Anionic Copolymerization of Diglycidyl Ether of Bisphenol A with Meldrum's Acid Derivatives Initiated by 4-(*N,N*-Dimethylamino) Pyridine

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ABSTRACT: The anionic copolymerization of diglycidyl ether of bisphenol A with 2,2,5,5-tetramethyl-4,6-dioxo-1,3-dioxane or 6,6-dimethyl-(4,8-dioxaspiro[2.5]octane-5,7-dione) with 4-(*N,N*-dimethylamino) pyridine as an initiator to form thermosets was studied with differential scanning calorimetry, and the kinetics were evaluated with isoconversional procedures. The evolution during the curing process of the epoxide, lactone, and linear ester bands was evaluated with Fourier transform infrared spectroscopy in the attenuated total reflection mode to clarify the reactions taking place. The shrinkage during curing, thermomechanical properties, and thermal degradability of the materials obtained by copolymerization with the different derivatives of Meldrum's acid were evaluated and related to the chemical structure of the final network. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1805–1815, 2009

Key words: crosslinking; recycling; ring-opening polymerization; thermogravimetric analysis (TGA)

INTRODUCTION

Shrinkage during curing can lead to serious problems when epoxy resins are used as coatings because it leads to the formation of microvoids, microcracks, and internal stress. These reduce the adhesion to the substrate and the durability of the coating and worsen the mechanical properties and capacity for protection.[1]

The cationic copolymerization of epoxy resins with lactones using Lewis acids as initiators has been widely studied.[2,3] Several studies on this topic developed in our research group[4–6] have demonstrated that even though the global shrinkage during curing remains the same, the shrinkage after gelation is notably reduced. This is of the greatest importance because internal stress appears in the material when there is no mobility in the network. This copolymerization, which leads to poly(ether ester) networks,

takes place through the *in situ* formation of spiroorthoesters and the subsequent ring-opening polymerization. Spiroorthoesters are considered expandable monomers because they can expand on polymerizing. Their use is a suitable strategy to reduce the shrinkage, but the synthesis of these monomers is in some cases very tedious.[7] Moreover, Meldrum's acid and its derivatives have demonstrated their expandable character in copolymerization with epoxy resins using lanthanide triflates as cationic initiators, which lead to thermosets with lower global shrinkage than pure epoxy resins.[8–10]

Brady et al.[11] reported that bicyclic monomers undergo copolymerization with epoxy resins via an anionic mechanism to reduce polymerization shrinkage of the resulting resins. Furthermore, they succeeded in the reduction of the shrinkage volume by adding small amounts of spirocyclic γ-lactones to anionic copolymerization systems with epoxy resins.[12] Endo and coworkers[13,14] suggested that this copolymerization follows an alternate pathway with a certain degree of homopolymerization depending on the ratio of the reactants. Nevertheless, they proposed that the homopolymerization of bislactone is not feasible. These authors used potassium *t*-butoxide or methyl lithium as an anionic initiator. However, tertiary amines, such as benzyldimethylamine, pyridine, triethylamine, imidazoles, 2,4,6-

tris(dimethylaminomethyl) phenol,[15,16] and 4-(*N*,*N*-dimethylamino) pyridine (DMAP),[17,18] are compounds that are more suitable as initiators from the point of view of technological applications because they can be used in an air atmosphere.

Spiro(γ-bislactone)s and diglycidyl ether of bisphenol A (DGEBA) were copolymerized with DMAP, 1,5-diazabicyclo[4.3.0]non-5-ene, and 1-methylimidazole as anionic initiators, and the alternating character of the copolymerization was demonstrated.[19] Among these initiators, the most efficient one was DMAP. The difference in the activity of these initiators might be attributed to the intrinsic activity of the tertiary nitrogens and also to the possibility of termination reactions, which allow refreshing of the initiator and therefore the retention of a sufficient amount of the active species in the reaction medium. The alternating copolymers obtained in this way should be advantageous as "reworkable thermosets" because of the presence of ester groups in the network. These labile groups impart higher thermal and hydrolytic degradability to the final material, and thus the permanency of these thermosets in the environment once their service life is over is reduced.[19,20]

Some authors[20–23] have incorporated tertiary ester groups into the network by polymerizing cycloaliphatic epoxy resins containing this moiety in their structure. The main drawbacks of this approach are that the epoxy monomers have to be synthesized previously, that cycloaliphatic epoxides are more difficult to crosslink than glycidylic ones, and that they do not polymerize with anionic initiators. Thus, the copolymerization of DGEBA, which is the most conventional and cheapest epoxy resin, with monomers that introduce breakable groups into the structure could be advantageous for increasing the degradability of the modified epoxy thermosets, enhancing the versatility of the materials, and reducing the economic costs.

In this article, we report the anionic copolymerization of DGEBA with two different Meldrum's acid derivatives—2,2,5,5-tetramethyl-4,6-dioxo-1,3-dioxane (MDM) and 6,6-dimethyl-(4,8-dioxaspiro[2.5]octane-5,7-dione) (MCP)—with DMAP as an initiator, which is the most efficient according to previous studies.[18,19]

In previous articles, we reported the cationic copolymerization of DGEBA epoxy resin with MCP[8,24,25] or MDM[9] using several Lewis acids as cationic initiators, and the reduction in the shrinkage was confirmed. In this work, we study the overall curing process and test if the global shrinkage is reduced under anionic conditions. In the curing process, the functionality of MCP and MDM is 2, and the functionality of DGEBA is 4. Therefore, this copolymerization leads to three-dimensional net-

works with a poly(ether ester) structure: the addition to DGEBA of MCP or MDM increases the distance between crosslinks, and this should reduce the fragility and retard the gelation point up to higher conversions.[26] In this way, the contraction after gelation is reduced, and the internal stress that is originated is much lower. MCP and MDM were selected because they have two tertiary ester groups in their structure, which facilitate the thermal β-degradation process, a relatively high dipolar moment, and a six-member ring that can show expandable behavior.

EXPERIMENTAL

Materials

DGEBA (Epikote Resin 827) from Shell Chemicals (Rotterdam, The Netherlands) (epoxy equivalent = 182.08 g/equiv) was used as received.

MCP (Aldrich) was used as received, and MDM was prepared according to the reported method.[9]

DMAP and phenyl glycidyl ether (PGE; Aldrich, München, Germany) were used without further purification.

Preparation of the curing mixtures

The samples were prepared through the mixing of DMAP with the corresponding amount of MDM or MCP and the addition of the required proportion of DGEBA with manual stirring in a mortar. The prepared mixtures were kept at −18°C before use. DMAP was added in molar ratios of 0.088 mol/mol of DGEBA and 0.044 mol/mol of MDM or MCP. Thus, mixtures of 3 mol of DGEBA with 1 mol of lactone contained 0.308 mol of the initiator.

Characterization and measurements

Calorimetric studies were carried out on a Mettler DSC-821e thermal analyzer (Greifensee, Switzerland) in covered Al pans under N_2 at 10°C/min. The calorimeter was calibrated with an indium standard (heat flow calibration) and an indium–lead–zinc standard (temperature calibration). The samples weighed approximately 7–9 mg. In the dynamic curing process, the degree of conversion by differential scanning calorimetry (α_{DSC}) was calculated as follows:

$$\alpha_{DSC} = \frac{\Delta H_T}{\Delta H_{dyn}} \qquad (1)$$

where ΔH_T is the heat released up to temperature T (obtained by integration of the calorimetric signal up to this temperature) and ΔH_{dyn} is the total reaction heat associated with the complete conversion of all reactive groups. The glass-transition temperature for each material was calculated after complete curing, by means of a second scan, as the temperature at the

half-way point of the jump in the heat capacity curve when the material changed from the glassy state to the rubbery state.

The isothermal curing process at 150°C was monitored with a 680 Plus Fourier transform infrared (FTIR) spectrophotometer from Jasco (Tokyo, Japan) with a resolution of 4 cm^{-1} in the absorbance mode. An attenuated total reflection (ATR) accessory with a thermal control and a diamond crystal (Golden Gate heated single-reflection diamond ATR, Specac-Teknokroma, Sant Cugat del Vallès, Spain) was used to obtain the FTIR spectra. The conversions of the reactive groups were determined from the normalized changes in absorbance by the Lambert–Beer law, as we explained previously.[4] After isothermal curing, in FTIR–ATR, a dynamic scan by differential scanning calorimetry (DSC) was always carried out to prove that the curing was complete. In any case, residual enthalpy was observed.

Thermogravimetric analyses were carried out with a Mettler TGA/SDTA 851e thermobalance. Cured samples with an approximate mass of 7 mg were heated between 30 and 600°C at a heating rate of 10°C/min in N_2 (200 cm^3/min) and measured under normal conditions.

The shrinkage was calculated from the densities of the materials before and after curing, which were determined with a Micromeritics AccuPyc 1330 gas pycnometer (Norcross, GA) thermostated at 30°C.

The dynamic mechanical thermal analyses were carried out with a TA Instruments DMTA 2980 analyzer (NJ). The samples were cured isothermally in a mold at 140°C for 3 h and subjected to postcuring for 2 h at 160°C. A three-point bending of 10 mm was performed on cylindrical samples (ca. 10 × 4.05 mm^2). The instrument was operated dynamically at 3°C/min from 35 to 200°C at a frequency of 1 Hz.

Kinetic Analysis

Integral nonisothermal kinetic analysis was used to determine the kinetic triplet {the pre-exponential factor (A), activation energy (E), and integral function of the degree of conversion [$g(\alpha)$]}.

Nonisothermal kinetic analysis may start with the kinetic equation:

$$\beta \frac{d\alpha}{dT} = A \exp\left(\frac{-E}{RT}\right) f(\alpha) \qquad (2)$$

where β is the heating rate, α is the degree of conversion, R is the universal gas constant, T is the temperature, and $f(\alpha)$ is the differential conversion function.

By using the Coats–Redfern[27] approximation to resolve the so-called temperature integral and considering that $2RT/E$ is much lower than 1, we can write the Kissinger–Akahira–Sunose equation as follows:[28]

$$\ln \frac{\beta}{T^2} = \ln\left[\frac{AR}{g(\alpha)E}\right] - \frac{E}{RT} \qquad (3)$$

For each conversion degree, the linear representation of $\ln[\beta/T^2]$ versus T^{-1} enables E and $\ln[AR/g(\alpha)E]$ to be determined from the slope and ordinate in the origin. If the reaction model, $g(\alpha)$, is known for each conversion, the corresponding value of A can be calculated for every value of E. In this study, to assign a reaction model to the systems studied, we used Criado's reduced master curves procedure,[29] which is described elsewhere.[30] Different kinetic models have been studied: diffusion (D_1, D_2, D_3, and D_4), Avrami–Erofeev (A_2, A_3, and A_4), power-law, phase-boundary-controlled reaction (R_2 and R_3), autocatalytic ($n + m = 2$ and 3), and n-order ($n = 1$, 1.5, 2, or 3).[30] We found that the curing of the studied systems follows an n-order kinetic model ($n = 1.5$) with $g(\alpha) = 2[-1 + (1 - \alpha)^{1/2}]$. The rate constant was calculated with E and A determined at $\alpha = 0.5$ with the Arrhenius equation.

RESULTS AND DISCUSSION

In previous works, we reported the cationic copolymerization of DGEBA with Meldrum's acid derivatives (MCP and MDM). Because of the characteristics of MCP, which has a highly strained cyclopropyl ring, a double ring opening of the skeleton could be suspected and could justify the expandable behavior observed.[8] However, MDM has also shown an expandable character.[9] Therefore, the opening of the Meldrum's acid ring should be responsible for these results.

In this work, we studied the copolymerization of DGEBA and these two lactones using DMAP as an anionic initiator because DMAP has been proved to be stable in an air atmosphere and to have great nucleophilicity.[17,18] Scheme 1 depicts the structure of the initial products and the reactive processes that could be expected. In anionic systems, the reactions between epoxide and γ-lactones have been reported to have an alternating character,[13,14] but there are no reported studies of anionic copolymerization with Meldrum's acid derivatives [Scheme 1(a)]. In addition, if epoxide is in excess in the reactive mixture, its homopolymerization should also occur [Scheme 1(b)].[31] The polymerization of lactones was studied several years ago,[32] and it was reported that the polymerizability of six-membered cyclic carbonyl-containing monomers markedly depends on their chemical structure. Alkyl and aryl substituents on a ring always decrease the polymerizability, and so the homopolymerization of MCP or MDM is
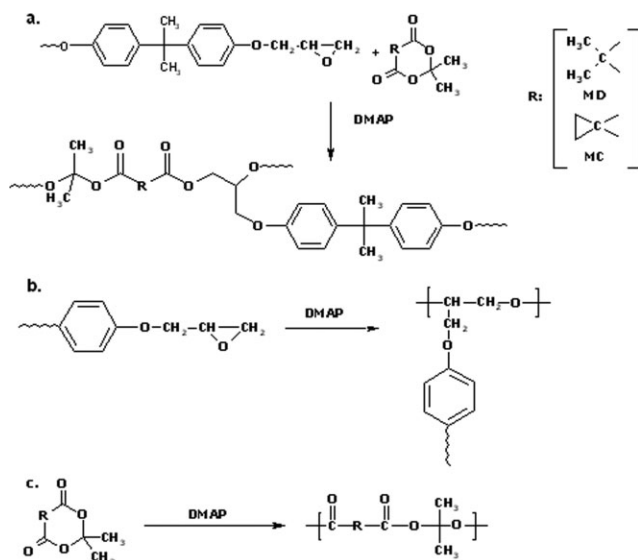
Scheme 1 Expected reactions taking place during curing.

uncertain [Scheme 1(c)]. The low proportion of lactone in the DGEBA/lactone formulation studied (3 : 1 mol/mol), in addition to the lower nucleophilicity of carboxylates in front of alkoxides, can reduce the probability of the lactone homopolymerization process.

Study of curing by calorimetry

Figure 1 shows the calorimetric curves and conversion degrees against temperature for pure DGEBA and for DGEBA/MDM and DGEBA/MCP mixtures, all initiated by DMAP. The curing of pure DGEBA exhibits a unimodal exotherm and higher conversion degrees at lower temperatures than the curing of DGEBA/lactone mixtures. On the addition of lactone, the calorimetric curve exhibits a more complex shape due to the concurrence of different reactive processes. Among Meldrum's acid derivatives, MCP produced a higher deceleration than MDM. The addition of both Meldrum's acid derivatives to DGEBA delayed the curing process. This fact could be attributed to the presence of carboxylate and alkoxide chain ends, the former being less reactive.

In Table I, the calorimetric results and the kinetic parameters of the curing process of pure DGEBA and its mixtures with MDM or MCP are collected. As can be seen, the addition of lactone leads to a decrease in the glass-transition temperatures of the materials because of the increase in the distance between crosslinks and the flexibility introduced into the network by the lactone structure.

The values of the total enthalpy per epoxy equivalent of the DGEBA/MDM and DGEBA/MCP formulations are quite similar and higher than the enthalpy of the pure DGEBA epoxy resin, probably

because of the heat generated by the ring opening of the lactone.

The dependence of the apparent activation energy on the degree of conversion calculated with the isoconversional method [eq. (3)] is presented in Figure 2. There is not a big variation in the activation energy values in the curing of pure DGEBA and its mixture with MCP, but the activation energy of the curing of the sample containing MDM shows a pronounced decrease from 85 to 45 kJ/mol in the conversion range 10–80%.

To calculate the frequency factors from the activation energies, the kinetic model that fits the experimental results best was determined. We used the reduced master curves procedure of Criado;[29] this consisted of comparing the experimental curves with the theoretical ones calculated with the different theoretical models mentioned in the Experimental section. The activation energies for each theoretical model by the Coats–Redfern method[27] were also calculated and compared with the experimental values. The results from both the Criado and Coats–Redfern methods showed that the $n = 1.5$ kinetic model produced the best correlation between the experimental and predicted kinetic data.

Knowing the activation energy and the kinetic model and using eq. (3), we could obtain the frequency factors for a conversion of 0.5.[33] To obtain the kinetic constants, we used the Arrhenius equation.

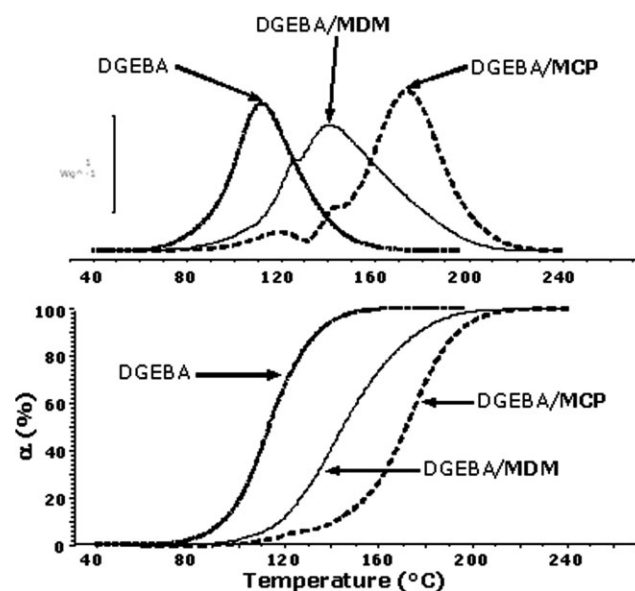Table I also collects the kinetic parameters of curing for the samples studied at a conversion of 0.5.

Figure 1 DSC scanning curves and conversion degree (α) values versus the temperature of curing of DGEBA and 3 : 1 mol/mol DGEBA/lactone mixtures initiated by DMAP at a heating rate of 10°C/min.

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TABLE I
Calorimetric Data and Kinetic Parameters of the Different Systems

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Entry	Formulation[a]	T_g (°C)[b]	ΔH (J/g)	ΔH (kJ/ee)	T_{max} (°C)	E_a (kJ/mol)[c]	ln A (s^{-1})[d]	$k_{150°C} \times 10^3$ (s^{-1})[e]
1	1 : 0.088 DGEBA/DMAP	140	466.4	84.9	112	65.2	15.40	42.94
2	3 : 1 : 0.308 DGEBA/MCP/DMAP	116	427.3	92.5	175	67.3	13.12	2.44
3	3 : 1 : 0.308 DGEBA/MDM/DMAP	97	423.1	91.8	141	59.6	12.12	8.03

ΔH = enthalpy per gram of mixture (J/g) or enthalpy per equivalent of epoxy groups (kJ/ee); A = pre-exponential factor for the kinetic model; E_a = activation energy; $k_{150°C}$ = rate constant at 150°C; T_g = glass-transition temperature; T_{max} = temperature of the maximum of the curing exotherm.
 [a] The compositions are given as molar ratios.
 [b] In entries 2 and 3, the T_g values were obtained by DSC in a second scan after dynamic curing. For entry 1, T_g was evaluated from a sample cured isothermally at 140°C for 3 h and postcured for 2 h at 160°C.
 [c] E_a was evaluated by the isoconversional integral method [eq. (3)] applied at a conversion of 0.5.
 [d] $n = 1.5$ {$g(\alpha) = 2[-1 + (1 - \alpha)^{1/2}]$ per $\alpha = 50\%$}.
 [e] $k_{150°C}$ was calculated with the Arrhenius equation: $\ln k = \ln A - \frac{E}{RT}$.

The calculated constant rates clearly show the order of reactivity observed by DSC (see Fig. 1).

In a previous work,[34] the anionic polymerization of DGEBA with some six-membered cyclic carbonates initiated by DMAP was studied. We observed a reduction in the glass-transition temperature for the materials due to the aliphatic structure introduced and also a decrease in the curing rate.

Study of the reactions on curing

Because the homopolymerizability of MCP or MDM is uncertain, first we studied whether these processes can occur in the presence of DMAP as an initiator. By DSC (Fig. 3), the thermal behavior of mixtures of lactone and DMAP was investigated. As can be seen, the MCP curve shows an exothermic process after melting, which can be attributed to the homopolymerization. The enthalpy per mole calculated from the DSC measurements was 24.3 kJ/mol. On the contrary, MDM shows only a broad endo-

therm, which can be related to both melting and sublimation.

By FTIR–ATR, it could be confirmed that MDM completely disappeared after heating at 150°C in the presence of DMAP because of sublimation. In contrast, MCP reacted as the initial lactone's carbonyl bands at 1768 and 1742 cm^{-1} disappeared and a new band at 1732 cm^{-1}, attributable to linear ester, appeared. Moreover, the band at 962 cm^{-1}, related to the deformation of the six-membered ring, completely disappeared. This band was assigned on the basis of calculations made with the program Gaussian 98.[35] However, the most striking observation was the complete disappearance of the absorption at 3115 cm^{-1}, which is typical from the C—H stretching of cyclopropenylic structures. This leads to the conclusion that DMAP can attack the cyclopropenylic ring in a way similar to that of other nucleophiles, as reported by some authors.[36,37] Figure 4 shows the FTIR–ATR spectra obtained for an MCP/DMAP mixture before and after the reaction. To elucidate the chemical structure of the product, we heated a
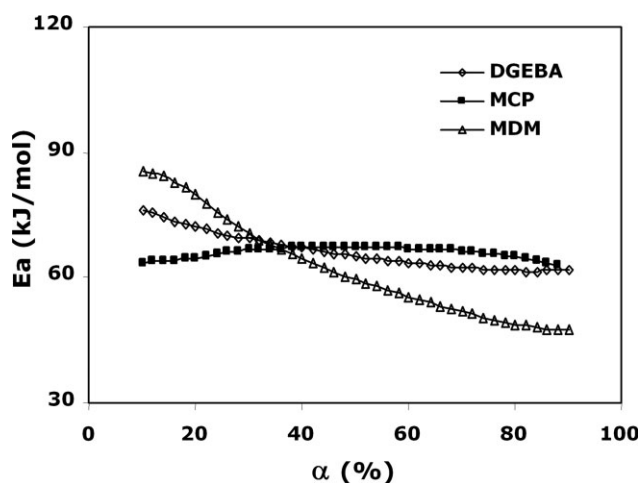

Figure 2 Dependence of the activation energy (E_a) on the degree of conversion (α) obtained by DSC in the curing of DGEBA and DGEBA/lactone formulations.
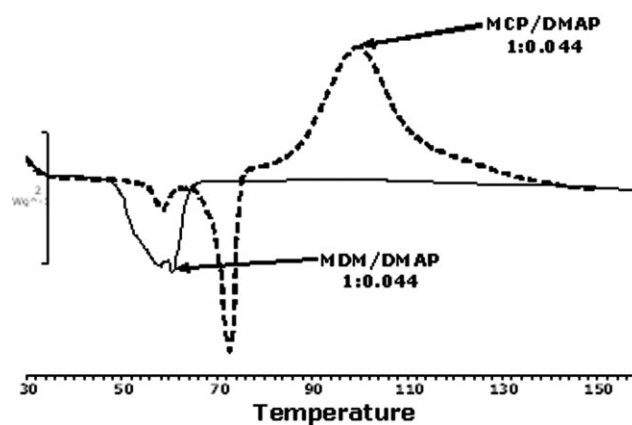

Figure 3 DSC scanning curves versus the temperature of both Meldrum's acid derivatives and 0.044 mol of DMAP/mol of lactone at a heating rate of 10°C/min.
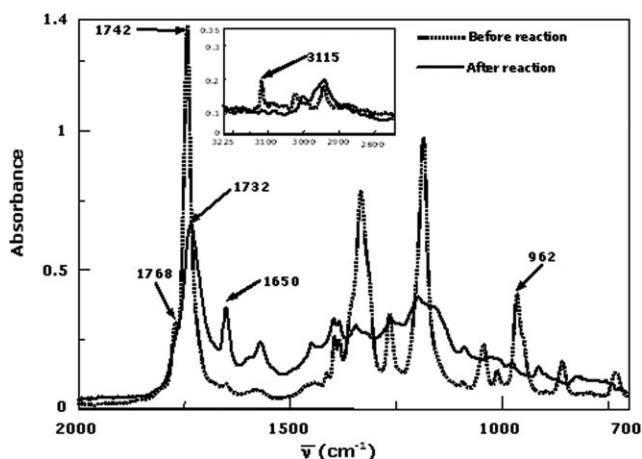
Figure 4 FTIR–ATR spectra of a mixture of MCP and DMAP initiated by DMAP before and after the reaction at 150°C.

convenient amount of the mixture at 150°C for 2 h in a reaction tube, and then we tried to record NMR spectra, but the product was partially insoluble in common deuterated solvents. This indicates that some crosslinking occurred and that MCP behaved as if it had a functionality higher than 2. These facts allow us to confirm that pure MCP can homopolymerize when heated with DMAP even though there is also an opening of the cyclopropenylic ring. Nonetheless, this result does not imply that this homopolymerization also occurs in the copolymerization with DGEBA.

Figures 5 and 6 show the FTIR–ATR spectra of the 3 : 1 mol/mol DGEBA/MCP and DGEBA/MDM formulations with 0.308 mol of DMAP as an initiator before and after curing at 150°C. The evolution of the carbonyl region during curing is shown in the insets. In the spectra of the uncured samples, there are two carbonylic absorptions at 1771 and 1747 cm^{-1} (MCP) and at 1782 and 1743 cm^{-1} (MDM) attributable to the stretching of the carbonyl groups of the initial lactones, a band at 965 cm^{-1} (MCP) and a band at 962 cm^{-1} (MDM) due to the deformation of the six-membered ring, and a band at 912 cm^{-1} due to the deformation of the oxirane ring. In the spectra of both cured samples, the epoxide and lactone ring deformation absorptions are absent, and this indicates that the epoxide and lactone are fully incorporated into the network. The times needed to achieve the complete reaction were 4335 and 1830 s for MCP and MDM mixtures.

The disappearance of the band at 965 or 962 cm^{-1} should indicate that MCP or MDM reacted, leading to an absorption at 1733 or 1734 cm^{-1} due to the carbonyl of the linear ester group. This band is more intense in the MDM sample, and this indicates that the proportion of linear ester groups in the network is higher in this case. The disappearance of the band
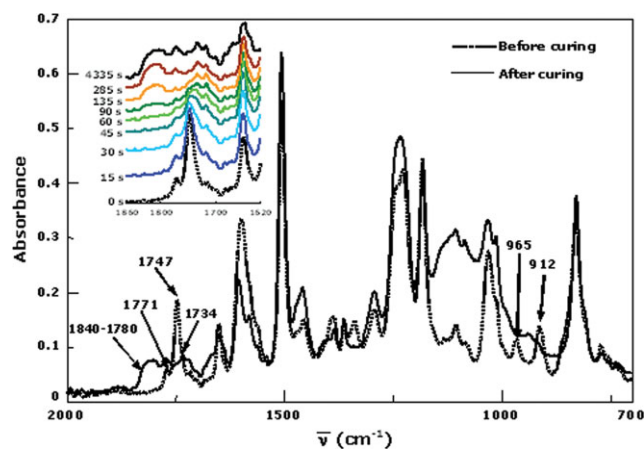

Figure 5 FTIR–ATR spectra of a 3 : 1 mol/mol mixture of DGEBA and MCP initiated by DMAP before and after curing at 150°C. The inset shows the evolution of the region between 1600 and 1880 cm^{-1} during curing. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

at 965 cm^{-1} indicates that the lactone ring was opened. Therefore, the low linear ester absorption in the MCP mixture was an unexpected result. In fact, when pure MCP polymerized with DMAP (Fig. 4), the linear ester band at 1732 cm^{-1} clearly appeared. One possible explanation could be found in the reactivity of the spiroacylal structure of MCP, which is susceptible to being attacked by a variety of nucleophiles to produce ring-opened products bearing a stabilized carbanion.[38] When MCP is copolymerized with DGEBA, DMAP first opens the oxirane ring to form an alkoxide, which can attack the cyclopropenylic structure, leading to a different structure than that formed by the direct attack of DMAP. However,
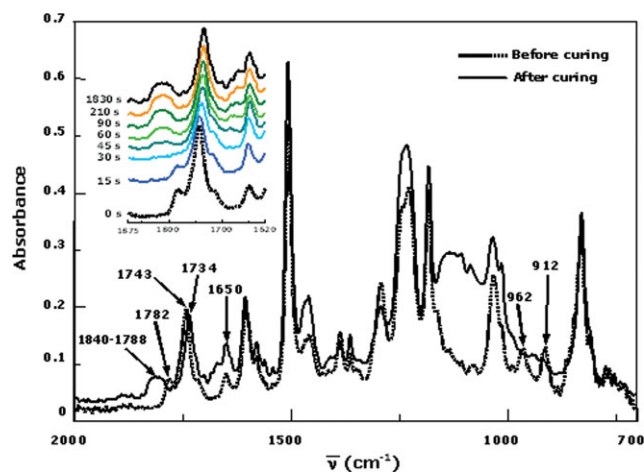

Figure 6 FTIR–ATR spectra of a 3 : 1 mol/mol mixture of DGEBA and MDM initiated by DMAP before and after curing at 150°C. The inset shows the evolution of the region between 1600 and 1880 cm^{-1} during curing. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
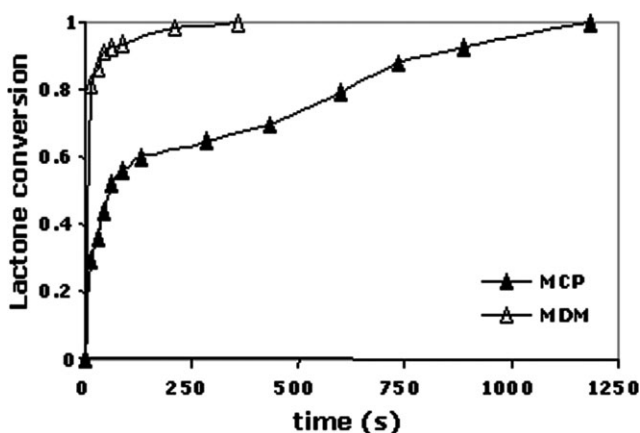
Figure 7 Conversion of lactone versus time in the curing of mixtures of DGEBA and lactone initiated by DMAP (obtained from FTIR spectra).

we could not observe any difference in the zone of 3100 cm^{-1} corresponding to the cyclopropanic C—H stretching because of the low proportion of MCP in the DGEBA/MCP mixture. Thus, in the curing of the mixtures, we could not experimentally prove the opening of the cyclopropenylic ring.

MDM was not able to homopolymerize with DMAP in the previous experiments, but the copolymerization with DGEBA resulted in the formation of linear esters. This seems to indicate that DMAP is not capable of directly attacking the lactone's ester group, but the alkoxide that forms in the opening of the oxirane ring is reactive enough to open the lactone structure.

Figure 7 shows the evolution of the lactone during curing by monitoring the diminution of the band at 962 (MDM) or 965 cm^{-1} (MCP) corresponding to the deformation of the lactone ring. As can be seen, MDM reacts faster, and at 360 s, the monitored band completely disappears, whereas MCP needs 1185 s to complete the reaction. Both lactones react at a high rate in the first stages of the curing, but the reaction of MCP slows down at a conversion of 0.55, a lower conversion than that in the case of MDM. Figure 8 shows the evolution of epoxide groups during curing in both mixtures by monitoring the disappearance of the band at 912 cm^{-1}. The disappearance of the epoxy group in the MDM mixture takes place very quickly until a conversion of 0.8 is reached. A different behavior shows the epoxy conversion curve in the MCP mixture. The disappearance of epoxide is slower from the beginning and slows down after a conversion of 0.5. Taking into account the molar ratio of epoxide to lactone, the results indicate that the homopolymerization of epoxide occurs from the first stages in the mixture with MDM. In the MCP mixture, the monomer consumption occurs more simultaneously in the first stages of the curing. For example, in Figure 7, it can

be seen that at 250 s, the lactone conversion is 0.6, which should correspond to an epoxy conversion of 0.1 if an alternate copolymerization occurred. Figure 8 shows that at 250 s, the epoxide conversion is 0.1, which implies a consumption of 0.6 mol of this group because of the molar ratio of the mixture. However, in the FTIR spectrum in Figure 5, the intensity of the linear ester band does not correspond to these conversions, and so the alternate copolymerization cannot be confirmed. This result may imply that some of the lactone reacts in another way.

Figures 5 and 6 show, in addition to the expected absorptions, a broad band above 1780 cm^{-1} in the spectra recorded after curing. Among all carbonyl groups that absorb at such a high wave number, anhydrides or vinylic esters are the most feasible candidates in our case. The formation of vinylic ethers has been described in the homopolymerization of epoxide with DMAP.[31] The reaction mechanism to form the analogous vinylic esters could imply the attack of an alkoxide to the lactone ring and the subsequent elimination reaction to recover the initiator, DMAP. This mechanism is depicted in Scheme 2. Dell'Erba and Williams[31] assigned the vinylic ether peaks to the band at 1642 cm^{-1}. Vinylic esters should produce an absorption in the region of 1690–1650 cm^{-1} due to the C=C stretching in addition to the carbonylic absorption.[39] In the insets of Figures 5 and 6, a band can be clearly seen in this zone that broadens as the curing process goes on; this seems to confirm the presence of these groups. Moreover, a possible mechanism that leads to the formation of anhydride moieties, which implies the loss of acetone, is shown in Scheme 3. This loss could be related to a clear weight loss at about 70°C observed when mixtures of DGEBA and MCP or DGEBA and MDM were cured in the presence of DMAP in the thermobalance. Therefore, according to
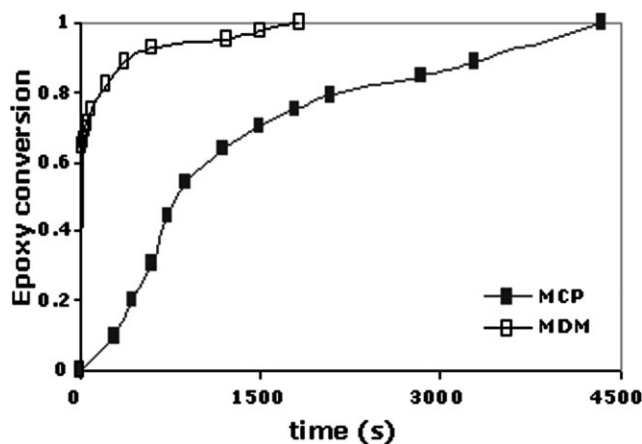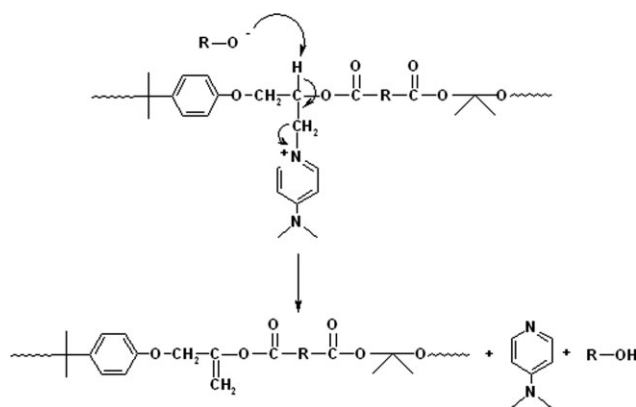

Figure 8 Conversion of epoxide versus time in the curing of mixtures of DGEBA and lactone initiated by DMAP (obtained from FTIR spectra).

Scheme 2 Formation of vinyl esters with regeneration of free iniator.

the FTIR data and the thermogravimetric analysis experiments, the formation of both vinyl esters and anhydride moieties is possible, and their presence could justify the broadness of the absorptions in the carbonylic region.

In a previous FTIR spectroscopy study[34] on the copolymerization of DGEBA and six-membered cyclic carbonates initiated by DMAP, an unexpected broad band centered at 1820 cm^{-1} could be observed and was attributed to the formation of a five-membered cyclic carbonate due to a back-biting process. Furthermore, the linear carbonate absorption was much lower than expected. These observations support the formation of the unexpected moieties that we postulate in this study. The high reactivity of the anionic groups at the end of the growing chains makes this possible.

To study in more detail the reactions that take place during the curing process, some experiments using PGE as a model compound were carried out with PGE kept at 150°C for 3 h in the presence of DMAP. Figure 9 shows the initial and final FTIR spectra and the evolution in the region between 1875 and 1615 cm^{-1} in the ATR during the reaction of a 6 : 1 mol/mol mixture of PGE and MCP. In contrast
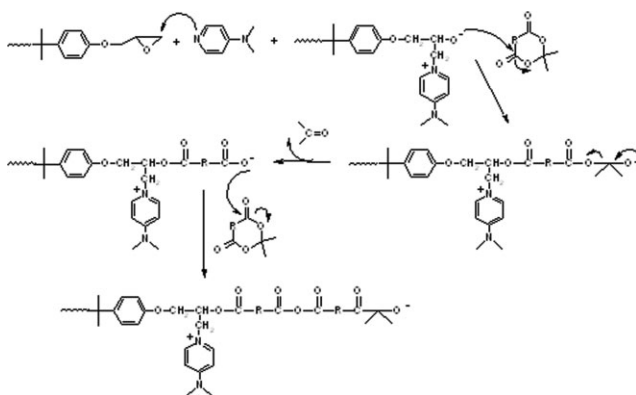
Scheme 3 Possible mechanism leading to the formation of anhydride moieties.

to the DGEBA/MCP mixture spectrum (Fig. 5), the model compound showed a big linear ester absorption after polymerization. However, as clearly shown in the inset of the aforementioned figure, there is a broad peak at 1800 cm^{-1} after 600 s, and as the reaction goes on, it diminishes. The appearance of this band can be attributed to the formation of an anhydride, which can be transformed into an ester by a reaction with an alkoxide. This last reaction is possible in this model study, but it is hindered for topological reasons in the curing of DGEBA/MCP because of the lack of mobility of the growing network. Thus, the anhydride can remain unreacted, and a low proportion of linear ester is formed in the thermoset. There is no evidence of the formation of any vinylic ester in this model study because the band at 1650 cm^{-1} does not broaden, as was observed in the curing mixture.

Study of the shrinkage

One of the main goals of our research is to reduce the shrinkage during curing to reduce the stress in the final material; therefore, the densities of the mixtures before and after the curing were measured. Table II shows these densities and the calculated global shrinkage. The values for pure DGEBA were added to the table to compare the effects of the addition of both lactones. As one can see, the addition of lactone leads to a reduction of the shrinkage, this effect being more important with MDM. This could be attributed to the higher chemical incorporation of this lactone by the formation of a linear ester. These results show the expandable character of Meldrum's acid derivatives in the anionic copolymerization with DGEBA.
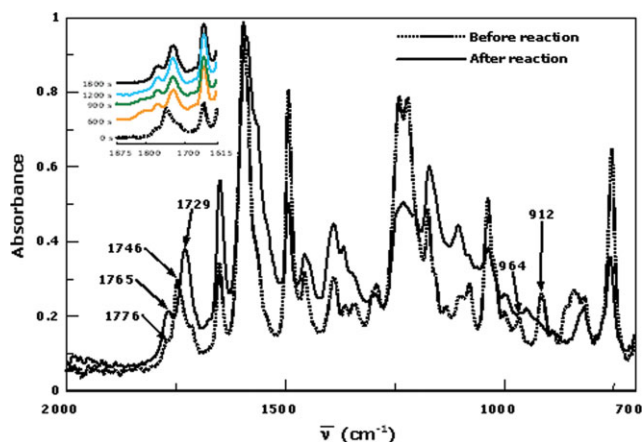

Figure 9 FTIR–ATR spectra of a 6 : 1 mol/mol mixture of PGE and MCP initiated by DMAP before and after the reaction at 150°C. The inset shows the evolution of the region between 1600 and 1880 cm^{-1} during the reaction. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Densities, Shrinkage Values, and Thermogravimetric and Thermodynamomechanical Parameters of the Systems with DMAP as the Initiator

Entry	Formulation[a]	$\rho_{initial\ mixture}$ (g/cm^3)	$\rho_{final\ material}$ (g/cm^3)	Shrinkage (%)	T (°C)	T_{max} (°C)	Char at 600°C (%)	Tan δ (°C)	E' (MPa)[b]
1	1 : 0.088 DGEBA/DMAP	1.155	1.192	3.2	337	430	16	146	35.2
2	3 : 1 : 0.308 DGEBA/MCP/DMAP	1.169	1.195	2.2	335	428	14	111	16.8
3	3 : 1 : 0.308 DGEBA/MDM/DMAP	1.159	1.181	1.9	252	425	13	87	7.5

$\rho_{initial\ mixture}$ = density of initial mixture; $\rho_{final\ material}$ = density of final mixture; E' = storage modulus; T = temperature of 2% weight loss calculated by thermogravimetry; T_{max} = temperature of the maximum degradation rate calculated by thermogravimetry.
[a] The compositions are given as molar ratios.
[b] E' was calculated at tan δ + 50°C.

In previous articles,[8,9] we reported the reduction of the shrinkage on the curing of DGEBA/MCP or DGEBA/MDM mixtures with cationic initiators. Three-to-one DGEBA/MDM mixtures led to a shrinkage of 2.2% with Yb(OTf)$_3$ and 2.7 with La(OTf)$_3$. Thus, anionic systems are the best for the reduction of the shrinkage on the curing of DGEBA/MDM formulations. However, MCP mixtures did not show this clear tendency. Three-to-one DGEBA/MCP formulations cured with Yb(OTf)$_3$ and La(OTf)$_3$ led to shrinkage of 1.7 and 2.5%, respectively, and with BF$_3$ · MEA, the shrinkage was 2.9%. In this case, the effect of Yb(OTf)$_3$ on the reduction of the shrinkage seems to be better than that of DMAP. The explanation of this fact can be found in the higher functionality of MCP in anionic systems. It can suffer the attack of an alkoxide to the cyclopropenylic structure, which leads to a higher degree of crosslinking and therefore to a more compact network. The curing mechanism of mixtures of DGEBA and Meldrum's acid derivatives does not lie in direct copolymerization but instead takes place by the formation of a spiroorthoester as a reaction intermediate. Because cationic initiators have different capabilities to polymerize these intermediates, which are expandable monomers, the global shrinkage can significantly vary. This fact is in accordance with our results.

From these studies, we can confirm that Meldrum's acid derivatives have an expandable character in anionic and cationic curing systems.

Study of the thermal degradability

To test if our modification procedure leads to more reworkable thermosets, the thermal degradability of the synthesized materials was analyzed by thermogravimetric analysis measurements. Figure 10 shows the thermogravimetric curves for the cured materials. In Table II, the thermogravimetric parameters for the studied materials are collected. The influence of the structure of the lactone on the degradability of the materials can be observed. The materials

obtained with MDM begin their degradation (2% weight loss) at a much lower temperature than pure DGEBA, and this can be attributed to the presence of tertiary ester linkages observed by FTIR. However, the addition of MCP does not produce any significant reduction. This is in accordance with the lower proportion of ester groups in the crosslinked structure. There are not many differences in the temperature of the maximum degradation rate and the char yield upon the addition of lactone because of the absence of ester groups at this temperature and the low proportion of the aliphatic moieties introduced.

Comparing these values to those obtained for cationic crosslinked materials initiated by lanthanide triflates,[9,24] we can conclude that the initial weight loss is related to the proportion of linear ester groups introduced into the network, regardless of the initiator used. However, the temperature of the maximum
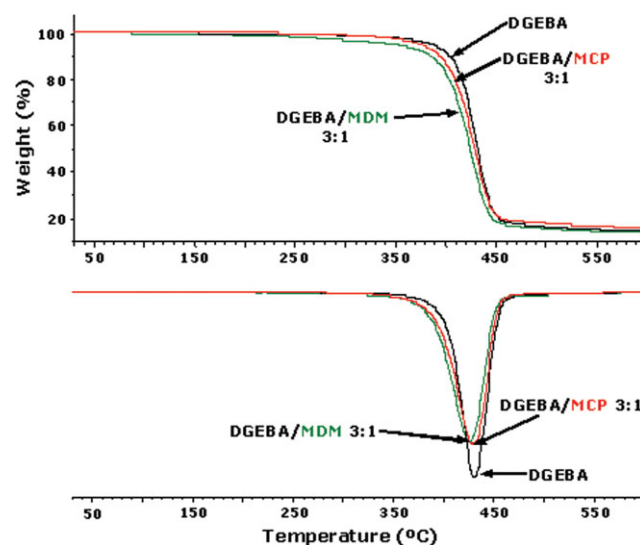

Figure 10 Thermogravimetric analysis and differential thermogravimetry curves at 10°C/min in an N$_2$ atmosphere of the crosslinked materials obtained. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

degradation rate is much lower for the lanthanide-initiated materials, and this can be attributed to the catalytic effect of these Lewis acids on the breakage of ether linkages.

Study of the thermomechanical properties

The copolymerization of epoxy resins with lactones with a functionality of 2 leads to less densely cross-linked networks with an increased distance between crosslinks; therefore, the mechanical properties should experience some changes. The thermomechanical properties of these materials were studied by means of dynamic mechanical thermal analysis. Figures 11 and 12 show the variation of the storage modulus and tan δ with the compositions of the obtained thermosets. The characteristic parameters from these experiments are shown in Table II. In Figure 11, it can be seen how the storage moduli of the copolymers show a relaxation at lower temperatures than pure DGEBA. The material obtained with MDM relaxes at the lowest temperature and leads to the lowest relaxed modulus. This could be related to the higher proportion of linear ester introduced, which leads to an increase in the distance between crosslinks. Figure 12 plots the values of tan δ against temperature, and this confirms the flexibility introduced into the network by the chemically incorporated lactone. The height of the tan δ peak is also an indicator of the significance of the relaxation of the material when it undergoes the glass transition. Therefore, we can state that the addition of lactone diminishes the glass-transition temperature and increases the flexibility of the network, this being more evident for the material obtained with MDM. The homogeneity of the copolymeric materials is quite similar to that of the material obtained from pure DGEBA.
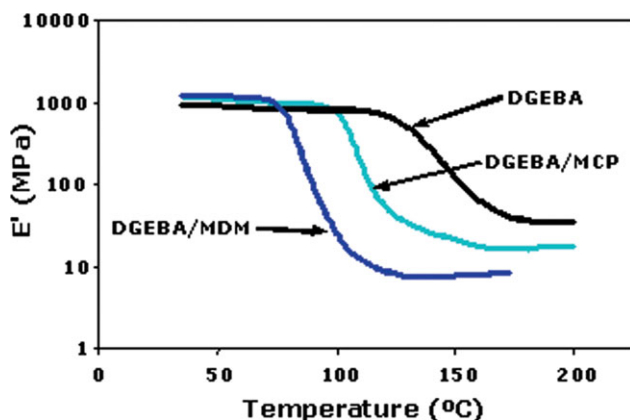

Figure 11 Storage modulus (E') versus the temperature for the materials obtained. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 12 Tan δ versus the temperature for the materials obtained. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
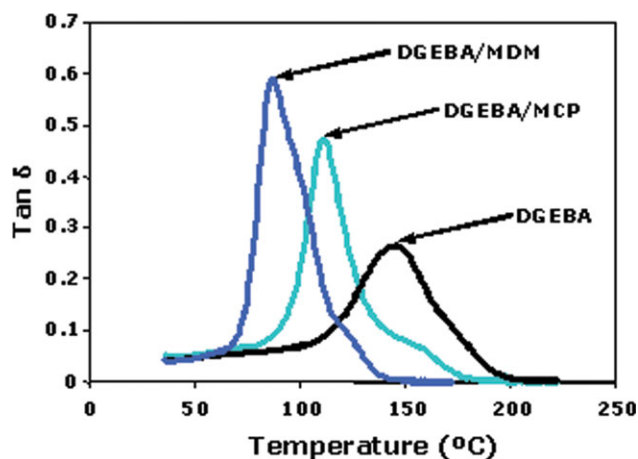
CONCLUSIONS

The addition of MCP or MDM to DGEBA using DMAP as an initiator produced a decelerative effect in the curing process.

The modification of DGEBA with MCP or MDM, initiated by DMAP, incorporated into the network the expected tertiary ester moieties as well as other carbonylic groups that were not observed under cationic conditions. The proportion of the linear ester depended on the type of lactone used, and it was higher for MDM.

The materials obtained by copolymerization presented lower values of the glass-transition temperature, tan δ, and relaxed modulus than those obtained in the absence of lactone because of an increase in the flexibility when the lactones were incorporated into the network.

The incorporation of MCP or MDM into DGEBA slightly increased the thermal degradability of the final materials. This effect was more pronounced when MDM was used because of the higher linear ester proportion that was yielded.

The expandable character of Meldrum's acid derivatives was demonstrated because the addition of MCP or MDM to DGEBA reduced the global shrinkage on curing.

References

1. Expanding Monomers: Synthesis, Characterization and Applications; Sadhir, R. K.; Luck, M. R., Eds.; CRC: Boca Raton, FL, 1992.
2. Matejka, L.; Chabanne, L.; Tighzert, L.; Pascault, J. P. J Polym Sci Part A: Polym Chem 1994, 32, 1447.
3. Fedtke, M.; Haufe, J.; Kahlert, E.; Müller, G. Angew Makromol Chem 1998, 255, 53.
4. Mas, C.; Ramis, X.; Salla, J. M.; Mantecón, A.; Serra, A. J Polym Sci Part A: Polym Chem 2003, 41, 2794.

5. Giménez, R.; Fernández-Francos, X.; Salla, J. M.; Serra, A.; Mantecón, A.; Ramis, X. J Polym Sci Part A: Polym Chem 2005, 46, 10637.
6. Mas, C.; Ramis, X.; Salla, J. M.; Mantecón, A.; Serra, A. J Polym Sci Part A: Polym Chem 2006, 44, 1711.
7. Canadell, J.; Mantecón, A.; Cádiz, V. J Polym Sci Part A: Polym Chem 2007, 45, 4211.
8. González, L.; Ramis, X.; Salla, J. M.; Mantecón, A.; Serra, A. J Polym Sci Part A: Polym Chem 2006, 44, 6869.
9. González, L.; Ramis, X.; Salla, J. M.; Mantecón, A.; Serra, A. J Appl Polym Sci 2008, 108, 1229.
10. González, L.; Ramis, X.; Salla, J. M.; Mantecón, A.; Serra, A. Eur Polym J 2008, 44, 1535.
11. Brady, R. F., Jr.; Simon, F. E. J Polym Sci Part A: Polym Chem 1987, 25, 231.
12. Sikes, A. M.; Brady, R. F. J Polym Sci Part A: Polym Chem 1990, 28, 2533.
13. Tadokoro, A.; Takata, T.; Endo, T. Macromolecules 1993, 26, 2388.
14. Chung, K.; Takata, T.; Endo, T. Macromolecules 1995, 28, 1711.
15. Mika, T. F.; Bauer, R. S. In Epoxy Resins: Chemistry and Technology, 2nd ed.; May, C. A., Ed.; Marcel Dekker: New York, 1998; p 465.
16. Pascault, J. P.; Sautereau, H.; Verdu, J.; Williams, R. J. J. Thermosetting Polymers; Marcel Dekker: New York, 2002.
17. Galià, M.; Serra, A.; Mantecón, A.; Cádiz, V. J Appl Polym Sci 1995, 56, 193.
18. Ribera, D.; Mantecón, A.; Serra, A. J Polym Sci Part A: Polym Chem 2002, 40, 3916.
19. Fernández-Francos, X.; Salla, J. M.; Mantecón, A.; Serra, A.; Ramis, X. Polym Degrad Stab 2008, 93, 760.
20. Chen, J. S.; Ober, C. K.; Poliks, M. D. Polymer 2002, 43, 131.
21. Wang, L.; Li, H.; Wong, C. P. J Polym Sci Part A: Polym Chem 2000, 38, 3771.
22. Li, H.; Wong, C. P. IEEE Trans Adv Packaging 2004, 27, 165.
23. Chen, J. S.; Ober, C. K.; Poliks, M. D.; Zhang, Y.; Wiesner, U.; Cohen, C. Polymer 2004, 45, 1939.
24. González, L.; Ramis, X.; Salla, J. M.; Mantecón, A.; Serra, A. Polym Degrad Stab 2007, 92, 596.
25. González, L.; Ramis, X.; Salla, J. M.; Mantecón, A.; Serra, A. Thermochim Acta 2007, 464, 35.
26. González, S.; Fernández-Francos, X.; Salla, J. M.; Serra, A.; Mantecón, A.; Ramis, X. J Appl Polym Sci 2007, 104, 3406.
27. Coats, A. W.; Redfern, J. P. Nature 1964, 201, 68.
28. Kissinger, H. E. Anal Chem 1957, 29, 1702.
29. Criado, J. M. Thermochim Acta 1978, 24, 186.
30. Ramis, X.; Salla, J. M.; Cadenato, A.; Morancho, J. M. J Therm Anal Calorim 2003, 72, 707.
31. Dell'Erba, I. E.; Williams, R. J. J. Polym Eng Sci 2006, 46, 351.
32. Hall, H. K.; Schneider, A. J. J Am Chem Soc 1958, 80, 6409.
33. Vyazovkin, S.; Linert, W. J Solid State Chem 1995, 114, 392.
34. Cervellera, R.; Ramis, X.; Salla, J. M.; Mantecón, A.; Serra, A. J Polym Sci Part A: Polym Chem 2006, 44, 2873.
35. Lee, I.; Han, I. S.; Kim, C. K.; Lee, H. W. Bull Korean Chem Soc 2003, 24, 1141.
36. Chen, B. C. Heterocycles 1991, 32, 529.
37. McNab, H. Chem Soc Rev 1978, 7, 345.
38. Singh, R. K.; Danishefsky, S. Organic Synthesis Collective; Wiley: New York, 1990; Vol. VII, p 411.
39. Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. Tablas para la Determinación Estructural por Métodos Espectroscópicos; Springer-Verlag Ibérica: Barcelona, 1998.