Kinetic Study of the Curing of Mixtures of DGEBA and Five-Membered Cyclic Carbonates with Lanthanum Triflate as Cationic Initiator

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ABSTRACT: Mixtures of diglycidylether of bisphenol A (DGEBA) with 1,3-benzodioxolane-2-one (CC) or 4-phenoxy-methyl-1,3-dioxolane-2-one (PGEC) were cured in the presence of lanthanum triflate. FTIR/ATR was used to study the evolution of carbonate and epoxide groups to follow the reactive processes that take place during curing. DSC was applied to study the thermal characteristics of the curing process and to determine the glass-transition temperatures of the cured materials. The kinetics of the curing was studied isothermally by means of FTIR and the kinetic model was selected through the isokinetic relationships. DSC experiments were used to study the kinetics in nonisothermal conditions by means of isoconversional procedures and the Coats–Redfern and Criado methodologies. By TMA we could monitor the evolution of the shrinkage during isothermal curing. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2875–2884, 2007

Key words: epoxy resins; carbonates; cationic polymerization; thermosets; lanthanide triflates

INTRODUCTION

Epoxy resins are among the most important thermosetting materials. They have numerous industrial applications because of their superior properties such as thermal and chemical stability. However, their use is sometimes limited because during the curing process they shrink by 4–5%. This shrinkage leads to internal stresses in the material, reduces adhesion to the substrate, and produces microvoids and microcracks, which reduce the durability of the material.[1]

Cyclic carbonates are known as expandable monomers[2,3] because the polymers formed have lower densities than the monomers from which they are derived. Moreover, cyclic carbonates react with oxiranes in the presence of a Lewis acid to give spiroortho carbonates (SOCs), which can be polymerized by cationic initiators to yield poly(ether-carbonate)s.[4,5]

In previous works[6,7] we studied the chemical incorporation of γ-butyrolactone (γ-BL) into the epoxy network. In these studies we proved that the shrinkage after gelation, when the stress is originated, was reduced. Moreover, the curing process was observed to be faster than in pure epoxy resins.

Rokicki and Nguyen[8,9] described that the reaction of oxirane with five-membered cyclic carbonates using $BF_3 \cdot OEt_2$ as initiator led to SOCs, poly(ether-carbonate), or polyether, depending on the oxirane ring substituent. They concluded that the incorporation of carbonate moieties in the material led to an increase in the strength of the resins and that the gel time and the pot-life of the epoxide cyclic carbonate compositions may be controlled by the amount of carbonate and initiator.

In a previous paper[10] we reported the curing of mixtures of diglycidylether of bisphenol A (DGEBA) or a cycloaliphatic epoxy resin (ECH) with a cyclic carbonate, 4-methyl-1,3-dioxolane-2-one (PC), using lanthanide triflates or $BF_3 \cdot MEA$ as cationic initiators and *N,N*-dimethylaminopyridine (DMAP) as an anionic initiator with the aim to obtain thermosets with carbonate groups in the polymeric chain and a low shrinkage during curing. However, we observed that the carbonate did not polymerize but remained in the network, acting as a plasticizer, lowering the T_g values of the cured materials. We could observe that PC accelerated the curing process.

The low boiling point of PC caused its partial evaporation during curing, which helped to displace the equilibrium of the SOC formation towards the initial products, such as that represented in Scheme 1.
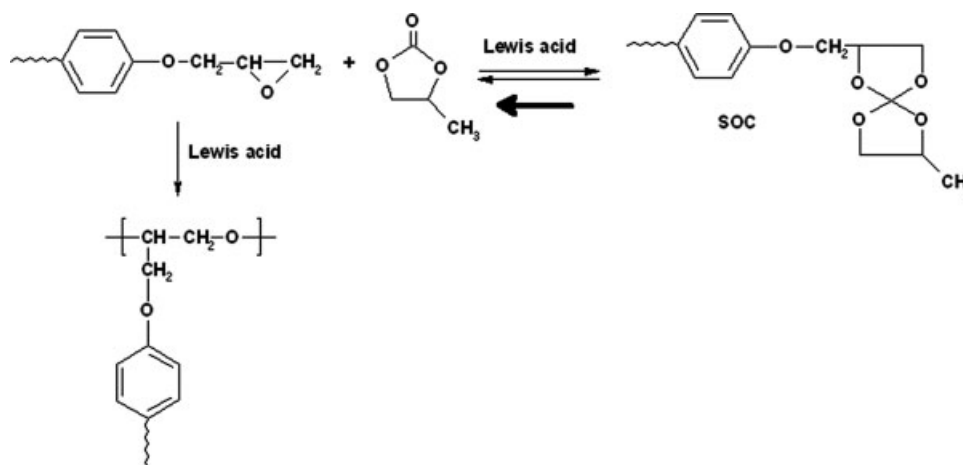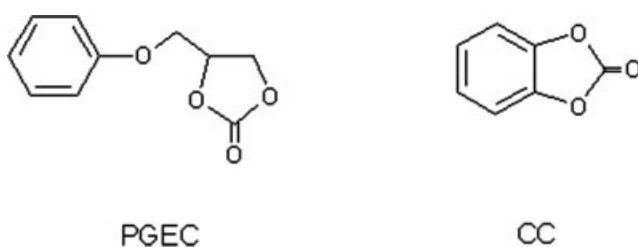
Scheme 1

The present work deals with the copolymerization of 4-phenoxymethyl-1,3-dioxolane-2-one (PGEC) and 1,3-benzodioxolane-2-one (CC), represented in Scheme 2, with DGEBA promoted by lanthanum triflate. In this case, because the carbonates are solid, the evaporation problem observed in PC formulations should be prevented. Moreover, the kinetic study of the curing is interesting to investigate the acceleration produced by the participation of the carbonates in the formation of the active initiating species.

Lanthanum triflate was selected as initiator because it proved to be an excellent Lewis acid initiator, stable in humid environments,[11] and was proved to be able to cure epoxy resins effectively.

EXPERIMENTAL

Materials

Diglycidylether of bisphenol A (DGEBA) Epikote Resin 828 from Shell Chemicals (Epoxy Equiv. = 187 g/eq) was used as-received. 4-Phenoxymethyl-1,3-dioxolane-2-one (PGEC) was prepared according to the reported method from phenyl glycidyl ether (PGE) and carbon dioxide.[12] 1,3-Benzodioxolane-2-one (CC) was prepared according to the reported method from cathecol and diphenyl carbonate.[13] Lanthanum (III) trifluoromethanesulfonate (Aldrich,

PGEC   CC

Scheme 2

Switzerland) was used as-received. The solvents were purified by standard methods.

Preparation of the curing mixtures

The mixtures were prepared by mixing lanthanum triflate in the corresponding amount of the selected carbonate and adding with stirring the required proportion of DGEBA. All the mixtures contained 1 phr of lanthanum triflate (one part of initiator per hundred parts of monomers, w/w). The prepared samples were kept at −18°C before use.

FTIR spectroscopy

The isothermal curing process, between 100°C and 160°C, was monitored with a FTIR Bomem Michelson MB 100 spectrophotometer with a resolution of 4 cm^{-1} in the absorbance mode. An attenuated total reflection accessory with thermal control and diamond crystal (Golden Gate Heated Single Reflection Diamond ATR, Specac-Teknokroma) was used to register FTIR spectra. The disappearance of the absorbance peak at 915 cm^{-1} (epoxy bending) was used to monitor the epoxy conversion. The peak at 1506 cm^{-1} (phenyl group) was chosen as an internal standard. After full cure, the peaks at 915 cm^{-1} disappeared completely. Absorbances were calculated in terms of peak areas. The conversion of the epoxy group was determined by the Lambert–Beer law from the normalized changes of absorbance at 915 cm^{-1} as[6,14,15]

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

where $\overline{A}^0$ and $\overline{A}^t$ are the normalized absorbance of the reactive group before curing and after reaction time t, $(\overline{A}^0_{915} = A^0_{915}/A^0_{1506}; \overline{A}^t_{915} = A^t_{915}/A^t_{1506})$.

After isothermal curing in the FTIR/ATR device, a dynamic scan by DSC was always carried out to confirm that the complete curing was achieved.

Differential scanning calorimetry

Calorimetric studies were carried out on a Mettler DSC-821e thermal analyzer in covered Al pans under N$_2$ at 10°C/min. The calorimeter was calibrated using an indium standard (heat flow calibration) and an indium–lead–zinc standard (temperature calibration). The samples weighed $\sim$ 5 mg. In the dynamic curing process the degree of conversion by DSC (α_{DSC}) was calculated as follows:

$$\alpha_{DSC} = \frac{\Delta H_T}{\Delta H_{dyn}} \tag{2}$$

where ΔH_T is the heat released up to a 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 (T_g) was calculated after complete curing by means of a second scan as the temperature of the halfway point of the jump in the heat capacity when the material changes from the glassy to the rubbery state.

Thermomechanical analysis

Thermomechanical analysis was carried out in a nitrogen atmosphere with a Mettler-Toledo TMA40 analyzer. The shrinkage ($\Delta L = L_t - L_0$) undergone by the resin during curing was measured by the application of a force of 0.01 N. The mixtures, impregnated in a silanized fiberglass support, were placed between two Al$_2$O$_3$ discs. Isothermal curing was carried out several times at temperatures between 110°C and 150°C. The degree of shrinkage in TMA was calculated as follows[16]:

$$\alpha_{TMA} = \frac{L_t - L_0}{L_\infty - L_0} \tag{3}$$

where L_0, L_t, and L_∞ are the values of the thickness of the sample at the onset, at time t, and on the completion of the reactive process, when the material is fully cured, respectively.

Kinetic methodology

The kinetics of the reaction is usually described by the following rate equation:

$$\frac{d\alpha}{dt} = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{4}$$

where t is time, A is the pre-exponential factor, E is the activation energy, T is the absolute temperature, R is the gas constant, and $f(\alpha)$ is the differential conversion function.

In general, the kinetic analysis was carried out using an isoconversional method. The basic assumption of this method is that the reaction rate at a constant conversion is only a function of the temperature.[17,18]

Isothermal methods

By integrating the rate equation in isothermal conditions we obtain:

$$\ln t = \ln\left[\frac{g(\alpha)}{A}\right] + \frac{E}{RT} \tag{5}$$

where $g(\alpha)$ is the integral conversion function, defined as:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \tag{6}$$

According to eq. (5) the activation energy and the constant $\ln[g(\alpha)/A]$ can be obtained, respectively, from the slope and the intercept of the linear relationship of $\ln t$ against T^{-1} for $\alpha = $ constant.

Nonisothermal methods

By integrating eq. (4) in nonisothermal conditions and reordering it, the so-called temperature integral can be expressed as:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^T e^{-(E/RT)}dT \tag{7}$$

where β is the heating rate.

By using the Coats–Redfern[19] approximation to solve eq. (7), and considering that $2RT/E \ll 1$, the following equation may be expressed as[20]:
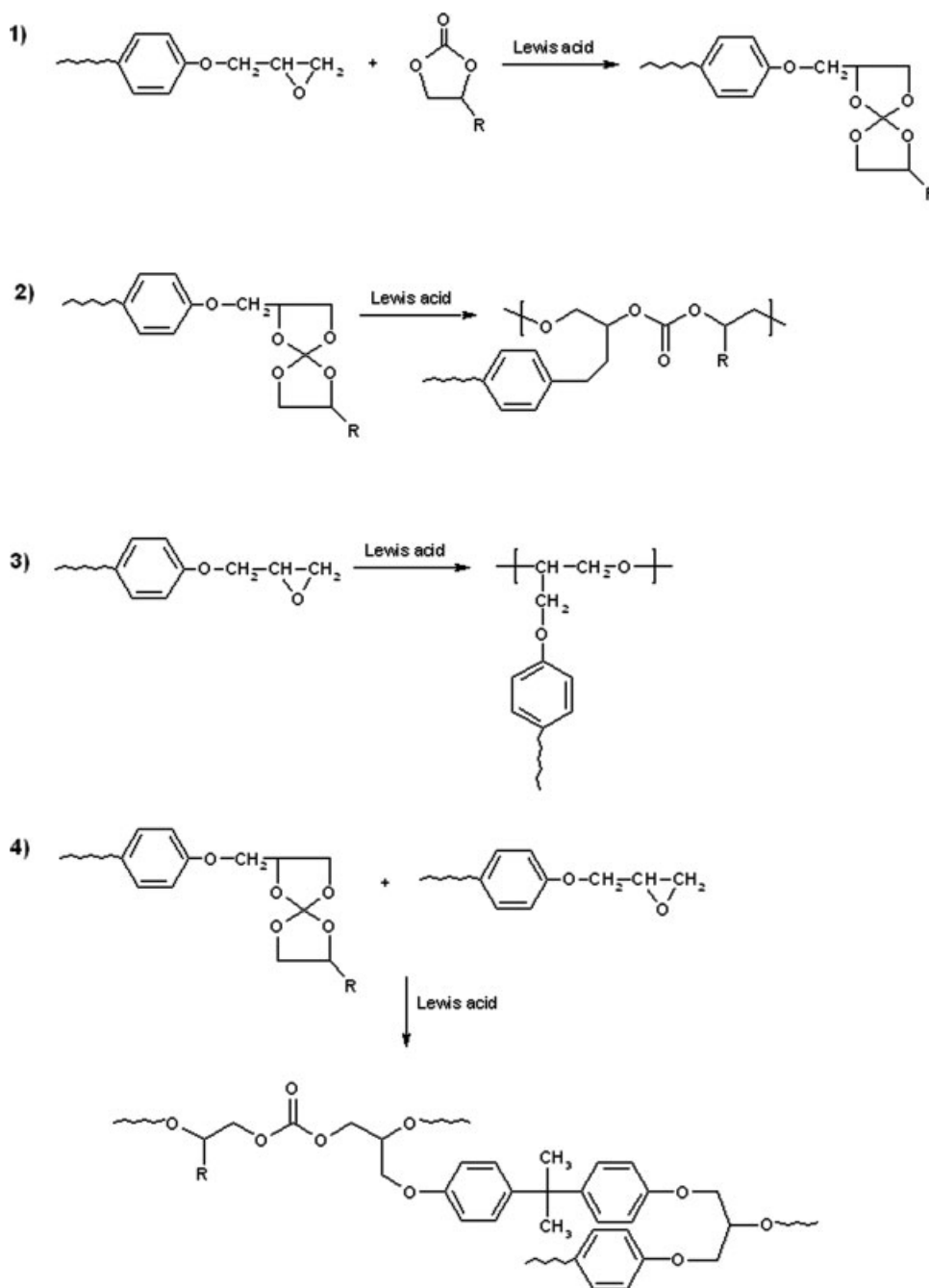
$$\ln\frac{g(\alpha)}{T^2} = \ln\left[\frac{AR}{\beta E}\right] - \frac{E}{RT} \tag{8}$$

For a given model, lineal representation of $\ln[g(\alpha)/T^2]$ against T^{-1} makes it possible to determine E and A from the slope and the ordinate at the origin.

By reordering eq. (8) we can write:

$$\ln\frac{\beta}{T^2} = \ln\left[\frac{AR}{g(\alpha)E}\right] - \frac{E}{RT} \tag{9}$$

The linear representation of $\ln[\beta/T^2]$ against T^{-1} makes it possible to determine E and the kinetic parameter $\ln[AR/g(\alpha)E]$ for every conversion degree.

Scheme 3

This isoconversional procedure is equivalent to Kissinger's method[21] and similar to Flynn–Wall[22] and Ozawa's method.[23]

The constant $\ln[AR/g(\alpha)E]$ is directly related by the R/E to the constant $\ln[g(\alpha)/A]$ of the isothermal adjustment. Thus, taking the dynamic data $\ln[AR/g(\alpha)E]$ and E from eq. (9) we can determine the isothermal parameters of eq. (5) and simulated isothermal curing without knowing $g(\alpha)$.[16,24]

If the reaction model, $g(\alpha)$, is known, for each conversion the corresponding pre-exponential factor can be calculated for every activation energy. In this

study, we used the reduced master curve procedure of Criado[25] and the Coats–Redfern method, described elsewhere,[24] to assign a reaction model to the system studied. The kinetic model which had the best linear correlation in the Coats–Redfern equation [eq. (8)] and which had an E value similar to that obtained isoconversionally (considered to be the effective E value, because was determined without know the model) was selected.

Different kinetic models have been tested: 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), order n ($n = 2$ and 3), and random nucleation (F_1).[20] We found that all systems studied follow a kinetic model of the surface-controlled reaction type, R_3, with $g(\alpha) = [1 - (1 - \alpha)^{1/3}]$. The rate constant, k, was calculated with E and A determined at the conversion of 0.5, using the Arrhenius equation.

Compensation effect (isokinetic relationship)

For complex processes (parallel reactions, successive reactions, physical changes, etc.) it is characteristic for the activation energy and the pre-exponential factor to depend on the degree of conversion. This generally reflects the existence of a compensation effect through the following equation[16,24,26–30]:

$$\ln A_\alpha = a E_\alpha + b = \frac{E_\alpha}{RT} + \ln\left[\frac{(d\alpha/dt)_\alpha}{f(\alpha)}\right] \qquad (10)$$

where a and b are constants and the subscript α represents the degree of conversion which produces a change in the Arrhenius parameters.

The slope $a = 1/RT_{iso}$ is related to isokinetic temperature T_{iso} and the intercept $b = \ln k_{iso}$ is related to the isokinetic rate constant. Equation (10) represents an isokinetic relationship (IKR). The appearance of IKR shows that only one model is present, whereas the existence of parameters that do not meet the IKR implies that there are multiple kinetic models.[31,32]

Isoconversional methods make it possible to determine easily the dependence of E on the degree of conversion in complex processes.

In this study, our aim was to determine the complete kinetic triplet [E, A, and $g(\alpha)$] in systems with $E = E(\alpha)$, by using isoconversional kinetic parameters, the slope and intercept of eqs. (5) and (9), and the IKR, eq. (10). In isothermal experiments, we selected the kinetic model whose IKR has the best linear correlation between the activation energy and pre-exponential factor and in which the associated T_{iso} value was near the experimental temperature range.

RESULTS AND DISCUSSION

We studied the cationic curing process of mixtures of DGEBA epoxy resin with two different five-membered cyclic carbonates, PGEC and CC (Scheme 2), in several molar proportions using 1 phr of lanthanum triflate as initiator.

Scheme 3 shows the individual reactions expected in the global curing process in cationic copolymerization of diglycidylic resins with cyclic carbonates. The first reaction (1) shows the formation of SOC from epoxide and cyclic carbonate. This reaction takes place with shrinkage because Van der Waals distances between both reactants convert into covalent bonds in
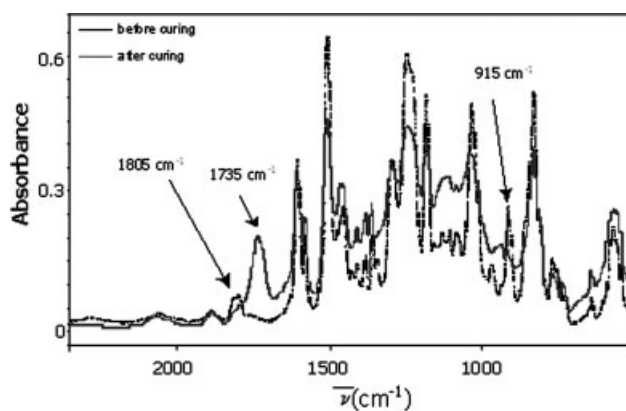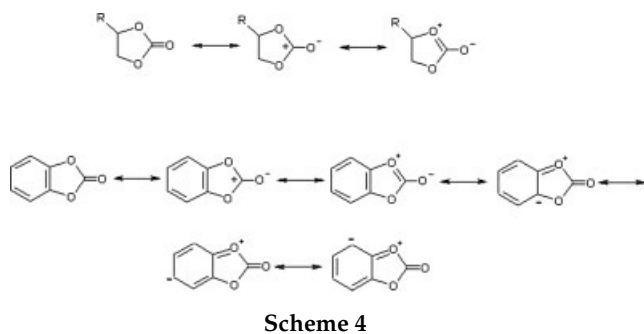

Figure 1 FTIR spectra of DGEBA/CC 2 : 1 (mol/mol) mixture with 1 phr of La(OTf)$_3$ before and after curing at 140°C.

the final product; the second reaction (2) is the polymerization of the SOC previously formed; the third (3) is the homopolymerization of DGEBA that leads to poly(ether) chains and the fourth (4) is the copolymerization of SOC and DGEBA that leads to a network containing carbonate and ether structures in proportions which depends on the composition of the initial mixture. Reactions 2 and 4, in which SOC polymerizes, should occur without shrinkage or even with expansion, because they are expandable monomers.[1] For thermodynamic reasons five-membered cyclic carbonate cannot homopolymerize[33] and thus its use simplify the chemical process. The low epoxy equivalent of the DGEBA resins used in this work makes negligible the polymerization initiated by hydroxylic groups with epoxides, and therefore, it has not been considered in Scheme 3.

It must be said that, in this type of copolymerization, the DGEBA resin acts as a tetrafunctional monomer and carbonate and SOCs act as bifunctional. Therefore, a higher proportion of DGEBA leads to a more densely crosslinked network, whereas a higher proportion of carbonate leads to a longer linear chain between crosslinks.

Figure 1 shows the FTIR spectra obtained from a mixture DGEBA/CC 2 : 1 (mol/mol) with 1 phr of lanthanum triflate before and after curing at 140°C. In the spectrum of the uncured sample, there is a absorption band at 1805 cm^{-1} attributable to the stretching of the carbonyl group of cyclic carbonate and a band at 915 cm^{-1} due to the deformation of the epoxy ring. In the spectrum of the cured sample, the epoxide absorption cannot be observed, which implies the complete reaction of epoxides, whereas a new carbonyl absorption, attributable to linear carbonate groups appears at 1735 cm^{-1}, which implies the polymerization of SOCs previously formed. We performed the same experiment with a DGEBA/PGEC mixture in the same proportions and we could see the disappearance of the band at 915 cm^{-1} of epoxy ring and a remaining carbonylic band at 1800 cm^{-1} corresponding to the cyclic

Scheme 4

Figure 3 Plot of the experimental and simulated degrees of epoxy conversion versus curing times for a sample DGEBA/ PGEC 2 : 1 (mol/mol) with 1 phr of lanthanum triflate at different temperatures. Open symbols represent experimental values, filled symbols (●) represent the isoconversional isothermal data obtained by eq. (5), and continuous line represents the curves obtained by using the function R_3 and the average isothermal kinetic parameters collected in Table I. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

carbonate. After curing in the FTIR a dynamic scan was always made in the DSC up to 250°C to prove that the curing was complete. In no case residual enthalpy was observed. These results indicate that whereas CC reacts, PGEC does not polymerize and remain entrapped in the material, similar to the results we obtained with PC.[10] The explanation to the higher reactivity of CC can be found in the higher electrophilic character of its carbonylic carbon, which has a higher $\delta(+)$ as is shown in Scheme 4. The aromatic ring directly attached to the oxygens of the carbonate group reduces their electronic density and therefore their electron release effect on the carbonylic carbon.

Figure 2 shows the plot of epoxy groups conversion against time in the pure DGEBA and DGEBA/cyclic carbonate 2 : 1 formulations with 1 phr of lanthanum triflate cured at 140°C in the FTIR/ATR. As we can see, the evolution of the epoxy group over time depends on the cyclic carbonate, CC being the fastest. In these systems the addition of carbonate accelerates the reaction in comparison with the curing of the pure resin.

Figures 3 and 4 show the degree of conversion of the epoxy group plotted against time for both mix-
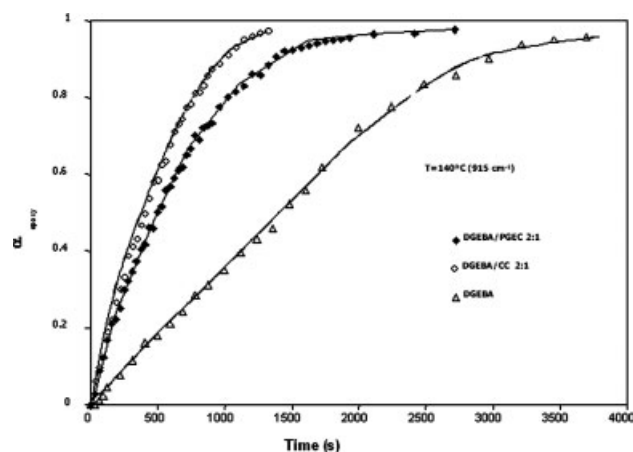
tures at different temperatures. These experimental curves (empty symbols) were used to determine the isoconversional kinetics of both reactive processes. By applying the eq. (5) at different degree of crosslinking we obtained the kinetic parameters collected in

Figure 2 Degree of epoxy conversion versus curing time obtained by FTIR of three different samples: pure DGEBA, DGEBA/PGEC 2 : 1 (mol/mol), and DGEBA/CC 2 : 1 (mol/ mol) mixtures with 1 phr of La(OTf)$_3$ at 140°C.
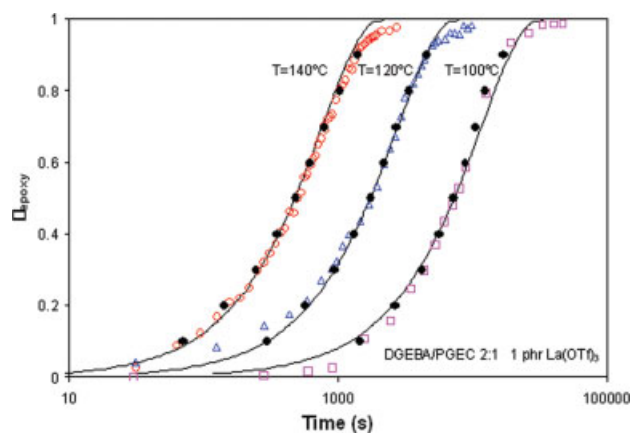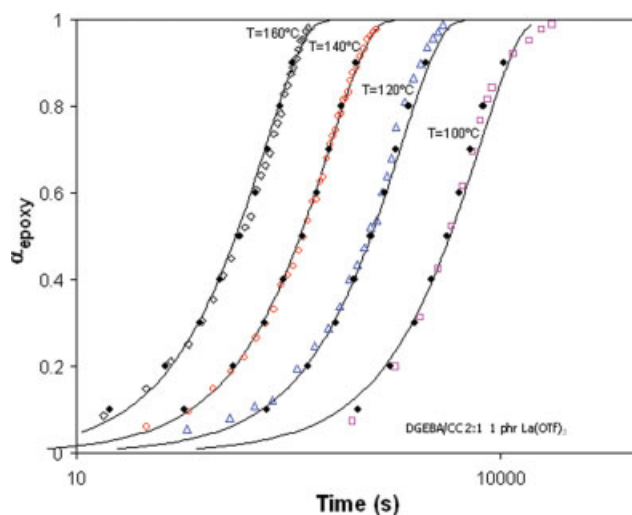

Figure 4 Plot of the experimental and simulated degrees of epoxy conversion versus curing times for a sample DGEBA/ CC 2 : 1 (mol/mol) with 1 phr of lanthanum triflate at different temperatures. Open symbols represent experimental values, filled symbols (●) represent the isoconversional isothermal data obtained by eq. (5), and continuous line represents the curves obtained by using the function R_3 and the average isothermal kinetic parameters collected in Table I. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Kinetic Parameters of the Isothermal Curing at 140°C of DGEBA/PGEC and DGEBA/CC 2 : 1 (mol/mol) Formulations with 1 phr of La(TfO)$_3$ Obtained by FTIR

	Epoxy (DGEBA/PGEC 2 : 1 sample)					Epoxy (DGEBA/CC 2 : 1 sample)				
α	E_a (kJ/mol)	ln[$g(\alpha)/A$] (s)	ln A (s^{-1})	$k_{140°C}\cdot(10^3)$ (s^{-1})	r	E_a (kJ/mol)	ln[$g(\alpha)/A$] (s)	ln A (s^{-1})	$k_{140°C}\cdot(10^3)$ (s^{-1})	r
0.1	97.6	−24.15	20.78	0.48	0.993	90.3	−22.09	18.72	0.51	0.995
0.2	93.9	−22.32	19.68	0.47	0.998	81.9	−19.01	16.37	0.56	0.998
0.3	91.2	−21.08	18.89	0.47	0.999	78.4	−17.45	15.27	0.52	0.999
0.4	88.7	−19.97	18.11	0.44	0.996	77.0	−16.76	14.90	0.54	1.000
0.5	86.5	−19.01	17.44	0.43	0.998	75.4	−15.98	14.40	0.52	1.000
0.6	85.3	−18.43	17.09	0.43	1.000	74.4	−15.45	14.12	0.53	1.000
0.7	83.0	−17.52	16.42	0.43	1.000	73.7	−15.06	13.95	0.54	1.000
0.8	79.8	−16.31	15.43	0.41	1.000	74.0	−14.92	14.04	0.55	1.000
0.9	80.6	−16.22	15.59	0.38	1.000	77.0	−15.57	14.95	0.57	0.999

Table I. In general, the activation energy is higher during the first stages of the curing process and then diminishes slightly. The figures compare the experimental α–t curves with those obtained from the kinetic parameters (full symbols) given in Table I. As can be seen, the curves agree with the experimental data and only little deviations are observed at the beginning and at the end of the curing.

To determine the kinetic model $g(\alpha)$, which describes the reactive processes in the curing, we used the isoconversional parameters and the IKRs. From the parameters ln[$g(\alpha)/A$] in Table I we obtained the pre-exponential factor for the different kinetic models used (Table II). Then, we looked for the IKR, eq. (10), for all the models and processes studied. Table III shows the results and the T_{iso} values determined from the slopes of the IKRs. Although some models have IKR, we considered that for the curing of both mixtures the R_3 model is the most suitable, because it had the best regression. In Table I we can see the pre-exponential factors determined for the model R_3. According to Vyazovkin and Linert,[34] if a T_{iso} in the experi-

mental range is obtained it is an indication that the kinetic model accurately describes the reactive process. In our case, we obtained T_{iso} in the experimental curing range at 121.7°C and 142.6°C for PGEC and CC mixtures, respectively. In Figures 3 and 4 we plotted the α–t curves for the R_3 model (continuous line) and using the average isoconversional kinetic parameters ($E = 87.4$ kJ mol^{-1}, ln $A = 17.71$ s^{-1}; and $E = 78$ kJ mol^{-1}, ln $A = 15.19$ s^{-1}) for PGEC and CC mixtures, respectively (Table I). It can be observed that the R_3 model accurately describes the reactive processes. The data obtained by this methodology are similar to those obtained by isoconversional adjustment and to the experimental values. This indicates that the methodology for determining the complete kinetic triplet E_a, ln A, and $g(\alpha)$ is correct and can be used to study other reactive systems. Models like R_2 or F_1 could be selected but they do not adjust the experimental data so correctly as R_3. Other models with good regressions (Table III) but with T_{iso} values that are substantially different from the experimental temperatures do not give good results.

TABLE II
Algebraic Expressions for $f(\alpha)$ and $g(\alpha)$ for the Kinetic Models Used

Model	$f(\alpha)$	$g(\alpha)$
A_2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
A_3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
$A_{3/2}$	$3/2(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	$[-\ln(1-\alpha)]^{2/3}$
A_4	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
D_1	$1/2(1-\alpha)^{-1}$	α^2
D_2	$-\ln(1-\alpha)$	$(1-\alpha)\ln(1-\alpha)+\alpha$
D_3	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)]^{-1/3}$	$[1-(1-\alpha)^{1/3}]^2$
D_4	$3/2(1-\alpha)^{1/3}[1-(1-\alpha)]^{-1/3}$	$(1-2/3\alpha)(1-\alpha)^{2/3}$
F_1	$(1-\alpha)$	$-\ln(1-\alpha)$
R_2	$2(1-\alpha)^{1/2}$	$[1-(1-\alpha)^{1/2}]$
R_3	$3(1-\alpha)^{2/3}$	$[1-(1-\alpha)^{1/3}]$
Power	$2\alpha^{1/2}$	$\alpha^{1/2}$
$n=2$	$(1-\alpha)^2$	$-1+(1-\alpha)^{-1}$
$n=3$	$(1-\alpha)^3$	$2^{-1}[-1+(1-\alpha)^{-2}]$
$n=1.5, m=0.5$	$\alpha^{0.5}(1-\alpha)^{1.5}$	$[(1-\alpha)\alpha^{-1}]^{-0.5}(-0.5)^{-1}$
$n=1.5$	$(1-\alpha)^{1.5}$	$[1-(1-\alpha)^{-0.5}](0.5)^{-1}$
$n=1.9, m=0.1$	$\alpha^{0.1}(1-\alpha)^{1.9}$	$[(1-\alpha)\alpha^{-1}]^{-0.9}(0.9)^{-1}$

TABLE III
Isokinetic Parameters for Samples DGEBA/PGEC and DGEBA/CC 2 : 1 (mol/mol) with 1 phr of La(TfO)$_3$
from the Compensation Curves for the Different Models Used

Model	Epoxy (DGEBA/PGEC 2 : 1)				Epoxy (DGEBA/CC 2 : 1)			
	a (mol kJ^{-1})	b (min^{-1})	T_{iso} (°C)	r	a (mol kJ^{-1})	B (min^{-1})	T_{iso} (°C)	r
A_2	0.3329	−10.53	88.3	0.9990	0.3151	−8.228	108.7	0.9980
A_3	0.3963	−15.35	30.5	0.9991	0.3832	−13.14	40.9	0.9931
R_2	0.3125	−9.256	111.9	0.9997	0.2952	−7.497	134.5	0.9998
R_3	0.3047	−8.918	121.7	0.9999	0.2894	−7.384	142.6	0.9999
D_1	0.2153	−1.132	285.6	0.9893	0.1858	0.6687	374.3	0.9866
D_2	0.1904	0.5775	451.6	0.9911	0.166	1.7471	451.6	0.9533
D_3	0.1589	2.0953	483.9	0.9924	0.1425	2.3465	571.1	0.8629
D_4	0.1801	0.0678	394.8	0.9919	0.1582	0.9388	487.3	0.9295
F_1	0.2878	−6.194	144.9	0.9998	0.277	−5.177	161.2	0.9971
Power	0.3917	−15.23	34.1	0.9992	0.3737	−12.67	48.8	0.9909
n + m = 2; n = 1.9	0.2475	−2.080	213.0	0.9905	0.2536	−2.761	201.2	0.9614
n + m = 2; n = 1.5	0.3378	−9.380	83.1	0.9998	0.3348	−8.506	86.2	0.9995
n = 2	0.2249	−0.214	261.8	0.9858	0.2334	−1.284	242.3	0.9343
n = 3	0.1472	7.1597	544.1	0.8697	0.1811	3.3666	391.2	0.7154

An alternative way to study the curing process is the nonisothermal curing in the DSC. One of the problems associated with this method is that the overall curing generally provides no kinetic information about the elemental processes. However, these studies can help to establish the curing conditions which should be used in the preparation of the cured material in isothermal conditions, such as is usual in technical applications.

To determine the kinetic model from nonisothermal parameters we used the Coats–Redfern method, eq. (8), to determine E_a and ln A for the different models. Table IV shows the results obtained at a heating rate of 10 K/min for the different formulations tested with both carbonates. We took R_3 as the correct model because it gave a better adjustment. Some other models had good regressions but we did not consider them because E_a is quite different from that obtained isoconversionally (considered to be the true E_a). We also used the reduced master curves procedure of Criado,[25] described elsewhere,[24] to decide the most accurate model, which was confirmed to be R_3.

Table V shows some calorimetric results of the curing process of DGEBA/cyclic carbonate mixtures catalyzed by 1 phr of lanthanum triflate. As can be seen, when the proportion of carbonate increases, the T_g value of the cured material decreases. The materials obtained with CC have higher T_g values than the materials obtained with PGEC, which can be attributed to the plasticizing effect of unreacted PGEC entrapped in the material. The heat released per epoxy equivalent is lower in the formulations with carbonate. For the mixture DGEBA/PGEC 1 : 1 (mol/mol) both T_g and enthalpy released were much lower than for the other formulations, which seems to indicate a lower degree of crosslinking. The apparent activation energies associated to the simultaneous reactive proc-

esses were calculated by an isoconversional integral method [eq. (9)] at a conversion of 0.5 and the pre-exponential factor for the R_3 kinetic model. Both parameters and the Arrhenius equation were then used to calculate the rate constants. The influence of carbonate on the kinetics depends on the monomer used. Thus, with PGEC, the addition of a small proportion of carbonate to DGEBA (entries 1 and 2) increases the rate constant, but successive additions of PGEC (entries 2–4) decrease it. Because PGEC is a solid it can not accelerate the curing process by dilution, but its effect on the rate of curing should be a compromise between the increase of viscosity and the formation of a more active initiating species in which PGEC and the initiator are involved. When CC was added the rate constant increases steadily (entries 1, 5, and 6). In this case it seems that the formation of the more active initiating species predominates over the increase of the viscosity.[7,8]

With the aim to compare the kinetic results obtained by FTIR and DSC we took the calculated nonisothermal DSC constant at 140°C at a conversion of 0.5 for DGEBA/PGEC 2 : 1 and DGEBA/CC 2 : 1 (mol/mol) mixtures, which are 2.76 × 10^{-4} s^{-1} and 4.11 × 10^{-4} s^{-1} respectively. These values are of the same order of magnitude than those obtained by FTIR at a conversion of α = 0.5 (Table I). The differences can be attributed to the fact that in the FTIR the cure is isothermal and is focused in the only evolution of the epoxy band, whereas in DSC the cure is dynamic and the information acquired reflects the global curing process.

The evolution of the shrinkage during curing was followed by TMA, and the normalized degree of shrinkage is plotted against the curing time in Figure 5. As can be seen, the shrinkage occurs in two stages separated by the gelation, at shorter times when CC is present in the mixture. In a previous study[7] we

TABLE IV
Arrhenius Parameters Determined by Coats–Redfern Method for the Samples Studied with 1 phr of La(TfO)₃

Model	DGEBA/PGEC 3:1			DGEBA/PGEC 2:1			DGEBA/PGEC 1:1			DGEBA/CC 3:1			DGEBA/CC 2:1		
	E_a (kJ/mol)	$\ln A$ (s⁻¹)	r	E_a (kJ/mol)	$\ln A$ (s⁻¹)	r	E_a (kJ/mol)	$\ln A$ (s⁻¹)	r	E_a (kJ/mol)	$\ln A$ (s⁻¹)	r	E_a (kJ/mol)	$\ln A$ (s⁻¹)	r
A_2	43.426	6.092	0.9977	41.125	5.288	0.9994	45.897	6.401	0.9995	46.912	1.604	0.9992	68.675	13.222	0.9949
A_3	26.512	1.106	0.9974	24.950	0.532	0.9994	28.083	1.306	0.9995	28.785	6.823	0.9991	43.324	6.033	0.9944
$A_{3/2}$	60.340	10.933	0.9979	57.300	9.877	0.9995	63.712	11.334	0.9995	65.039	11.881	0.9993	94.023	20.265	0.9951
A_4	18.056	−1.529	0.9971	16.862	−1.989	0.9993	19.176	−1.378	0.9994	19.721	−1.140	0.9990	30.649	2.322	0.9937
D_1	142.244	32.574	0.9928	134.579	30.043	0.9885	149.627	33.374	0.9889	153.377	34.787	0.9959	223.389	54.497	0.9996
D_2	164.318	39.216	0.9979	156.336	36.568	0.9958	172.823	40.197	0.9958	176.573	41.643	0.9987	251.407	62.668	0.9999
D_3	175.783	40.163	0.9999	167.269	37.322	0.9995	185.178	41.229	0.9995	189.027	42.745	0.9999	269.789	65.422	0.9986
D_4	163.329	36.541	0.9990	155.114	33.809	0.9973	171.983	37.510	0.9973	175.824	38.995	0.9993	252.737	60.608	0.9997
F_1	94.164	20.382	0.9980	89.650	18.839	0.9995	99.344	20.987	0.9995	101.298	21.787	0.9993	144.730	34.153	0.9954
R_2	79.662	15.389	0.9993	75.474	13.969	0.9979	83.971	15.882	0.9979	85.925	16.651	0.9995	124.934	27.803	0.9994
R_3	84.229	16.342	0.9999	79.936	14.883	0.9994	88.818	16.871	0.9994	90.781	17.651	0.9999	131.203	29.193	0.9985
Power	30.075	1.926	0.9894	28.095	1.221	0.9829	31.747	2.121	0.984	32.741	2.514	0.9942	50.313	7.796	0.9995
$n = 2$	130.297	30.972	0.9737	125.059	29.145	0.9797	137.572	31.839	0.9809	139.384	32.682	0.9881	193.126	47.887	0.9776
$n = 3$	174.594	43.823	0.9391	168.558	41.667	0.9481	184.429	45.009	0.9504	185.959	45.880	0.9712	251.765	64.426	0.9553
$n = 1.5, m = 0.5$	61.491	12.275	0.9708	58.832	11.326	0.9774	65.014	12.706	0.9789	65.955	13.145	0.9869	92.876	20.940	0.9760
$n = 1.5$	111.075	25.355	0.9886	16.211	23.676	0.9926	117.236	26.084	0.9931	119.140	26.909	0.9951	167.494	40.628	0.9878
$n = 1.9, m = 0.1$	116.537	27.239	0.9734	111.815	25.597	0.9794	123.064	28.018	0.9807	124.693	37.780	0.9880	173.073	42.502	0.9774

TABLE V
Calorimetric Data and Isoconversional Kinetic Parameters at Conversion of 0.5 of the Systems Studied Catalyzed by 1 phr of Lanthanum Triflate

Entry	Formulations[a]	Eq. catalyst/eq. epoxide	T_g (°C)	T_{max} (°C)	Δh[b] (kJ/ee)	E_a[c] (kJ/mol)	$\ln A$[d] (s⁻¹)	$k_{140°C} \cdot (10^4)$[e] (s⁻¹)
1	DGEBA	0.0032	127	192	108.7	80.3	14.73	1.76
2	DGEBA/PGEC 3:1	0.0037	68	179	78.4	77.6	14.59	3.35
3	DGEBA/PGEC 2:1	0.0042	58	185	94.3	72.9	13.03	2.76
4	DGEBA/PGEC 1:1	0.0048	25	198	63.8	82.4	15.20	1.52
5	DGEBA/CC 3:1	0.0032	104	178	83.9	67.6	11.30	2.29
6	DGEBA/CC 2:1	0.0035	90	157	78.9	72.5	13.31	4.11

[a] The compositions of the formulations are given in molar ratios.
[b] Enthalpies are expressed by equivalent of epoxy groups.
[c] Values of activation energies were evaluated by isoconversional integral method applied at conversion of 0.5.
[d] The values of pre-exponential factor for kinetic model R_3 in which $g(\alpha) = [1 − (1 − \alpha)^{1/3}]$.
[e] The values of rate constant at 140°C calculated using the Arrhenius equation $\ln k = \ln A − \frac{E}{RT}$.
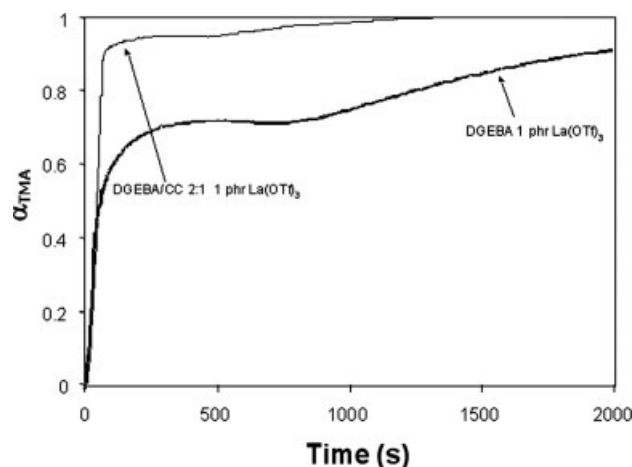
Figure 5 Degree of shrinkage versus the curing time for DGEBA and DGEBA/CC 2 : 1 (mol/mol) mixture initiated by 1 phr of lanthanum triflate obtained by heating in the TMA at 140°C.

proved that at the final of the first stage the material became insoluble. It should be said that the contraction after gelation is the responsible for the apparition of stress and the formation of voids and cracks, which diminish the capability of protection of the coating. Although the initial contraction, whereas the material has mobility, is much higher on adding CC, after gelation the contraction is practically negligible. This behavior is similar to that observed in the copolymerization of DGEBA with lactones,[6,7] carbonates,[5] and SOCs.[35] Similar studies made with PGEC mixtures did not give the desired results because this carbonate did not copolymerize with epoxides in cationic conditions.

CONCLUSIONS

Lanthanum triflate allows to copolymerize DGEBA with a five-membered cyclic carbonate, CC. However, PGEC does not react but remains entrapped in the cured material. The different reactivity of the two carbonates can be related to the different electrophilicity of the carbonyl group.

FTIR makes it possible to analyze the chemical processes that take part in a complex curing processes such as the cationic crosslinking of DGEBA/five-membered cyclic carbonate mixtures.

Isoconversional methods allow the evaluation of the kinetic parameters which vary with the degree of conversion. Using these methods in combination with the IKRs enable us to determine the complete kinetic triplet E_a, A, and $g(\alpha)$ in the isothermal curing. In nonisothermal curing, isoconversional method can be used in combination with Coats–Redfern method.

It has been established that the cationic curing of DGEBA with five-membered cyclic carbonate is similar under isothermal and nonisothermal conditions. In

both cases the curing follows a kinetic model of the surface-controlled reaction type R_3.

Although the shrinkage in the liquid state before gelation is higher when carbonate copolymerizes with DGEBA, the shrinkage after gelation is notably reduced.

References

1. Sadhir, R. K.; Luck, M. R., Eds. Expanding Monomers. Synthesis, Characterization and Applications; CRC Press: Boca Raton, FL, 1992.
2. Takata, T.; Sanda, F.; Ariga, T.; Nemoto, H.; Endo, T. Macromol Rapid Commun 1997, 18, 461.
3. Matsuo, J.; Sanda, F.; Ariga, T.; Endo, T. Macromol Chem Phys 1998, 199, 2489.
4. Sakai, S.; Fujinami, T.; Sakurai, S. J Polym Sci Polym Lett Ed 1973, 11, 631.
5. Cervellera, R.; Ramis, X.; Salla, J. M.; Mantecón, A.; Serra, A. J Polym Sci Part A: Polym Chem 2005, 43, 5799.
6. Mas, C.; Ramis, X.; Salla, J. M.; Mantecón, A.; Serra, A. J Polym Sci Part A: Polym Chem 2003, 41, 2794.
7. Mas, C.; Mantecón, A.; Serra, A.; Ramis, X.; Salla, J. M. J Polym Sci Part A: Polym Chem 2004, 42, 3782.
8. Rokicki, G.; Nguyen, T. X. Macromol Rep A 1995, 32, 265.
9. Rokicki, G.; Nguyen, T. X. Polym Polym Compos 1996, 4, 45.
10. Cervellera, R.; Ramis, X.; Salla, J. M.; Mantecón, A.; Serra, A. J Appl Polym Sci 2006, 102, 2086.
11. Kobayashi, S., Ed. Lanthanides: Chemistry and Use in Organic Synthesis. Topics in Organometallic Chemistry; Springer Verlag: Berlin, 1999.
12. Kihara, N.; Endo, T. J Polym Sci Part A: Polym Chem 1993, 31, 2765.
13. Bialas, N. J.; Kühling, S.; Keul, H.; Höcker, H. Makromol Chem 1990, 191, 1165.
14. Matéjka, L.; Chabanne, P.; Tighzert, L.; Pascault, J. P. J Polym Sci Part A: Polym Chem 1994, 32, 1447.
15. Zhiqiang, Z.; Bangkun, J.; Pingsheng, H. J Appl Polym Sci 2002, 84, 1457.
16. Ramis, X.; Cadenato, A.; Morancho, J. M.; Salla, J. M. Polymer 2003, 44, 2067.
17. Fridman, H. J Polym Sci Part C: Polym Symp 1963, 6, 183.
18. Vyazovkin, S.; Sbirrazzuoli, N. Macromol Chem Phys 1999, 200, 2294.
19. Coats, A. W.; Redfern, J. P. Nature 1964, 201, 68.
20. Vyazovkin, S.; Dollimore, D. J Chem Inf Comput Sci 1996, 36, 42.
21. Kissinger, H. E. Anal Chem 1957, 29, 1702.
22. Flynn, J. H.; Wall, L. A. J Res Natl Bur Stand Sect A 1966, 70, 487.
23. Ozawa, T. Bull Chem Soc Jpn 1965, 38, 1881.
24. Ramis, X.; Salla, J. M.; Cadenato, A.; Morancho, J. M. J Therm Anal Calorimetry 2003, 72, 707.
25. Criado, J. M. Thermochim Acta 1978, 24, 186.
26. Vyazovkin, S.; Linert, W. Int Rev Phys Chem 1995, 14, 355.
27. Salla, J. M.; Ramis, X.; Morancho, J. M.; Cadenato, A. Thermochim Acta 2002, 388, 355.
28. Linert, W. Chem Soc Rev 1989, 18, 477.
29. Vyazovkin, S. Int J Chem Kinet 1996, 28, 95.
30. Vyazovkin, S.; Wight, C. A. Annu Rev Phys Chem 1997, 48, 125.
31. Vyazovkin, S.; Linert, W. J Solid State Chem 1995, 114, 392.
32. Salla, J. M.; Cadenato, A.; Ramis, X.; Morancho, J. M. J Therm Anal Calorimetry 1999, 56, 771.
33. Ivin, J. K.; Saegusa, T., Eds. Ring Opening Polymerization; Elsevier: London, 1984.
34. Vyazovkin, S.; Linert, W. Chem Phys 1995, 193, 109.
35. Cervellera, R.; Ramis, X.; Salla, J. M.; Serra, A.; Mantecón, A. Polymer 2005, 46, 6878.