Crosslinking of Mixtures of DGEBA with 1,6-Dioxaspiro[4,4]Nonan-2,7-Dione Initiated by Tertiary Amines. I. Study of the Reaction and Kinetic Analysis

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ABSTRACT: The anionic copolymerization of a Diglycidyl ether of bisphenol A (DGEBA) epoxy resin and a bislactone has been studied with different initiators. The kinetics of the process has been dealt with in detail, and it has been detected the existence of different competing curing mechanisms: a quasi-alternating copolymerization between the epoxy monomer and the bislactone, and homopolymerization of the epoxy resin. In presence of an excess of DGEBA, the copolymerization first takes place, and then the excess of epoxy monomer can homopolymerize. The bislactone induces an apparent accelerating effect because it reduces the extent of epoxy homopolymerization and therefore the termination reactions associated with it, thus allowing a complete cure with a reduced amount of initiator. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2304–2315, 2008

Key words: anionic polymerization; thermosets; DSC; FTIR; kinetics

INTRODUCTION

Cationic copolymerization of epoxy monomers with lactones, which leads to *in situ* formation and opening of spiroorthoesters (SOEs) during the curing process, has been previously studied with the purpose of taking advantage of the beneficial expanding effect of SOEs opening during curing.[1–8] The most relevant results are a significant reduction in shrinkage after gelation, an increase in the flexibility of the materials and a somewhat lower thermal stability, which can be regarded positive in terms of reworkability. Some authors[9] stated that the introduction of tertiary esters into the structure of thermosets permits their controlled thermal degradation, which would permit recovery of the substrate, although we observed that the introduction of primary or secondary ester groups eases the thermal degradation of these materials as well and makes it possible to recover and rework a fraction of them via hydrolysis.[5]

It has been observed that some bislactones have an expandable structure,[10] though we have only used them as a comonomer under cationic conditions.[1,2,5] Some authors studied the copolymerization of bislactones and epoxides with anionic initiators,[11–14] and stated that an isomerization of the bislactone takes place during the process, as can be seen in Scheme 1. This isomerization with anionic initiators leads to a double ring-opening polymerization, which is typical of expandable monomers. In these conditions bislactones act as bifunctional monomers instead of their potential tetrafunctionality in cationic mechanisms, thus changing the stoichiometry of the reaction process. In this case, therefore, since each epoxy group would react with a s(γBL) molecule, a stoichiometric reaction between Diglycidyl ether of bisphenol A (DGEBA) and s(γBL) would demand a 1 : 2*M* ratio between the two monomers.

It has been previously stated[11,12] that in the anionic curing, epoxy-bislactone copolymerization is the most favorable process, which results in an early consumption of the bislactone and provokes a reduction in shrinkage prior to gelation. Other authors[13,14] stated that this copolymerization proceeds in an almost alternating way, with certain degree of homopolymerization depending on the feed ratio of the reactants, but bislactone homopolymerization in the absence of other coreactants is not feasible because it would require anhydride formation,[13] which would be energetically unfavorable and hamper further polymerization.

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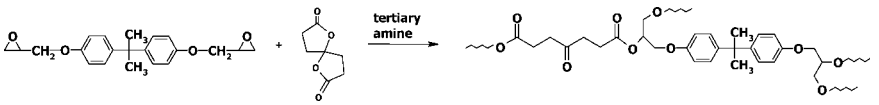


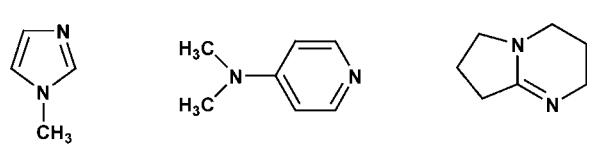
Scheme 1 Anionic copolymerization of a DGEBA epoxy resin and the s(γBL) spirobislactone.

The present work aims at studying in detail the kinetics of the copolymerization of a DGEBA epoxy resin with a spiranic bislactone, 1,6-dioxaspiro[4,4]-nonan-2,7-dione (s(γBL)), and test the efficiency of several anionic initiators which are already used for the homopolymerization of DGEBA and other epoxy resins[15–19] and the copolymerization of epoxides with cyclic carbonates,[20–22] namely 1-methylimidazole (1MI), 4-(N,*N*-dimethyl)aminopyridine (DMAP) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN). Scheme 2 depicts the structures of these initiators. Murayama et al.[22] calculated the theoretical activities of different tertiary amines and determined that DBN-like initiators were the most efficient ones because the double-bonded nitrogen bore the highest net electronic charge. However, different other effects are to be taken into account: (1) a resonance effect between the different atoms in the structure that stabilizes the positive charge after the initiation step[18] (2) electrostatic hindrance by neighboring groups[23] or (3) the occurrence of termination and regeneration reactions,[17,18] which might help keep a certain amount of active centers depending on the ability of the initiator to restart the process during the curing. Scheme 3 shows two possible generic regeneration mechanisms[17,18] (a and b) and also a cyclization reaction without regeneration that has been proposed for DMAP[18] (c).

EXPERIMENTAL

Materials

DGEBA epoxy resin (Epikote 827, Shell, 182 g/ee), 1,6-dioxaspiro[4,4]-nonan-2,7-dione (s(γBL)) (Aldrich, 156 g/mol), 1-methylimidazole (1MI) (Aldrich, 82 g/mol), 4-(*N*,*N*-dimethyl)aminopyridine (DMAP) (Aldrich, 122 g/mol) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (Aldrich, 122 g/mol) were used without purification.



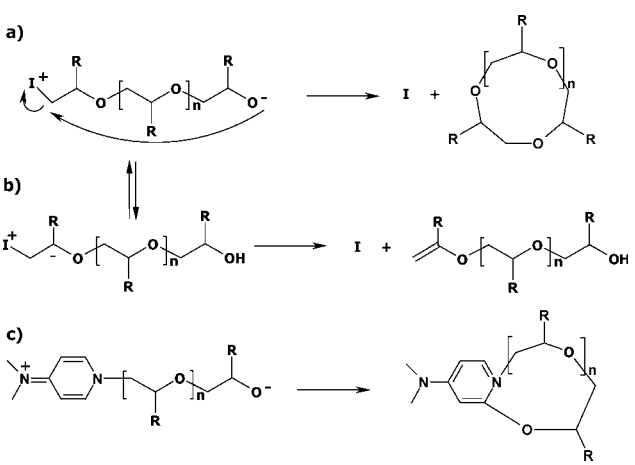
Scheme 2 Structure of the several anionic initiators used in this study.

Preparation of the curing mixtures

The various formulations were prepared by mixing and heating the right proportions of DGEBA and s(γBL) so that an homogeneous dissolution is obtained. Then they were cooled down to room temperature to add the initiator and subsequently stirred. The samples were degassed under vacuum to prevent the appearance of bubbles during the curing process. Table I shows details on the notation and composition of the formulations studied in this work. They are numbered XYZ, where XY correspond to the molar ratio between DGEBA and s(γBL) and Z is the amount of added initiator in phr (parts per 100 parts of mixture, w/w).

DSC calorimetry

A Mettler DSC-822e with a TSO801RO robotic arm calibrated using indium standards was used to dynamically cure 10 mg samples in pierced covered aluminum pans, from 0 to 200–300°C at different heating rates, to determine the reaction heat and to study the kinetics of the process. The degree of conversion α up to a temperature T can be calculated as follows



Scheme 3 Generic mechanisms proposed for the regeneration of the initiator and for the termination step (cyclization without regeneration) in the homopolymerization of DGEBA initiated by DMAP.

TABLE I
Notation and Composition of the Different Formulations Used in This Work, in Molar Ratio (n/n) and Equivalent Ratio (eq/eq) (init Stands for Initiator)

Formulation	$n_{DGEBA}/n_{s(\gamma BL)}$	$eq_{epoxy}/eq_{s(\gamma BL)}$	eq_{init}/eq_{epoxy}	$eq_{init}/eq_{s(\gamma BL)}$
DGEBA-1MI 102	1/0	1/0	0.044	–
DGEBA-1MI 105	1/0	1/0	0.111	–
DGEBA-s(γBL)-1MI 212	2/1	4/1	0.054	0.216
DGEBA-s(γBL)-1MI 122	1/2	1/1	0.082	0.082
DGEBA-DMAP 105	1/0	1/0	0.074	–
DGEBA-s(γBL)-DMAP 212	2/1	4/1	0.036	0.145
DGEBA-s(γBL)-DMAP 122	1/2	1/1	0.055	0.055
DGEBA-s(γBL)-DMAP 142	1/4	1/2	0.081	0.040
DGEBA-s(γBL)-DBN 212	2/1	4/1	0.036	0.145
DGEBA-s(γBL)-DBN 122	1/2	1/1	0.055	0.055

DGEBA equivalent = 182 g/eq. s(gBL) equivalent = 156 g/eq (the whole s(γBL) unit).

$$\alpha = \frac{\Delta h_T}{\Delta h_{\text{total}}}$$

where Δh_T and Δh_{total} are the heat released up to the temperature T and the total heat released respectively, providing full cure has occurred.

FTIR spectroscopy

FTIR spectroscopy was used to monitor the isothermal curing of the different samples and to determine the degree of curing of nonisothermally cured samples with DSC. A FTIR spectrometer Bomem Michelson MB 100 was used, with a resolution of 4 cm^{-1} in the absorbance mode. An attenuated total reflection accessory with thermal control and a diamond crystal (Golden Gate Heated Single Reflection Diamond ATR, Specac-Teknokroma) was employed to determine the FTIR spectra.

The analysis of the different peaks in the FTIR spectra was carried out on the basis of previous works[1,5,6] and a handbook on analytical chemistry.[24] The disappearance of the absorbance peak at 915 cm^{-1} (oxirane ring bending) was used to monitor the epoxy conversion. The disappearance of the s(γBL) C=O stretching peak at 1795 cm^{-1} accounted for the isomerization reaction and consumption of the bislactone, along with the increase of a double peak at 1738 cm^{-1} and 1725 cm^{-1} (carbonyl stretching of linear ester and ketone groups). A mathematical deconvolution[1,5,6] of the overlapping of the different carbonyl bands was necessary to study the s(γBL) conversion, either via appearance or disappearance of the peaks. Peak deconvolution was also needed to monitor the epoxy conversion because of overlapping with a peak at 932 cm^{-1} corresponding to s(γBL). The peak at 1510 cm^{-1} was chosen as an internal standard. Thus, the normalized absorbances at a wavenumber *xxxx* were calculated as follows:

$$\overline{A}_{xxxx} = \frac{A_{xxxx}}{A_{1510}}$$

The conversion of the starting monomers was determined by the Lambert-Beer law from the normalized changes of absorbances as

$$\alpha_{epoxy} = 1 - \left(\frac{\overline{A}^{t}_{915}}{\overline{A}^{0}_{915}}\right)$$

$$\alpha_{s(\gamma BL)} = 1 - \left(\frac{\overline{A}^{t}_{1795}}{\overline{A}^{o}_{1795}}\right) = \left(\frac{\overline{A}^{t}_{1738+1725}}{\overline{A}^{\infty}_{1738+1725}}\right)$$

where $\overline{A}^{t}_{xxxx}$, $\overline{A}^{o}_{xxxx}$ i $\overline{A}^{\infty}_{xxxx}$ are normalized absorbances of peaks at wavenumber *xxxx* at a time t, at the beginning and at the end of the reaction process, respectively.

Theoretical analysis

The kinetics of a curing process can be analyzed on the basis of the following kinetic equation $d\alpha/dt = k \cdot f(\alpha)$ where $d\alpha/dt$ is the reaction rate, $f(\alpha)$ is the differential function of the kinetic model that governs the curing process and k is the kinetic constant, which can be expressed in its Arrhenius form as $k = A\exp(-E/RT)$, where A is the preexponential factor, E the activation energy, R the gas constant and T the curing temperature. The preexponential factor, the activation energy and the kinetic model constitute the so-called kinetic triplet, which is commonly used to completely describe a reactive process.

Isoconversional kinetic analysis of calorimetric data obtained from dynamic curing at different heating rates were performed to study the evolution of

the activation energy along the conversion of the curing processes. Isoconversional methodology has long proved useful to obtain reliable kinetic information on many different processes.[25] Regarding cure kinetics, it has the advantage that it is not needed to carry out long isothermal experiments. In theory, the most reliable kinetic data would be obtained from isothermal experiments, but baseline instability at the beginning of the curing process migh sometimes lead to loss of data and therefore erroneous results. A set of kinetic parameters can be obtained for each degree of conversion providing the kinetic model ($f(\alpha)$ or its integral version $g(\alpha)$) does not depend on the temperature program. Integral and differential activation energies were obtained using Vyazovkin integral and advanced modified methods, respectively.[2,25–27] Integral and differential activation energies might be different at the same degree of conversion because integral values represent an average activation energy up to that conversion whereas differential values represent the activation energy at that conversion, being only equivalent when the activation energy throughout the whole process is constant. Therefore, changes in reaction mechanisms resulting in changes in activation energy can be detected analyzing the differential activation energy whereas integral activation energy can conceal such changes.[2,25,27]

The basis for the Vyazovkin integral method lies in the solution of the so-called temperature integral. For experiments with constant heating rate β, it takes the form:

$$g(\alpha) = \frac{A_\alpha}{\beta}\int_0^{T_\alpha} \exp(-E_\alpha/RT)dT = \frac{A_\alpha}{\beta} I(E_\alpha, T_\alpha)$$

$$I(E_\alpha, T_\alpha) = \frac{E_\alpha}{R} p(x)$$

where $p(x)$ is a function of $x = E_\alpha/RT_\alpha$, for instance the Senum and Yang's approximation.[2,26,28] The integral activation energy is the one that minimizes the following expression:

$$\phi(E_\alpha) = \sum_i^n \sum_{j\neq 1}^n \frac{I_i(E_\alpha, T_{\alpha,i})/\beta_i}{I_j(E_\alpha, T_{\alpha,j})/\beta_j}$$

where the subscripts refer to the experiments with different heating rates. The modified method makes use of $J(E_\alpha, T_\alpha) = I(E_\alpha, T_\alpha) - I(E_\alpha, T_{\alpha-\Delta\alpha})$ instead of $I(E_\alpha, T_\alpha)$ in the minimization function $\phi(E_\alpha)$ to obtain the differential activation energy.

By making use of the same procedure, average activation energies within a conversion range could be calculated by minimization of the $\phi(E_\alpha)$ function using $H(E_\alpha, T_{\alpha_1}, T_{\alpha_2}) = I(E_\alpha, T_{\alpha_2}) - I(E_\alpha, T_{\alpha_1})$ instead of $I(E_\alpha, T_\alpha)$ ($E_{\text{int,ave}}$ in Table IV). Alternatively, a rough estimate can be made by simple averaging of differential activation energy within that range ($E_{\text{diff,ave}}$ in Table IV). Both methods should give the same result providing the differential activation energy is constant throughout the conversion range. However, it is by its definition that in the first method the activation energy is considered constant throughout the process from α_1 to α_2.

Reaction rates can be calculated using the differential isoconversional activation energy E_α and the factor $A_\alpha f(\alpha)$, which can easily be obtained taking into account that

$$\frac{1}{f(\alpha)} = \frac{d(g(\alpha))}{d\alpha} = \frac{g(\alpha) - g(\alpha - \Delta\alpha)}{\Delta\alpha}$$

$$\text{and} \quad g(\alpha) - g(\alpha - \Delta\alpha) = \frac{A_\alpha}{\beta} J(E_\alpha, T_\alpha),$$

then

$$A_\alpha f(\alpha) = \frac{\beta\Delta\alpha}{J(E_\alpha, T_\alpha)}$$

The $A_\alpha f(\alpha)$ factor was therefore calculated by averaging of the last expression evaluated at the different heating rates. The reaction rate was finally calculated as $d\alpha/dt = A_\alpha f(\alpha)\exp(-E_\alpha/RT)$, which is simply a rearrangement of the rate expression shown above.

RESULTS AND DISCUSSION

Kinetic analysis using DSC

Overall characterization

Figure 1 shows the thermograms corresponding to the dynamic curing of the different formulations using 1MI as initiator. When no s(γBL) is present in the curing mixture, homopolymerization of DGEBA is the only process taking place. On comparing the curves obtained for DGEBA-1MI 105 and DGEBA-1MI 102 formulations, we observed that the latter releases a lower heat and its curing extends up to higher temperatures than the former, which means that at least the curing of 102 formulation is not able to reach completion, contrary to what is suggested by Ooi et al.[17] Trapping or depletion of active species due to termination reactions might account for this phenomenon. It has been verified by FTIR that formulation 105 is able to cure completely at moderate temperatures. In addition, Table II shows that the heat released per epoxy equivalent of 105 formulation with 1MI is about the acknowledged value of 100 kJ/equiv for epoxy rings.[29] Indeed, Heise and Martin[30] showed that a minimum of ca 4-5 phr was

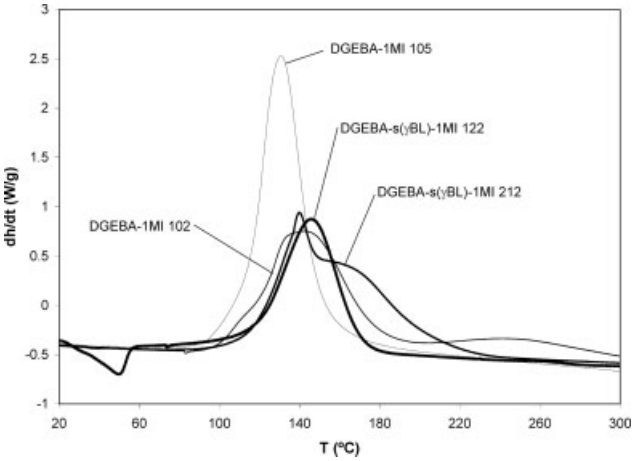


Figure 1 DSC thermograms of the dynamic curing at 10 K/min of the different formulations with 1MI.

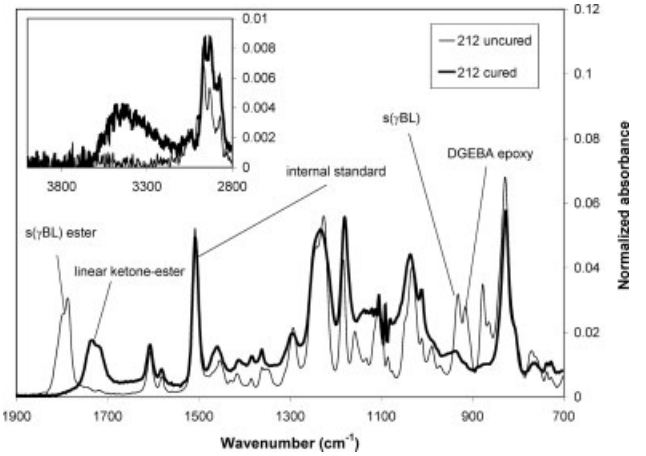


Figure 2 FTIR spectra of 212 formulation with 1MI before and after dynamic curing. FTIR scans performed at 30°C.

needed to completely cure DGEBA, although they used other imidazoles.

On the contrary, formulations with s(γBL), 212 and 122 (excess epoxy and stoichiometric formulation, respectively), are able to cure completely with a smaller amount of initiator, only 2 phr. It was verified by FTIR that complete cure had been achieved, as seen in Figures 2 and 3. Figure 2 shows the FTIR spectra of the formulation 212 with 1MI obtained before and after curing. The most significant peaks of the uncured sample are the ones corresponding to the s(γBL) C=O stretching at 1795 cm^{-1} and epoxy bending at 915 cm^{-1}. The cured sample reveals that neither s(γBL) nor epoxy groups are present and that a double peak related to linear ester and ketone appears as a consequence of the s(γBL) opening with isomerization. A broad band around 3400 cm^{-1} is also present (inset in Fig. 2) due to the occurrence of termination and transfer reactions[17,18] in which the initiator is refreshed and hydroxyl groups are generated [see Scheme 3(b)]. Figure 3 shows the FTIR spectra of the formulation 122 with 1MI before and after curing. It can be observed that no quantifiable traces of epoxy or s(γBL) ester groups are present after curing. However, the overlapping of epoxy peak at 915 cm^{-1} with a peak from s(γBL) hinders the study of epoxy conversion along the curing process. Moreover, both formulations exhibited a heat released (see Table II) close to 100 kJ/equiv, on the basis that the opening of the epoxy ring is responsible for the heat release during curing,[5] which is not unreasonable if it is considered that, for instance, the ring-opening of γBL is only 5 kJ/equiv.[31]

From the shape of the curves of the 212 and 122 formulations in Figure 1 it can be sensed what was stated by Sikes and Brady[11,12] and other authors[13,14] as to the curing mechanism. It is supposed that in formulation 212 (excess of DGEBA) a copolymerization between DGEBA and s(γBL) first occurs, and once the s(γBL) is exhausted homopolymerization of DGEBA takes place, which produces a quasi bimodal exotherm. On the contrary, in formulation

TABLE II
Reaction Heat of the Different Formulations Cured Dynamically with DSC at 10 K/min, in J/g and kJ/ee (Epoxy Equivalent)

Formulation	Δh (J/g)	Δh (kJ/ee)
DGEBA-1MI 105	550	102.3
DGEBA-s(γBL)-1MI 212	429.6	96.8
DGEBA-s(γBL)-1MI 122	275.6	95.0
DGEBA-DMAP 105	483.4	92.4
DGEBA-s(γBL)-DMAP 212	404.4	91.2
DGEBA-s(γBL)-DMAP 122	282.2	97.3
DGEBA-s(γBL)-DMAP 142	186.5	94.0
DGEBA-s(γBL)-DBN 212	412.4	93.0
DGEBA-s(γBL)-DBN 122	280.3	96.6

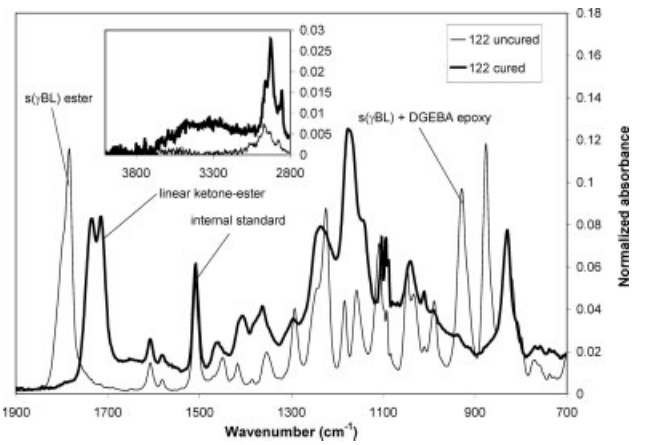


Figure 3 FTIR spectra of 122 formulation with 1MI before and after dynamic curing. FTIR scans performed at 30°C.

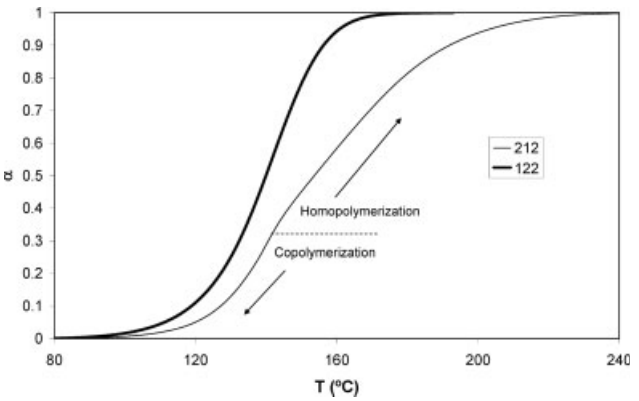


Figure 4 Conversion-temperature profiles of the dynamic curing at 10 K/min of 212 and 122 formulations with 1MI.

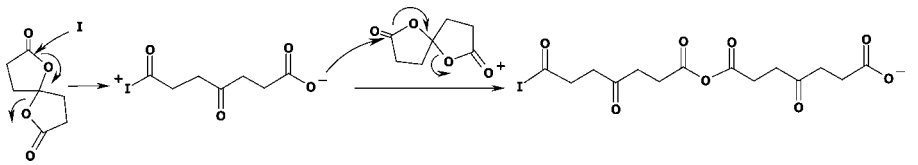
122, using stoichiometric amounts of reactants, the perfect unimodal curve indicates that an only process takes place, which must be assigned to an alternating copolymerization between DGEBA and s(γBL). The endothermic peak that appears in the 122 thermogram can be attributed to the melting of s(γBL), which is unable to completely dissolve in DGEBA once the initiator has been added, and remains finely dispersed in the mixture in the solid state. However, since the reaction starts clearly after the melting endotherm, it is supposed that it does not interfere with the curing process and its kinetics.

Figure 4 compares the conversion–temperature profiles of the dynamic curing at 10 K/min of 212 and 122 formulations with 1MI as initiator. It is shown, as in Figure 1, that the curing process of 122 formulation is faster than the 212. Moreover, a change of slope in the 212 profile above 0.3 conversion is observed, which is related to the presence of different peaks, as is seen in Figure 1. Taking into account the 4 : 1 equivalent ratio between DGEBA and s(γBL), this value is somewhat close to the theoretical value of 0.25 that would result from an alternate copolymerization between DGEBA and s(γBL) prior to DGEBA homopolymerization. The reaction slowdown after this process seems to indicate that the DGEBA homopolymerization is a less favorable process than its copolymerization with s(γBL), probably due to the existence of termination reactions[17,18] or the inability to restart the reaction after the regeneration of the initiator (see Scheme 3), which reduces the amount of active species in the reaction medium, in accordance with the higher amount of initiator needed in the homopolymerization of DGEBA, as seen above.

In Figure 1 it is also observed that the beginning of the curing process is delayed when s(γBL) is added to the reaction mixture. But since curing reaches completion at lower temperatures as the s(γBL) content increases, it would seem that the addition of s(γBL) has an accelerative effect on the curing of DGEBA under anionic catalysis with a small amount of initiator. A similar behavior was reported in the anionic copolymerization of DGEBA with cyclic carbonates,[20,21] and resembles the observed effect in the cationic copolymerization of DGEBA with s(γBL).[5] Formulation 142, with an excess of s(γBL), has been studied to ascertain the observed apparent accelerating effect. It has been verified that 142 and 122 reaction profiles are extremely similar and the curing process occurs within the same range of temperatures, which means that the use of an overstoichiometric proportion of s(γBL) to the reaction mixture does not really enhance the reaction rate. It can thereby be said that the kinetic process is basically the same alternating copolymerization between s(γBL) and DGEBA. The apparent accelerating effect of s(γBL) observed when formulations 102, 212, and 122 with 1MI are compared (see Fig. 1) can be attributed to the fact that its presence favors the copolymerization process and reduces the occurrence of DGEBA homopolymerization and the subsequent termination reactions that reduce the amount of active species, thus resulting in complete DGEBA conversion at lower temperatures, because it has to be remembered that the reaction starts earlier with pure DGEBA even with 2 phr of initiator although it cannot reach completion.

It has been verified, as it was suggested,[13] that s(γBL) homopolymerization in the absence of coreactants is not feasible. The initiator is activated indeed, but the process is unable to go past the first stages due to the formation of an anhydride-like structure which would prevent further s(γBL) reaction (see Scheme 4). However, it has been seen that the copolymerization of DGEBA with an excess of s(γBL), formulation 142, might favor s(γBL) homopolymerization to a certain extent, because it is expected a maximum degree of s(γBL) conversion of 0.5 and a somewhat higher value is observed by FTIR.

It has been observed that 212 and 122 formulations with DMAP and DBN show similar curing profiles to the ones using 1MI as initiator. Dell'Erba and Williams[18] pointed out that a minimum amount of ca 5 phr was needed to cure DGEBA completely due to the existence of termination reactions that reduce the amount of the initiating species present in the curing mixture. It was indeed verified that DMAP was not able to cure completely with 2 phr of DMAP, and that 5 phr were necessary to cure it completely, in a similar way to 1MI. In contrast, DBN was proved unable to completely homopolymerize DGEBA even with 5 phr, in accordance with what observed by Murayama et al.,[22] which might be caused by excessive occurrence of termination reactions and inability to regenerate. Table II summarizes enthalpy data



Scheme 4 Formation of an anhydride-like structure which inhibits further homopolymerization of s(γBL).

obtained from the dynamic DSC curing at 10 K/m of the different formulations, except those unable to achieve complete curing. The heat released per epoxy equivalent are quite similar to each other, coherent with the data reported by other authors using similar initiators,[17,18,30] close to 100 kJ/equiv for epoxy rings and the enthalpies we obtained in the cationic copolymerization of DGEBA and s(γBL), taking into account that the opening of the epoxy ring is mainly responsible for the reaction heat evolved.[5] It has been verified by FTIR that the mixtures have reacted completely, except formulation 142, in which a significant amount of s(γBL) remains unreacted.

Kinetic analysis

Figure 5 shows the reaction rate-conversion curves along with the differential and integral activation energy profiles with respect to the degree of conversion for the 122 formulation with 1MI. An almost constant activation energy is observed, between 75 and 80 kJ/mol, in agreement with the occurrence of a single-step mechanism, the alternate copolymerization between s(γBL) and DGEBA. Figure 6 compares the differential activation energies and reaction rate profiles at 5 K/min of 122 formulations. Since the curing processes are similar, the values of activation energy are close to each other except at the beginning of the curing process. It has also been determined that DMAP and DBN are the most efficient initiators for this formulation, but this is something which is not self-evident if only activation energies are analyzed and the pre-exponential factors are ignored, unless the differences at the beginning of the curing process do really exert such a great influence. For that matter, the reaction rates of the different formulations have been calculated at 0.5 conversion and temperatures of 100 and 150°C using differential isoconversional data and presented in Table III. On comparing 122 formulations, they all show similar rates, but it is clear that, at any temperature, 1MI is the least efficient initiator in terms of rate whereas DMAP and DBN behave almost equally.

The homopolymerization of DGEBA has also been studied. Figure 7 compares the differential activation energies and reaction rate profiles at 5 K/min of 105 formulations with 1MI and DMAP because, as has been stated above, DBN is unable to homopolymerize completely DGEBA even with 5 phr of initiator. Formulations 105 exhibit a low and rather constant value of activation energy at the beginning of the process and it increases significantly above 0.7 conversion. Dell'Erba and Williams reported 62.4 kJ/mol as the activation energy for the polymerization of phenyl glycidyl ether (PGE) with DMAP[18] by averaging isoconversional integral energies at different degrees of conversion under the assumption that the fact that there were no significant variations accounted for constancy throughout the process, indeed they did not notice such an increase in acti-

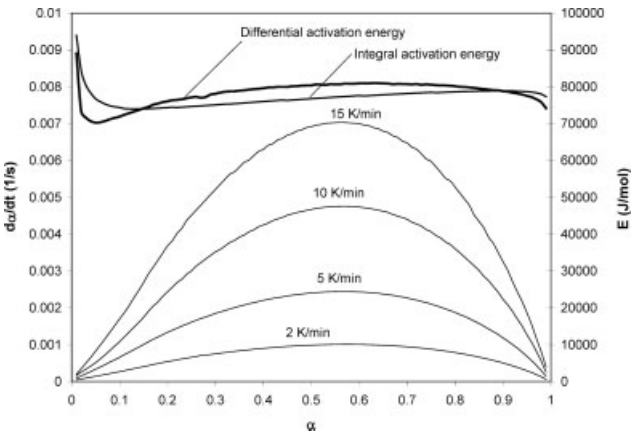


Figure 5 Differential and integral activation energy and reaction rate (at different heating rates) profiles with conversion of the thermal curing of 122 formulation with 1MI.

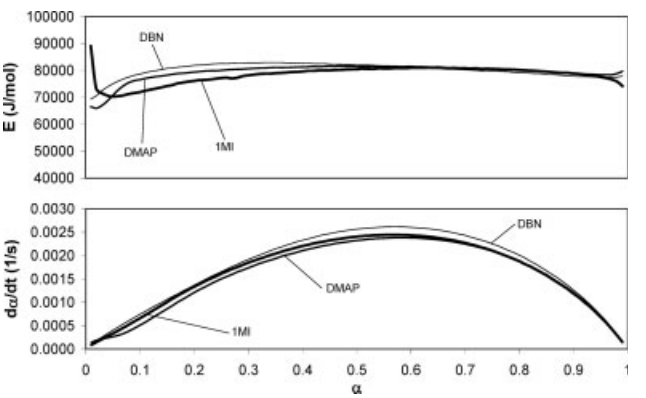


Figure 6 Comparison of the differential activation energies (upper graph) and reaction rate at 5 K/min (lower graph) of the curing of 122 formulations with the different initiators.

TABLE III
Reaction Rates at 100 and 150°C ($d\alpha/dt_{100°C}$ and $d\alpha/dt_{150°C}$) Calculated at 0.5 Conversion Using Only Isoconversional Differential Data

Formulation	$d\alpha/dt_{100°C}$ (min^{-1})	$d\alpha/dt_{150°C}$ (min^{-1})
105 1MI	0.0836	0.6880
105 DMAP	0.2072	1.2501
212 1MI	0.0074	0.1212
212 DMAP	0.0104	0.1339
212 DBN	0.0076	0.0781
122 1MI	0.0187	0.4014
122 DMAP	0.0225	0.5011
122 DBN	0.0223	0.5086

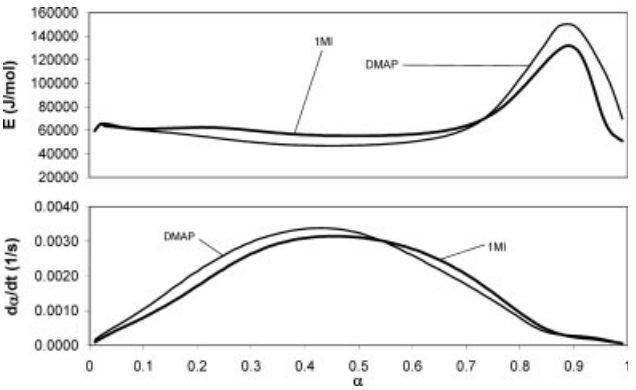


Figure 7 Comparison of the differential activation energies (upper graph) and reaction rate at 5 K/min (lower graph) of the curing of 105 formulations with 1MI and DMAP.

vation energy. Their value is higher than the observed differential values up to 0.7 conversion in Figure 7 and the averages shown in Table IV, but care has to be taken to compare activation energies and averages because of the way they are defined. Despite not matching any of the methods given in the theoretical analysis section, we have calculated a value of 58.3 kJ/mol between 0.1 and 0.7 conversion by simply averaging the isoconversional integral activation energy, which is in fair agreement with their result taking into account that DGEBA and PGE might not behave exactly the same. Ooi et al. reported an integral energy of 73.3 kJ/mol for the cure of DGEBA with 2 phr of 1MI,[17] which is somewhat higher than our integral energy up to 0.7 but it has to be taken into account that a different DGEBA was used and the amount of initiator was different from ours. Other authors,[32] in contrast, reported lower values ranging from 34.3 to 63.8 along the curing process using 2,4-EMI as initiator.

With both initiators, the large increase in activation energy at the end of the cure can be attributed to the existence of noncatalyzed reaction between epoxy groups and hydroxyl groups at high temperatures, the hydroxyl groups already present in DGEBA or coming from termination and regeneration reactions [see Scheme 3(b)]. In the lower graph of Figure 7 a shoulder at the end of the curing process is observed which seems to be related to this phenomenon. Oh et al.[33] studied the curing of epoxy resins with hydroxyl terminated hyperbranched polymers and linear polyols without initiator and found that the greater the hydroxyl content, the faster and higher the extent of cure. They calculated an integral activation energy using the Ozawa method and obtained values ranging from 99.1 to 110.8 kJ/mol depending on the amount of hydroxyl groups (the lower the amount the higher the activation energy) and the type of polyol (higher with linear polyols than with hyperbranched polymers). The integral activation energies along the curing process of 105 formulations also show a maximum at the end of the cure process of 113.7 for 1MI and 127.5 for DMAP, which is in fair agreement with the referred values. In addition, the temperature at which the aforementioned shoulder appears in the curing of 105 formulations lies within the curing range of these epoxy-hyroxyl systems.[33] It is hypothesized that either depletion of active species or trapping of active centers during curing might account for the existence of noncatalyzed epoxide-hydroxyl reaction at the end of the cure process.

The shape of the reaction rate profiles shown in Figure 7 might lead to wrong conclusions as to the efficiency of the initiators in terms of reaction rate, because they are extremely similar. It has to be taken into account, however, that reaction proceeds at lower temperatures with DMAP than with 1MI and, for that matter, DMAP is more efficient than 1MI. In addition, it is shown in Table III that the reaction rate of 105 formulation with DMAP is significantly higher than with 1MI at any temperature.

Figure 8 plots the conversion profiles and activation energy for the 212 formulation with 1MI. Two

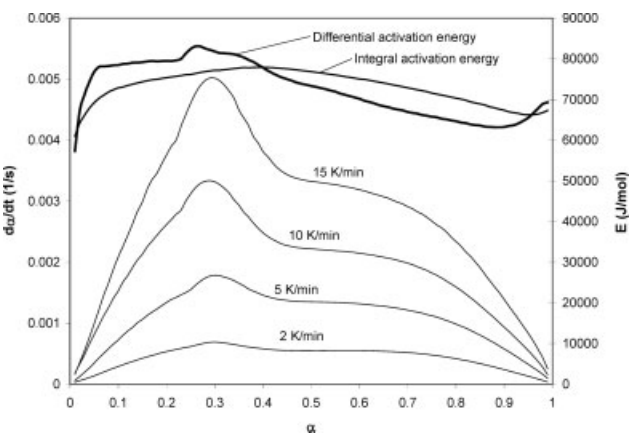


Figure 8 Differential and integral activation energy and reaction rate (at different heating rates) profiles with conversion of the thermal curing of 212 formulation with 1MI.

TABLE IV
Calculated Averages of Activation Energy Within the Specified Conversion Ranges for the Different Formulations

Formulation	Range	$E_{diff,ave}$ (kJ/mol)	$E_{int,ave}$ (kJ/mol)
105 1MI	0.1–0.7	58.7	59.2
105 DMAP	0.1–0.7	51.6	52.4
212 1MI	0.05–0.25	79.2	79.5
	0.4–0.9	69.0	65.7
212 DMAP	0.05–0.25	78.3	77.8
	0.4–0.9	63.1	62.2
212 DBN	0.05–0.25	79.3	78.8
	0.4–0.9	57.4	56.6
122 1MI	0.1–0.9	78.9	79.3
122 DMAP	0.1–0.9	80.4	80.2
122 DBN	0.1–0.9	81.1	80.4

$E_{diff,ave}$ is the result of arithmetical averaging the differential isoconversional activation energy and $E_{int,ave}$ is the average calculated using the method using the modification of the Vyazovkin integral method described in the theoretical analysis section.

main processes can be distinguished from the two peaks of the reaction rate curves and from the differential activation energy but, as has been stated in the theoretical analysis section, it is not so evident from the integral activation energy. At the early stages of curing the activation energy is around 80 kJ/mol, and at conversions greater than 0.3 it decreases to 65 kJ/mol. The first process would correspond mainly to the copolymerization between DGEBA and s(γBL) and the second one to the DGEBA homopolymerization, which is in agreement with the values obtained for 122 and 105 formulations, as seen in Figures 6 and 7 and Table IV. It would seem that DGEBA homopolymerization is kinetically a more favorable process because of the lower value of the activation energy. Nevertheless, the curing slows down during DGEBA homopolymerization, which means that additional factors should be taken into account from the kinetics point of view: the pre-exponential factor of the expression of the Arrhenius kinetic constant and the kinetic model $f(\alpha)$,[34] which is likely to change on switching from copolymerization to DGEBA homopolymerization.

Very similar results were obtained with DMAP and DBN. Figure 9 compares the differential activation energies and reaction rate profiles at 5 K/min of 212 formulations with the different initiators. It can be seen that at the early stages of curing, the values of activation energy are very similar to each other. However, at conversions higher than 0.25 the decrease is far more pronounced with DMAP and DBN than with 1MI, which leads to a difference in the DGEBA homopolymerization process after copolymerization. It has indeed been observed that the rate of DGEBA homopolymerization in 212 formulation with 1MI is enhanced with respect to the other initiators when the heating rate is increased, a phenomenon which is related to its higher activation energy along this process. As shown in Table III, 1MI appears to be the least efficient initiator for the 212 formulation at low curing temperatures, but it can compare to DMAP and even outperform DBN when the curing temperature is sufficiently raised. Taking into account that the rates have been calculated at a conversion at which DGEBA homopolymerization is taking place in this formulation, the different termination, transfer, and regeneration reactions related to DGEBA homopolymerization depicted in Scheme 3 and reported in the literature[17,18] might account for these differences in activation energies and reaction rate. An influence of the heating rate on the initiation to propagation ratio cannot be disregarded either.[15,16] In addition, differences exist between the different initiators as to the transition between the two processes, as can be observed in the rate profiles in Figure 9, which might account for certain differences regarding the copolymerization process as well.

The above discussion about the processes taking place in the curing of these systems is summarized in Figure 10 and Table IV. Figure 10 compares the differential activation energy of the different formulations with DMAP (122, 212, and 105). As stated before, formulation 122 presents a practically constant activation energy, and it can be noticed that 212 exhibits a very similar behavior at the beginning of the curing process due to the occurrence of the same curing mechanism. Once s(γBL) is exhausted, DGEBA homopolymerization starts and the activation energy drops down to a level which is close to the average activation energy of 105 formulation before its large increase after 0.7 conversion. Accordingly, the slight increase in the activation energy of

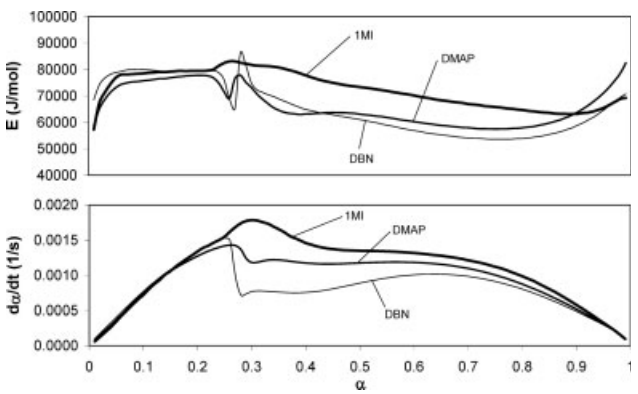


Figure 9 Comparison of the differential activation energies (upper graph) and reaction rate at 5 K/min (lower graph) of the curing of 212 formulations with the different initiators.

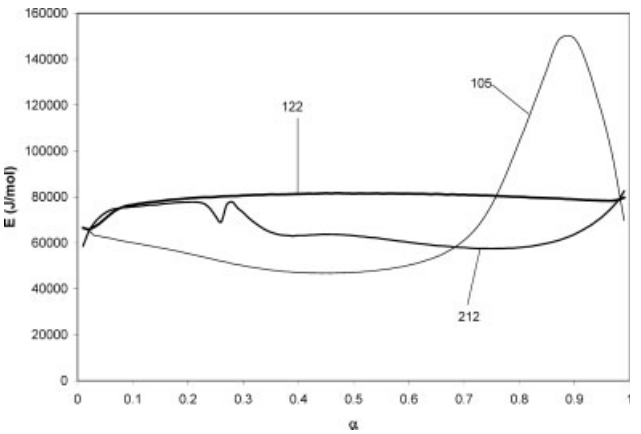


Figure 10 Comparison of the differential activation energies of the curing of 122, 212 and 105 formulations with DMAP.

212 formulation at the end of the curing process could be related to the one observed in 105 formulation. Table IV compares the average activation energies of the curing of all these systems using the two methods described in the theoretical analysis. The values have been calculated within ranges where it could be considered that there was only one process and the differential activation energy did not experience significant variations. As a consequence, the different averaging methods give very similar results. On comparing the activation energies for the copolymerization process, that is, for the 122 formulations and first process in 212 formulations, one can see good agreement between the different initiators and formulations. Accordingly, a fair agreement is observed between the values corresponding to the DGEBA homopolymerization, but the ones of 105 formulations are somewhat lower than the ones of 212 formulations.

FTIR analysis

Because of excessive overlapping of an s(γBL) peak with the epoxy peak it has not been possible to study the different conversions in formulations 122 (see Fig. 4). However, it has not been noticed any abnormal behavior by FTIR, that is, an irregular decrease of lactone and epoxy peaks, and complete conversion is achieved anyway. Therefore, only 212 formulations have been studied in detail.

Figure 11 plots the evolution of the most relevant reactive groups during the isothermal curing of formulation 212 with 1MI at 100°C in the FTIR. The disappearance of cyclic ester groups from the s(γBL) and the appearance of a linear ketone–ester structure have been used to monitor the s(γBL) conversion. It can be seen that both profiles overlap, which is logical taking into account that they are related to the same reactive process. It can also be noticed that the s(γBL) conversion profile follows an almost linear behavior typical of a zero-order reaction. However, it has to be remembered that calorimetric data mainly reflect on the conversion of DGEBA epoxide groups, and the profile of epoxy conversion in Figure 11 does not look so linear. Taking into account the stoichiometry of the reaction for the 212 formulations (see Table I), the number of reacted moles of epoxy groups with respect to s(γBL) has been calculated (*n* epoxy series) by multiplying the epoxy conversion by the equivalents ratio between the two reactants (see Table I). If an alternate copolymerization was the only process taking place, this profile should overlap the one corresponding to s(γBL), but epoxy conversion is slightly lower than expected, either due to certain degree of s(γBL) homopolymerization or due to errors in the mathematical deconvolution of the peaks.

Formulation 212 with 1MI has been tested at different temperatures, and it has been verified that the lactone conversion follows an almost linear behavior, which would mean that it roughly followed a zero-order kinetic model. From a simple kinetics point of view, it could mean that the rate of the copolymerization process is not so dependent on the s(γBL) concentration as it might be on epoxy concentration, which remains high along this process until s(γBL) exhaustion. An activation energy can be easily calculated for this process, because the slope of the conversion profiles matches the kinetic constant in zero-order reactions. A value of 78.9 kJ/mol has been obtained, which is in excellent agreement with the values obtained at the beginning of the curing of 212 formulations and the average values for 122 formulations (see Figs. 6, 8, and 9 and Table IV). It can therefore be stated that the process that takes place

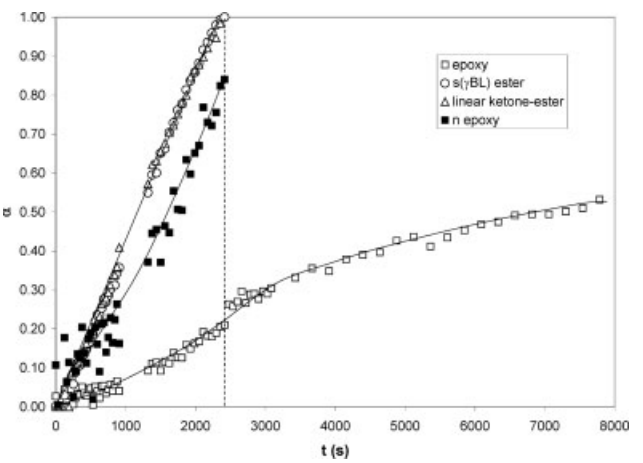


Figure 11 FTIR conversion-time profiles of the different reactive groups of the isothermal curing of 212 formulation with 1MI at 100°C.

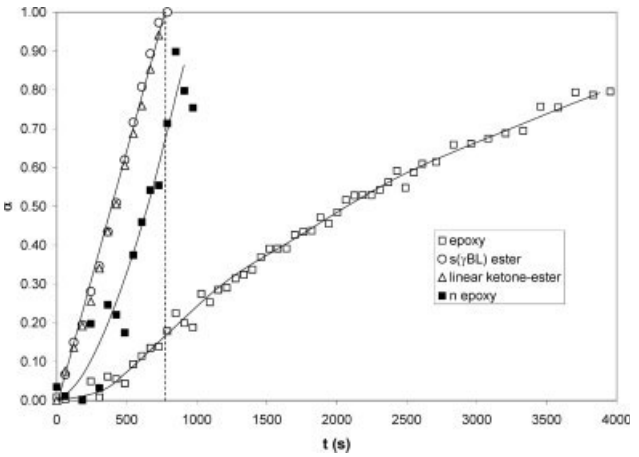


Figure 12 FTIR conversion-time profiles of the different reactive groups of the isothermal curing of 212 formulation with DMAP at 100°C.

at the beginning of the curing of 212 formulations is very similar to the one that takes place along the curing of 122 formulations, namely, an almost alternate copolymerization between DGEBA and s(γBL).

Figures 12 and 13 show the conversion profiles for 212 formulations with DMAP and DBN respectively, cured isothermally at 100°C. The profiles are very similar to that of the formulation with 1MI, but the reaction process is much faster. As pointed out in the DSC kinetic analysis, 1MI was the least efficient initiator at moderate temperatures, as it is the case. The conversion of s(γBL) with DMAP and DBN proceeds at a very similar pace, but there are significant differences regarding epoxy conversion. Using DBN as initiator, epoxy conversion with respect to s(γBL) overlaps s(γBL) conversion, which means that a 1 : 1 and possibly a true alternating copolymerization is taking place indeed. As it is seen in Figure 9, the copolymerization and homopolymerization processes do not exactly show the same profiles for the three initiators. Once s(γBL) is exhausted and DGEBA homopolymerization is the only possible process, it can be seen that in formulation 212 with DMAP epoxy conversion increases from 0.18 to 0.80, whereas with DBN it only increases from 0.24 to 0.63. Therefore, epoxide homopolymerization with DBN proceeds slower than with DMAP, in agreement with the information in Table III. To sum up, it seems that 1MI and DMAP favor certain degree of s(γBL) homopolymerization at the beginning of the curing process, whereas an alternate copolymerization would take place using DBN as initiator, which is the least efficient one for DGEBA homopolymerization.

As it has been previously stated, the appearance of hydroxyl bands in the curing of these systems could result from the occurrence of termination reactions and regeneration of the initiator. Further confirmation of this phenomenon could be obtained by studying the coloration of the samples during curing by direct observation of samples on the FTIR/ATR device and monitoring of the curing. Dell'Erba and Williams observed a severe darkening of the samples on curing, which they attributed to the fact that a fraction of the polyether chains is attached to the initiator and a double-bond conjugation effect between the different atoms in the initiator structure.[18] It has been observed that 122 formulations undergo yellowing on curing but they retain certain degree of transparency. On the contrary, 212 formulations experience serious darkening but only after s(γBL) is exhausted and DGEBA homopolymerization takes place, being this behavior the less pronounced with DBN, whereas 105 formulations exhibit this darkening from the very beginning of the curing process except with DBN, which is unable to homopolymerize DGEBA and only shows yellowing. In addition, the hydroxyl band at 3400 cm^{-1}, which is more important with 1MI and DMAP than with DBN, becomes only noticeable after s(γBL) exhaustion. It is therefore concluded that darkening takes place as a consequence of the initiation step of the curing process of samples in which DGEBA homopolymerization is the main process, such as 105 and 212 formulations, and that regeneration and reinitiation reactions do occur and new polyether chains are started, as it has been deduced from the darkening and the appearance of hydroxyl groups observed in 212 formulations after s(γBL) exhaustion.

CONCLUSIONS

The thermal curing of the DGEBA with s(γBL) using different anionic initiators has been studied. Different processes taking place during the curing of this

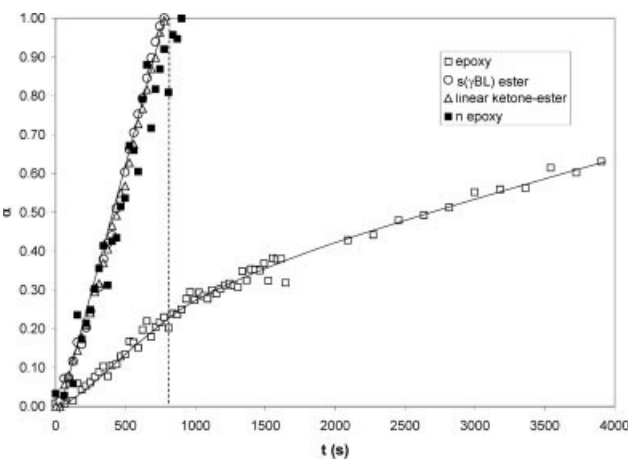


Figure 13 FTIR conversion-time profiles of the different reactive groups of the isothermal curing of 212 formulation with DBN at 100°C.

system have been identified with DSC and FTIR: (1) an almost alternating copolymerization between epoxy groups and s(γBL) and (2) homopolymerization of epoxy groups in excess of DGEBA. When s(γBL) is present, the copolymerization occurs in the first place, and once it is exhausted, DGEBA homopolymerization takes place.

The existence of termination, transfer, and regeneration reactions associated with DGEBA homopolymerization could be determined with FTIR due to the appearance of a broad band corresponding to OH groups and darkening of the samples once s(γBL) is exhausted. As a consequence, a minimum amount of initiator is needed to achieve complete DGEBA homopolymerization due to the reduction in the amount of active species along the curing process.

The addition of s(γBL) brings about an apparent acceleration effect, and allows the complete curing with a smaller amount of initiator. This acceleration effect is, however, of a different nature from the one observed in the cationic curing of DGEBA with s(γBL), because the curing process starts earlier in its absence, and the use of an overstoichiometric amount of s(γBL) does not further accelerate the curing process. It is concluded that s(γBL) inhibits DGEBA homopolymerization at the beginning of the process in favor of its copolymerization with DGEBA, thus allowing complete epoxy conversion due to a reduction in the occurrence of termination reactions associated with DGEBA homopolymerization.

Among the different initiators tested, DMAP is the most efficient one in all the formulations studied in this work. 1MI appears to be the least efficient one, but its performance can be greatly improved with respect to the others in 212 formulations if the curing temperature is high enough. DBN is an efficient initiator for the copolymerization of DGEBA with s(γBL), but it far less efficient for DGEBA homopolymerization. These differences might be attributed not only to the intrinsic activity of the tertiary nitrogens but also to the chances of undergoing termination reactions which allow to refresh the initiator and keep a sufficient amount of active species in the reaction medium and to the different network structure which is developing during curing, which in addition might confer different mechanical and thermal properties on the materials.

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