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Kinetic parameters of a cyanate ester resin catalyzed with different proportions of nonylphenol and cobalt acetylacetonate catalyst

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Abstract

The isothermal cure of a dicyanate ester monomer has been investigated by differential scanning calorimetry (DSC) in the presence of different quantities of a catalyst system formed by nonylphenol (NP) and cobalt (II) acetylacetonate ($Co(AcAc)_2$). Two sets of experiences were studied. Firstly, the NP composition was varied from 0 to 10 per hundred resin (phr) and secondly, the $Co(AcAc)_2$ loadings were changed at 2 phr of NP. It has been observed that the cyanate conversion increases significantly after the first addition of the metal catalyst and, also, at the same time the thermal stability improves. Moreover, the kinetic data have been fitted with a second-order equation respect to the cyanate conversion in the kinetically conversion regime. Also, both the activation energies and the kinetic order respect to the NP and the $Co(AcAc)_2$ have been determined.

Keywords: Cyanate resin; Catalyst; Cure behaviour; Kinetics

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1. Introduction

Cyanate ester resins are among the most important thermosetting polymers developed in the last decades. This family of resins has been receiving attention in the high-technology area of aerospace and electronics due to their excellent properties. The outstanding properties of these matrices are low water absorptivity and outgassing, excellent mechanical properties, dimensional and thermal stability, flame resistance, good adhesive properties, high glass transition temperatures and good chemical resistance, among others [1–5]. Cyanate resins can be processed in a manner similar to epoxies while they are relatively tougher than other thermosets, however the most serious restriction for cyanates to replace epoxies is the high price of cyanate [1].

Cyanate esters undergo thermal polycyclotrimerization to give polycyanurates, that is, sym-triazine rings linked by aryl ether linkages which result in a tightly cross linked structure [1,2,5–9]. Different catalysts systems may be used for the curing to be more efficient in terms of attaining high conversion degrees but minimizing weight losses by volatility. Generally, these catalyst packages comprise a transition metal, carboxylate or chelate, and an alkyl phenol known as co-catalyst used

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to dissolve the former [1,10–21]. It has been observed that the choice of the ratio transition metal/co-catalyst is important to attain a more efficient cure without degradation. In this direction, many papers have investigated the cure behaviour of cyanate resins at a fixed concentration of metal catalyst and co-catalyst [1,10–13,16,18–21] while very scarce literature can be found related to the kinetic study as a function of catalyst concentration [14,15,17].

In this regard, the polycondensation kinetics have been studied by several techniques such as differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy, size exclusion chromatography (SEC), Raman, NMR... [1,10–21]. From all of them, the DSC technique has been widely used since the polycondensation reaction is very exothermic and allows to obtain the complete conversion versus cure time curve. Mostly, in the kinetic-conversion regime, during the first stage of the reaction, the uncatalyzed cyanate conversions have been fitted by a second-order autocatalytic expression that takes into account both the catalyzed and the uncatalyzed reaction [1,2,6,11,15,17]. For systems in which the temperature or the catalyst concentration is high enough to neglect the initial phases of the reaction [1,2,15,16,19,21] a simple *n*th-order kinetic expression can describe the experimental data. Moreover, the activation energies have been found to follow an Arrhenius dependence with small differences between both systems denoting the same reaction path.

In this paper we have monitored the cyanate conversion in the presence of different concentrations of the catalytic system: cobalt (II) acetylacetonate catalyst (from 0 to 1000 ppm) and nonylphenol (from 0 to 10 per hundred resin, phr) by DSC. The aim of this paper is to mainly highlight the kinetic parameters as a function of the catalyst ratio without devoting many details to the chemical mechanisms.

2. Materials and methods

2.1. Materials

A bisphenol A-based cyanate resin, BADCy, (4,4′-dicyanato-2,2′-diphenylpropane) monomer with the trade name AroCy B10 (99.5% purity and a cyanate

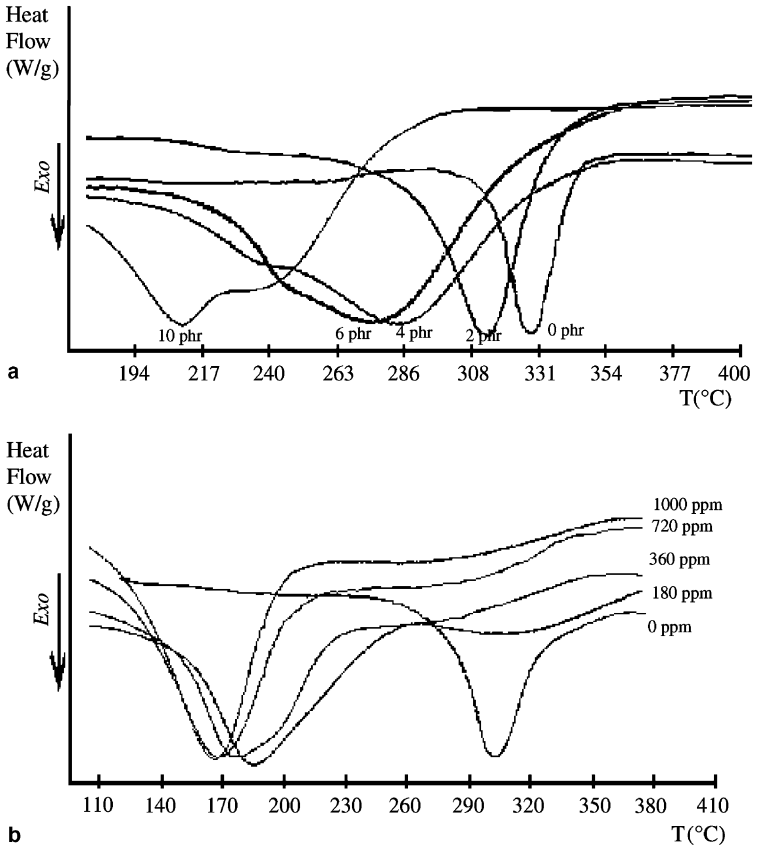

Fig. 1. Dynamic DSC scans of Arocy B10 at 10 °C/min with different catalyst loadings: (a) without $Co(AcAc)_2$ and the nonylphenol content from 0 phr to 10 phr; (b) with 2 phr of nonylphenol and $Co(AcAc)_2$ from 0 ppm to 1000 ppm.

equivalent of 139 g/eq) was gently supplied by Ciba-Geigy. The complex metal cobalt (II) acetylacetonate, $Co(AcAc)_2$, and the co-catalyst nonylphenol, NP, (technical grade) were purchased from Aldrich and used as catalyst system.

2.2. Sample preparation

The dicyanate monomer was blended with the required amount of the catalytic system, $Co(AcAc)_2$ and NP, at different concentrations prior to cure. The required amount of metal catalyst was predissolved in NP at 100 °C with continuous stirring until an homogeneous mixture was obtained and then cooled down to room temperature. The catalytic blend was added to the preselected weight of the molten cyanate resin at 90 °C, stirred for 5 min to obtain an homogeneous mixture and immediately quenched before any reaction could occur. Prior to cure, the catalyzed samples were stored in a desiccator and placed in the refrigerator to avoid moisture absorption.

2.3. Methods

Differential scanning calorimetry, DSC, measurements were performed with a Perkin–Elmer DSC7 supported by a Perkin–Elmer Computer running DSC7 software kit (version 3.1) for data acquisition. The DSC was calibrated with high purity indium and zinc. Eight to ten milligrams of samples were weighed into DSC aluminium pans and sealed with holed aluminium lids. The experiments were conducted under an argon flow of 20 ml min^{-1}. Isothermal curing was carried out at different temperatures ($T_c = 150$–190 °C) with several proportions of the catalytic mixture. All the samples were subjected to a dynamic DSC scan from 30 to 380 °C at 10 °C/min to determine the residual heat of reaction, ΔH_{res}, and the glass transition temperature, T_g, of the cured material. The temperature corresponding to the onset of the transition was taken as the T_g, and the residual heat of reaction was calculated from the exothermic peak by integrating the area between the heat flow curve and the base line. The conversion of each sample under isothermal conditions, assuming a single reaction mechanism, can be calculated by:

$$x = \frac{(\Delta H_{\text{iso}})_t}{\Delta H_{\text{iso}} + \Delta H_{\text{res}}} \qquad (1)$$

where $(\Delta H_{\text{iso}})_t$ is the heat of reaction at a time t calculated from the isothermal mode, and $(\Delta H_{\text{iso}} + \Delta H_{\text{res}})$ is the total heat of reaction obtained from the sum of the total heat from the isothermal mode, ΔH_{iso}, and the residual one. The accuracy of the values $(\Delta H_{\text{iso}} + \Delta H_{\text{res}})$ is ±10 J/g with respect to the polymerization enthalpies, ΔH_{tot}, calculated from dynamic scans at 10 °C/min. Specifically we have obtained $\Delta H_{\text{tot}} = (710 \pm 10)$ J/g for AroCy B10, in agreement with literature data [1,2,6,14–16,21].

A Setaram 92-12 thermobalance was used for *thermogravimetric analysis* (TGA). Uncured samples, either catalyzed or uncatalyzed, of approximately 3 mg in weight, were scanned from 30 to 600 °C at a heating rate of 10 °C/min under argon atmosphere.

3. Results and discussion

Cyanate ester resins polycyclotrimerize upon heating to form a thermostable network. This process is more often carried out in the presence of a catalytic mixture formed by a metal complex and a co-catalyst. In this work we have employed the following catalytic mixture:

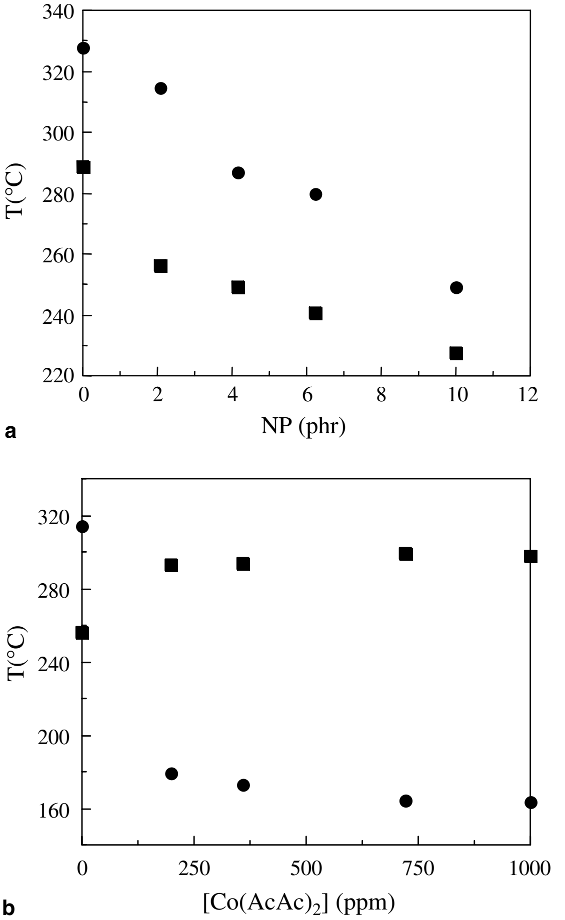

Fig. 2. Plot of the maximum temperature of the exothermic peak (T_p), ●, and of the maximum glass transition temperature ($T_{g\infty}$), ■, as a function of: (a) the nonylphenol content without $Co(AcAc)_2$; and (b) the $Co(AcAc)_2$ content with 2 phr of nonylphenol.

cobalt (II) acetylacetonate and nonylphenol, being the kinetics of the process investigated as a function of the amount of both components.

Then, in order to study the role of the co-catalyst (NP) in the cure behaviour, Fig. 1a shows representative DSC thermograms of the NP-catalyzed samples. These DSC traces exhibit an exotherm peak, broader as the amount of NP increases, which appears to comprise a shoulder preceding the main exotherm. This shoulder has been explained by Barton et al. [22] as a possible heat of reaction caused by the co-catalyst when forming the active catalytic species, or the formation of the imidocarbonate intermediate. The main exothermic peak shifts to lower temperatures as the NP concentration increases.

We have also investigated the influence of the different amounts of metal catalyst, $Co(AcAc)_2$, at 2 phr of co-catalyst, NP, on the cure behaviour. In this respect, Fig. 1b shows dynamic DSC scans of the resin with different $Co(AcAc)_2$ concentrations ranging from 0 to 1000 ppm and 2 phr of NP. General features of these thermograms include a broad exothermic peak above 100 °C with the maximum peak temperature, T_p, slightly moving to lower values as the concentration of metal catalyst increases, which indicates a higher reaction rate more accentuated by the first addition of catalyst. The 100 °C wide shoulder at the high temperature side is related to vitrification and diffusion-controlled cured, as deduced from temperature modulated DSC [23]. These results are also in good agreement with those found by Barton et al. [22] with a copper (II) naphthenate catalyst and by Harismendy et al. [14] with a copper (II) acetylacetonate catalyst. The polymerization enthalpy obtained by integrating the trimerization exotherm, ΔH_r, is independent of the addition of catalyst denoting that any side reaction which occurs during curing of the dicyanate monomer happens with the same extent in both the uncatalyzed and catalyzed systems [24]. The shoulder at high temperatures has been attributed to a competing autocatalytic reaction [25,26]. The magnitude of this shoulder decreases as the metal concentration increases. This fact should indicate that autocatalytic effect is reduced by the addition of a catalyst.

Fig. 2 depicts the plot of the peak temperature of the dynamic scan, T_p, and the glass transition temperature after a dynamic scan, $T_{g\infty}$, or maximum glass transition temperature attained by the cyanate matrix with different NP loadings (part a) and as a function of the metal catalyst added with 2 phr of NP (part b). It can be seen that the addition of NP reduces both T_p and $T_{g\infty}$. For example, the value of T_p decreases from 328 °C to 249 °C indicating that the addition of NP increases the reaction rate while decreases the maximum glass transition temperature from 289 °C to 228 °C due to plastification [1,14,17]. These results are similar to that reported by Lin et al. [17] who studied the cure behaviour of 4-4′-thiodiphenyl cyanate catalyzed with NP but without metal catalyst. As the concentration of $Co(AcAc)_2$ is increased from 0 to 1000 ppm (Fig. 2b) the variation of T_p and $T_{g\infty}$ is the opposite. As seen, T_p decreases from 314 °C to a plateau value of approximately 163 °C, being that decreasing more accentuated by the first addition of metal catalyst, whereas $T_{g\infty}$ goes from 256 °C without metal catalyst to a constant value of 298 °C independent of the amount of metal catalyst present. Similar data have been obtained with 4 phr of NP suggesting that the reaction is less influenced by

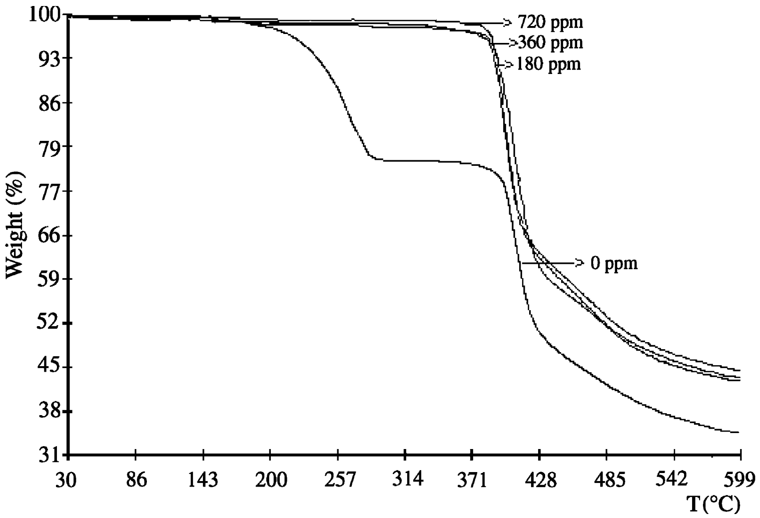

Fig. 3. TGA scans for Arocy B10 with different catalyst loadings.

the NP concentration than by the metal catalyst. These results indicate that the addition of $Co(AcAc)_2$ reduces the T_p, giving a higher reaction rate which also minimizes losses of volatility of the resin, and increases $T_{g\infty}$ of the cured material. Therefore, these experiments strongly recommend the use of a metal catalyst. The volatility of the uncatalyzed or only NP catalyzed samples is very significant. Heating the sample in a sealed pan greatly reduces the loss of material from the system, but it is still possible for the monomer to evaporate from the floor of the pan to condense on the underside of the sealed lid. It can be concluded that the addition of only NP is not as effective as the addition of metal catalyst and 2 phr of NP as co-catalyst is enough to dissolve the metal catalyst.

On the other hand, the effect of metal concentration on the thermal stability of the AroCy B10 was investigated using dynamic TGA experiments in the temperature range of 25–600 °C. The TGA thermograms for AroCy B10 in presence of different quantities of $Co(AcAc)_2$ with 2 phr of NP, and without catalyst mixture are shown in Fig. 3. As can be seen, the thermogram for the cured sample without metal catalyst shows two major stages of weight loss, the first onset with a weight loss of ≈20% at 200 °C and a second one at ≈375 °C. The addition of metal catalyst considerably increases the thermal stability of the resin by eliminating the first weight loss and moving to ≈360 °C the temperature, which is independent of the amount of $Co(AcAc)_2$ added. This fact suggests the presence of unstable products in the network formed without metal catalyst that decomposes at low temperatures.

Differential scanning calorimetry has been reported to be a reliable technique to monitor the overall kinetics of thermosets although we are aware that it detects only the functions liable to react. So, in order to investigate how the amount of co-catalyst (NP) and metal catalyst ($Co(AcAc)_2$) affect the curing reaction, DSC isothermal scans, at temperatures from 150 °C to 190 °C, have been conducted. All of them show bell-shaped exotherms (figures not shown for simplicity) corresponding to the polycyclotrimerization reaction for 4 h curing at constant temperature. These curves allow to evaluate the cyanate conversion as a function of time at every curing temperature (Eq. (1)). The basic assumption made when treating the calorimetric data to obtain reaction kinetics is that the heat of reaction evolved at any time is proportional to the number of moles of reactant consumed.

In this regard, Fig. 4 shows cyanate conversion as a function of curing time, at a cure temperature, T_c, of 180 °C, for different NP loadings from 0 to 10 phr. It is evidenced an increase of the reaction rate and higher final conversion with an increase of NP content. Fig. 5 shows the variation of the extent of reaction versus time for samples catalyzed with 2 phr of NP and different quantities of $Co(AcAc)_2$ (0–1000 ppm) at $T_c = 150$, 160, 170 and 180 °C. It can be observed an increase of the reaction rate and plateau or final conversion with the addition of metal catalyst and curing temperature.

Chemically speaking, the thermal polymerization of cyanate ester is a complex process involving large changes in viscosity and changes of state. For these reasons, the kinetics derived from DSC must be only treated as a phenomenological analysis. A practical problem that requires the knowledge of the overall kinetics is predicting the progress of cure at different temperatures. If an external catalyst is added to the system, the autocatalytic reaction will be suppressed and the overall reaction becomes of *n*-order,

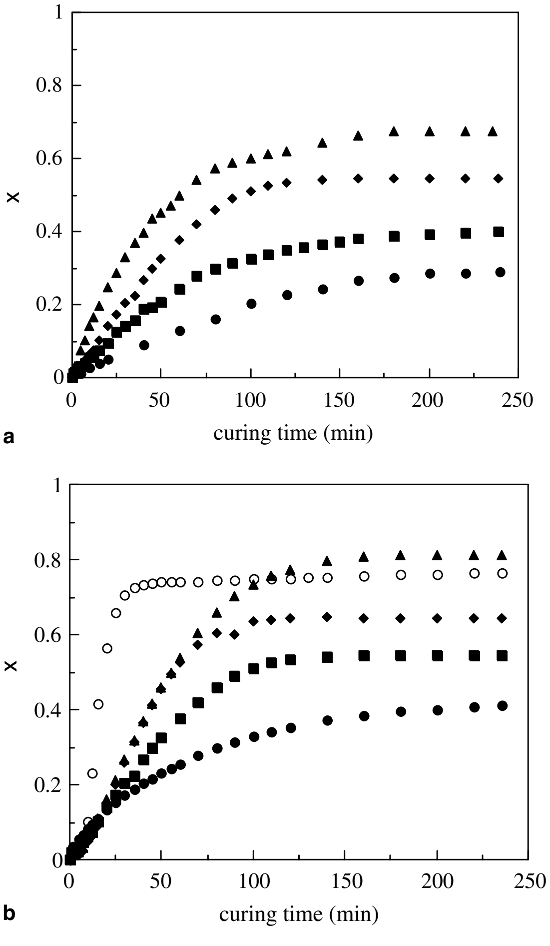

Fig. 4. Cyanate conversion as a function of curing time (a) at different curing temperatures for Arocy B10 with 2 phr nonylphenol, $T_c = 160$ °C (●), 170 °C (■), 180 °C (◆) and 190 °C (▲); (b) at $T_c = 180$ °C for different nonylphenol loadings, 0 phr (●), 2 phr (■), 4.16 phr (◆), 6.24 phr (▲) and 10 phr (○).

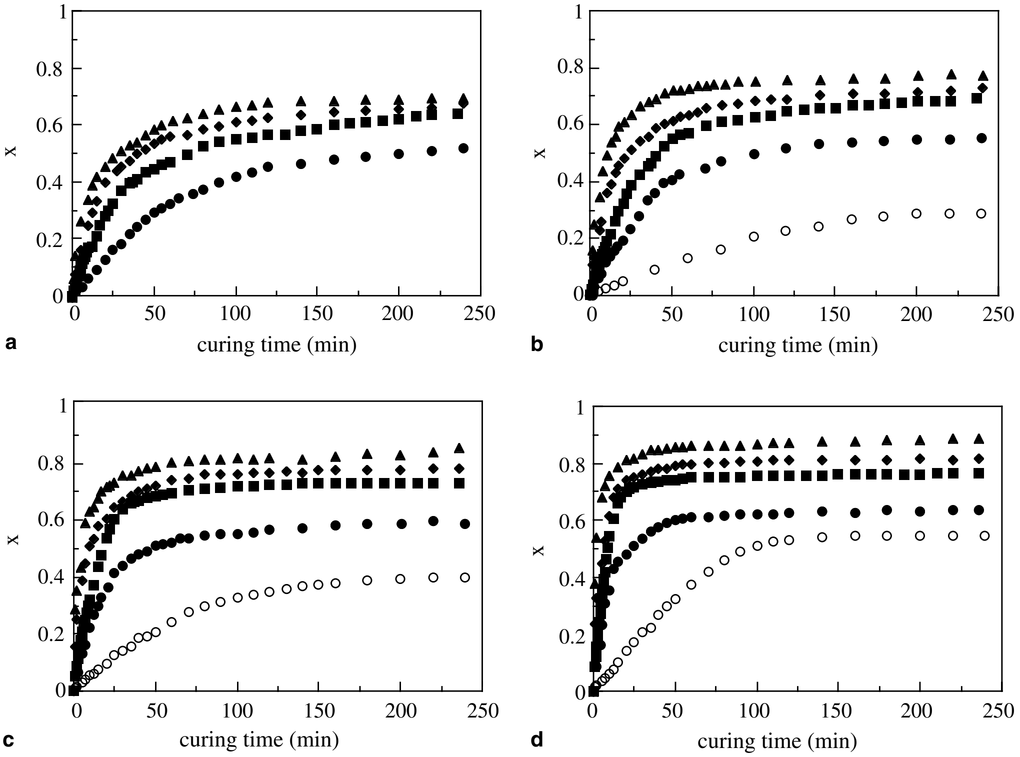

Fig. 5. Cyanate conversion as a function of curing time for different curing temperatures: (a) 150 °C; (b) 160 °C; (c) 170 °C and (d) 180 °C for Arocy B10/2 phr of nonylphenol with different of Co(AcAc)$_2$ loadings, that is, (○) 0 ppm; (●) 180 ppm; (■) 360 ppm; (◆) 720 ppm and (▲) 1000 ppm.

$$\frac{dx}{dt} = k_{app}(1-x)^n \tag{2}$$

where the rate constant k_{app} is, in turn, an apparent rate constant that includes the catalyst concentration. The parameters n and k_{app} were evaluated from the conversion data in the kinetic-controlled regime. Thus, for the different cure temperatures and catalyst concentrations assayed the optimum values of n were in the range of 1.8–2.4. This induces us to take $n = 2$ as a representative value, that is, the kinetics of cyclotrimerization is second-order with respect to the cyanate as measured by the disappearance of the cyano groups, which is in agreement with other authors [2,10,15,16,19,21].

In order to obtain kinetic rate constants, the conversion data plotted in Figs. 4 and 5 were fitted with a second-order rate expression. All the data gave good linear fittings in the kinetic-controlled regime and the analysis of the different parameters was carried out as a function of catalyst concentration and curing temperature.

Conversion data of AroCy B10/2 phr NP at different curing temperatures (Fig. 4a) were fitted with Eq. (2) ($n = 2$) and the k_{app} rate constants obtained. These constants follow the Arrhenius dependence with temperature, given by

$$\ln(k_{app}) = A - \frac{E_a}{R}\frac{1}{T} \tag{3}$$

where A is the pre-exponential factor and E_a the activation energy. The Arrhenius plot gives good correlation coefficient (Fig. 6a) from which ordinate and slope $A = 2.0 \times 10^6\ \text{min}^{-1}$ and $E_a = 106.7$ kJ/mol are obtained, respectively.

Moreover, it has been shown that the catalytic rate constant is proportional to the amount of catalyst added [4,15,17,27], that is $k_{app} = k[\text{NP}]^m$. In order to test this dependence, kinetic constants have been obtained from conversion data as a function of NP concentration at 180 °C (Fig. 4b). Therefore, Fig. 6b depicts the plot of $\ln(k_{app})$ as a function of ln[NP] computed by fitting Eq. (2) with $n = 2$ in the kinetically conversion range. From the slope of this plot we obtain that the order with respect to the nonylphenol concentration is 1.2. Thus, it can be considered that the reaction rate is first-order with respect to the nonylphenol.

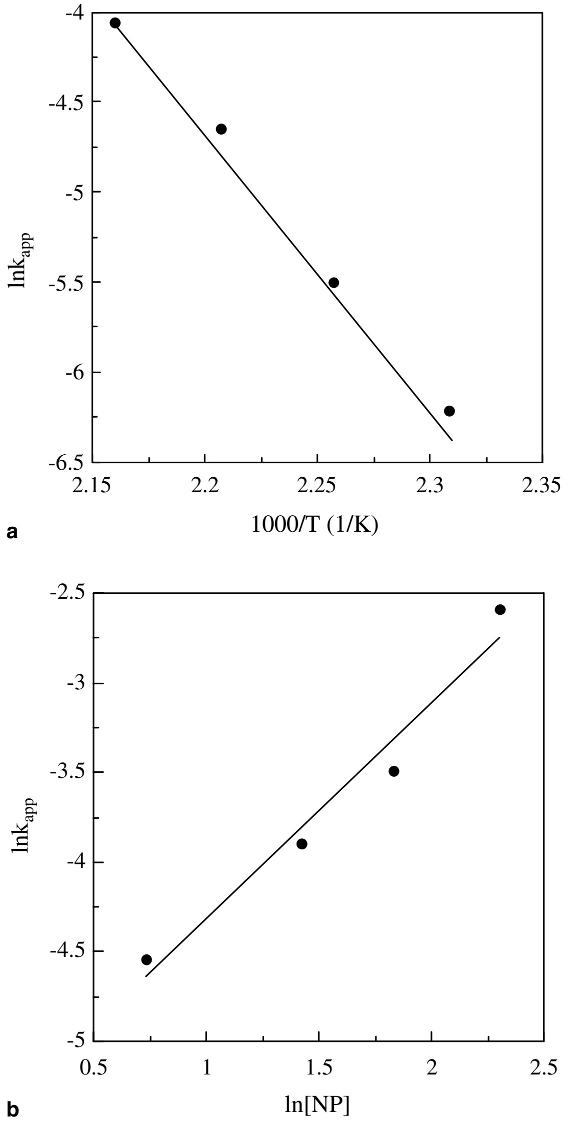

Fig. 6. (a) Arrhenius plot of the apparent rate constant for the system Arocy B10/2 phr NP; (b) plot of lnk against ln[NP] for Arocy B10/NP system cured at 180 °C.

Now, to elucidate the dependence with the curing temperature as a function of Co(AcAc)$_2$ concentration at 2 phr of NP we will analyze the conversion data depicted in Fig. 5. The fit of these data to Eq. (2) (with $n = 2$) gives the rate constants summarized in Table 1. It is observed that the rate constants increase as the curing temperature and the Co(AcAc)$_2$ concentration increase. Computed values of E_a and A (Eq. (3)) are also compiled in Table 1. Values of E_a slightly decrease as the concentration of Co(AcAc)$_2$ increases and are in good agreement with literature data [1,2,16,21]. To ascertain the dependence with the metal catalyst concentration for every curing temperature, we assume a relation such as: $k_{app} = k[\mathrm{Co(AcAc)_2}]^q$. From this expression we obtain that the order with respect to the Co(AcAc)$_2$ is 2 in the range of 160–180 °C curing temperature, also in good agreement with other literature data [15]. Then, it is clear that the increase of metal catalyst and curing temperature also increase the reaction rate while keeping the $T_{g\infty} = 298$ °C except at 1000 ppm.

4. Conclusions

The kinetic parameters of AroCy B10 in presence of different concentrations of the catalytic system Co(AcAc)$_2$/NP have been investigated by DSC at different curing temperatures. The conversion data has been fitted with a second-order kinetic equation in the kinetically controlled conversion regime. From this analysis frequency factors, activation energies and the kinetic order with respect NP and Co(AcAc)$_2$ concentrations have been obtained. It is noticed that the activation energy $E_a = 106.7$ kJ/mol in presence of NP is slightly higher than the value obtained in presence of the metal catalyst (around 92 kJ/mol). The reaction kinetics is first-order with respect the NP concentration and second-order with respect Co(AcAc)$_2$. It is observed that the presence of Co(AcAc)$_2$ is very effective to attain a high conversion degree without altering the final T_g of the polycyanurate network.

Table 1
Kinetic parameters as a function of the cobalt (II) acetylacetonate (Co(AcAc)$_2$) and curing temperature for the cyanate resin in presence of 2 phr of nonylphenol

(Co(AcAc)$_2$) (ppm)	$k_{app\ (150\ °C)}$ (min^{-1})	$k_{app\ (160\ °C)}$ (min^{-1})	$k_{app\ (170\ °C)}$ (min^{-1})	$k_{app\ (180\ °C)}$ (min^{-1})	$10^{-7}\ A$ (min^{-1})	E_a (kJ mol^{-1})
200	0.005	0.012	0.0315	0.079	6.5	99.0
360	0.016	0.0225	0.059	0.120	1.7	92.7
720	0.0235	0.040	0.087	0.151	5.6	89.6
1000	0.027	0.079	0.183	0.366	9.3	87.3

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