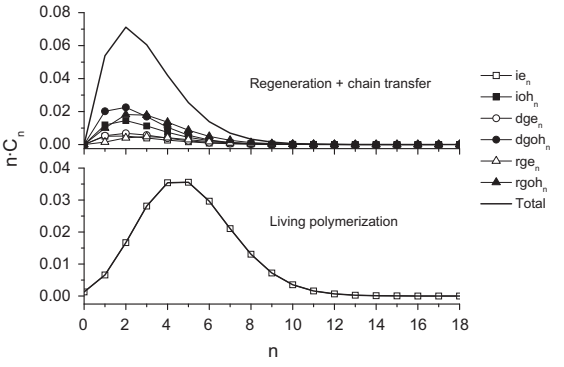


Fig. 5. Primary chain distribution at gelation for two different curing situations using DGEBA with an initial oligomer concentration of 0.1 and an initiator concentration of 0.04. The living polymerization has been modeled with $k'_{ini} = k'_p$. The regeneration and transfer polymerization has been modeled with $k'_{ini} = k'_p$, $k'_{inicat} = 10{\cdot}k'_{ini}$, $k'_{gen} = 0.2{\cdot}k'_p$ and $k'_{trans} = 10{\cdot}k'_p$.

though such possibility was not contemplated in that previous work [10]. Whether this is significant or not can be

calculated easily. For instance, water impurity content of 1 wt.% in undried DGEBA represents ca 0.1 mols per epoxy equivalent, and a total amount of protons of ca 0.2 mols per epoxy equivalent. This is exemplified in Table 5, where the gel conversion in both cases is calculated using the above kinetic scheme and network build-up model. In the first case, the presence of a small molecular weight impurity is modeled by means of adding a relatively high amount of methanol (32 g/mol). In the second case, such impurity is not present. For this simulation it has been assumed that $k_i' = k_p' = 0.01\ s^{-1}$, $k_{inicat}' = 0.1\ s^{-1}$ (proton donors have only a catalytic effect on the initiation mechanism shown in Scheme 1a, though it need not be strictly true), $k_{trans}' = 0.1\ s^{-1}$, $k_{gen}' = 0.004\ s^{-1}$, $k_{gen2}' = 0.003\ s^{-1}$. It is observed how in the first case, in spite of the lower initiation concentration, the conversion at gelation is higher than in the second case, where it has been considered that no impurities were present. The first case would represent a situation closer to that of one reference [10] and the second case to the other [16]. If there were no impurities in the first case, the gel conversion would be 0.259, the crosslinking density would be 0.357 and the sol fraction would be 0.062. Therefore, the curing of undried DGEBA may lead to materials with somewhat different properties with respect to those coming from properly dried DGEBA, because the presence of proton donors can have a deep effect on the network structure, not only on the curing kinetics [11]. However, very little data is available for comparison in the literature concerning the crosslinking density [9,14] and it is reported that, for instance, relaxed modulus measurements using DMA may not provide a direct measurement of the crosslinking density as deviations from the ideal elastomer behavior may occur [14,41].

Barton et al. [7] reported a conversion at gelation for the curing of DGEBA, using phenlyglycidyl ether-ethylmethyl imidazole adducts as initiators, of 0.39–0.43. It was stated that these values were lower than the expected using, mistakenly, the classical Flory expression for step-wise polymerizations. Although the primary chain definition should be altered to account for the structure and presence of hydroxyl groups in the imidazole adducts, one can roughly estimate, using the same constants as in the preceding case, an approximate conversion of ca 0.44 assuming hydroxyl groups from the imidazole adduct act like monoprotic added impurity. If one considered the real adduct structure, the conversion at gelation would be somewhat lower due to an increase in kinetic chain length, getting closer to the reported values [7].

Table 5
Determination of structural parameters for the curing of DGEBA with 1-methyl imidazole in two cases selected according to literature results [10,16].

	Case 1 (Ref. [10])	Case 2 (Ref. [16])
DGEBA eq. weight (g/ee)	190.5	182
Initiator content (phr)	2	5
$dgoh_{0,t=0}$	0.072	0.042
$roh_{0,t=0}$	0.150	0.000
$i_{t=0}$	0.047	0.112
x_{gel}	0.452	0.325
n_{cross}	0.166	0.385
w_{sol}	0.126	0.098

Dell'Erba and Williams reported that the average chain-length of polymerized phenyl glycidyl ether with benzydimethylamine (BDMA) as initiator is around 4 for an initiator-epoxy molar ratio of 0.08 [9]. When 4-(dimethylamino) pyridine (DMAP) is used as initiator, in the same molar ratio, the average chain length is around 7 [9]. Assuming a living polymerization model and complete polymerization, one would expect an average chain length of 12.5. In both cases, this rather low chain length can be explained by the occurrence of regeneration reactions, as pointed out in the discussion of the reaction mechanism. Moreover, the authors argued that the difference between both initiators could be explained by the higher propagation rate of the alkoxide anion using DMAP because of the absence of a mobile counter-cation. For non-crosslinking processes using monoepoxides, the kinetic-structural model can also be used to predict the true polymer chain distribution, which would be equal to the primary chain distribution. It has been calculated the primary chain length P_n (see appendix) at the end of the curing process of a formulation with no oligomeric DGEBA and no added monoalcohol, using a different set of reaction parameters than those of the preceding examples, since the amines are different. For BDMA it has been assumed that the initiation mechanism shown in Scheme 1b takes place, leading to the formation of a mobile couter-ion, and is therefore highly dependent on the hydroxyl content. Thus, in this case $k_p' = 0.01\ s^{-1}$, $k_i' = 0.005\ s^{-1}$, $k_{iniOH}' = 0.05\ s^{-1}$, $k_{trans}' = 0.1\ s^{-1}$, $k_{gen}' = 0.003\ s^{-1}$, $k_{gen2}' = 0.004\ s^{-1}$, and a value of P_n of 4.3 is obtained. For DMAP it has been assumed that initiation takes place according to the mechanism shown in Scheme 1a and that it is faster and less dependent on the hydroxyl content. The value of the propagation constant has been increased to account for the supposedly absence of a mobile counter-ion. The new set of constants is $k_p' = 0.03\ s^{-1}$, $k_i' = 0.02\ s^{-1}$, $k_{inicat}' = 0.01\ s^{-1}$, $k_{trans}' = 0.1\ s^{-1}$, $k_{gen}' = 0.003\ s^{-1}$, $k_{gen2}' = 0.004\ s^{-1}$, which gives a value of P_n of 6.8. One should also take into account that the likelihood of regeneration should not be the same and consider the effect of the different termination reaction reported for DMAP [9], but the sole change in initiation and propagation rate constants helps to explain the differences reported in the literature, as suggested [9].

Given that the proposed model can be used to explain a variety of experimental results, it can be concluded that the kinetic-structural model proposed in this work has the potential of simulating real curing situations. Model validation requires, on one hand, that the proposed model can properly simulate the curing kinetics properly. In the present case, it implies that the relative rates of initiation, propagation and regeneration and the catalytic effect of added proton donors and those resulting from elimination regeneration should produce consistent kinetic results for a variety of formulations, as suggested in a previous work [26]. Different initiators may have different initiation mechanisms and likelihood of regeneration or termination. One might also consider more complex reactivity issues such as the formation of equilibrium complexes, as shown for the epoxy-amine polycondensation [28,29,42,43]. On the other hand, this kinetic-structural model should produce characteristic

network build-up parameters such as the conversion at gelation, the crosslinking density or the sol fraction [26,30], to name a few, comparable to those determined experimentally. Experimental work with monoepoxides as model compounds [9] would shed light on the real primary chain distribution during curing and, consequently, on the network build-up model. In that case, the strategy of chain-coupling used in this work may not be applicable and a real distribution of primary chains should be determined. On the basis of the study of crosslinking and non-crosslinking processes, the assumption of independent reactivity of epoxy groups, random recombination and absence of primary chain cyclization could be verified as well.

This model could also be adapted to other cases such as the curing of epoxy-anhydride thermosets with tertiary amines as initiators, as it is claimed that added proton donors or impurities play an important role in the curing kinetics and network build-up [20,26,44], as well as tertiary amine regeneration [22,26,45,46]. Experimental work is currently under way to test the applicability of the proposed kinetic-structural model for epoxy homopolymerization and epoxy-anhydride copolymerization using tertiary amines as anionic initiators.

4. Conclusions

A network build-up model for the anionic curing of epoxides using tertiary amines as initiators has been proposed. A primary chain-based statitstical network build-up method is used to determine a series of relevant statistical averages such as the gel point conversion, the crosslinking density and the gel fraction.

Several issues have been considered in this model: the effect of proton donors such as the hydroxyl groups in the DGEBA oligomeric structure and added monoalcohols, different initiation mechanisms, tertiary amine regeneration, chain-transfer, and unequal reactivity of certain species. All these factors contribute to the network build-up process to different extents depending on the formulation composition and the purity of the components. While added monoalcohol can increase significantly the number of primary chains thus reducing the average chain length and increasing conversion at gelation, because of their role as chain-transfer agents and initiating sites, hydroxyl groups coming from DGEBA oligomer may even have an opposite effect because of the crosslinking character of the DGEBA oligomer. Substitution and elimination regeneration reactions have counter-acting effects during curing, the former leading to chain coupling, thus decreasing gel point conversion and increasing crosslinking density, while the latter leads to the opposite.

The proposed model has a potential to model properly the curing process of epoxy resins with tertiary amines with initiators. It can even be extended to the study of other thermosetting formulations that share common reactivity issues such as epoxy-anhydride formulations.

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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.2014.03.022.

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