Kinetic Study of Polyurethane Synthesis Using Different Catalytic Systems of Fe, Cu, Sn, and Cr

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ABSTRACT: This work presents a comparative study between alternative catalytic systems, metal-β-diketones complexes (iron, copper, chromium, and tin), and the commercial catalyst dibutyltin dilaurate, DBTDL, in the polyurethanes synthesis obtained from isophorone diisocyanate (IPDI) and polyols as polypropyleneglycol/diethyleneglycol and 1,6-hexanodiol polyadipate (polyester A-Mn = 2000 g/mol and polyester B-Mn = 1000 g/mol) reactions. The polyurethanes synthesis was followed by the IPDI consumption in time, verified by infrared spectroscopy (FTIR) through the decrease of free NCO characteristic band at 2300–2200 cm^{-1}. The FTIR data was used to determine the polyurethanes formation kinetic behavior. It was verified that for the reactions with polyethers excess, DBTDL catalyst was more effective when compared to metal-β-diketones complexes, while for the reactions with polyester, A and B, the metal-β-diketones complexes were more effective. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1797–1802, 2010

Key words: polyurethanes; catalysts; kinetics

INTRODUCTION

Polyurethanes are a versatile kind of polymers mainly due to the great raw materials availability and the possibility of variation in the synthesis parameters. The polyurethanes molecular structures can vary from rigid with crosslinking to highly elastomeric, increasing considerably the use of these polymers in different applications.[1–3]

Polyurethanes can be obtained through the polyisocyanate and polyalcohol polycondensation reaction.[1] The isocyanate structure is very important in the NCO group reactivity, which can be increased for a more electrophilic substituent in the diisocianate structure increasing the positive charge in the carbonyl carbon, attached to NCO group. Thus, aliphatic isocyanates are less reactive when compared to aromatic one. In addition to electronic effect the esteric effect is also important, bulky substituents close to the NCO group decrease the reaction rate and influence the catalysts specificity, because they need to approach the reaction site to exercise its catalytic effect.[4]

The polyurethane properties also depend on the molecular structure of the alcohol utilized in the synthesis, influencing properties such as flexibility/hardness and processing characteristics. High functionality polyalcohols promote the formation of crosslink, which gives the final material properties such as stiffness, hardness, and chemical resistance.[5,6]

The urethanes formation can be catalyzed by amines and a wide variety of Lewis acid. In these categories DABCO (1,4-diazobicyclo-[2,2,2]-octane) and DBTDL (dibutiltin (IV) dilaurate) are commercially utilized. Preferably amine catalysts are used in the catalytic reactions between isocyanates and water, while organometallic compounds, in particular tin-based compounds, are more active in the catalytic reaction between isocyanates and alcohols.[7] Acetylacetonates metal compounds are widely used in the urethane forming reaction due to the Lewis acid behavior, coordinating itself a molecule of diisocyanate or alcohol.[8]

The polyurethanes importance in different technology segments has directed to the development of new polymers and processing methods.[9] For this purpose, it is necessary to study the kinetics of these processes in which the properties are directly related to factors such as monomers molar ratio, processing temperature, catalyst amount and solvent, among others.[4,10,11]

One of the most usual methods for the kinetics study of diisocyanates reactions is through infrared
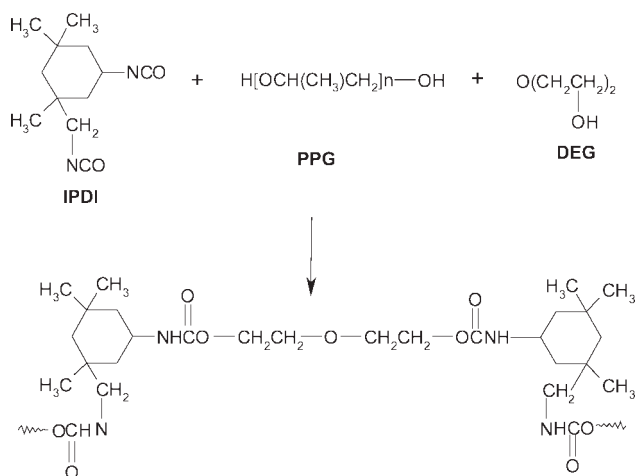
Figure 1 Scheme of reaction between isophorone diisocyanate (IPDI) and polypropyleneglycol/diethyleneglycol.

spectroscopy (FTIR), by determining the residual content of the NCO group, whose characteristics band appears in 2300–2200 cm^{-1}.[12–16]

In this work, we present a comparative study between metal-diketones complexes and DBTDL as catalysts, evaluating the use of these alternative systems, in the polyurethane resins production for paints and adhesives, and also check the kinetics of reactions. The polyurethanes formation kinetic studies, described in the literature, usually deal with reactions not catalyzed or using DBTDL as a catalyst,[1,17,18] so the goal was to study the kinetics in systems with DBTDL and metal β-diketones complexes systems, which can be an alternative to commercial one because they are synthesized through metal salts using techniques widely known in literature.[19–21]

MATERIALS AND METHODS

Materials

The metallic complex β-diketonates (M(acac)x) were obtained from the reaction between a metal salt and acetylacetonate as described in literature.[19–21] The commercial DBTDL was used without further purification.

The polyurethanes syntheses were performed using the catalytic systems acetylacetonates and commercial DBTDL through the one-step method to obtain prepolymers.

The catalytic reactions were performed under N$_2$ atmosphere in a glass reactor with mechanical stirring at 30°C, using acetone as solvent. Reactions were accompanied by FTIR analysis, by the decreasing of the characteristic band of the isocyanate group (NCO).[1]

Synthesis of organometallic complexes

The metallic complex β-diketonates were synthesized using the Schlenk technique under inert atmos-

phere, from the reaction between metals salts [iron (III) nitrate (5 mmol, Vetec), copper (II) sulfate (13 mmol, Dinâmica), chromium (III) chloride (10 mmol, Vetec), tin (II) chloride (24 mmol, Merck)] and acetylacetone (Vetec).[19–21] The characterization of the catalytic systems was conducted based on the FTIR spectrum of the precursor, acetylacetone, according to the literature.[22,23]

Catalytic reactions

The prepolymers were obtained by the reaction between the isophorone diisocyanate (IPDI) and the mixture of polyols polypropyleneglycol-PPG (M_n = 1300 g/mol)/diethyleneglycol-DEG (M_n = 106.12 g/mol), Figure 1, and 1,6-hexanodiol polyadipate (polyester A-Mn = 2000 g/mol and polyester B-Mn = 1000 g/mol), Figure 2.

In the reaction between the IPDI (22 mmol, Degussa) and the mixing of polyether PPG (90 mmol, The Dow Chemical Company) and DEG (112 mmol, Vetec), the proportion of NCO/OH = 1/10 was used. The catalytic systems were DBTDL, Fe(acac)$_3$, and Cu(acac)$_2$ in the proportion of ∼ 0.1% by weight (5 mmol of catalyst).

Reactions between IPDI (112.0 mmol, Degussa) and polyester 1,6-hexanodiol polyadipate (polyester A and polyester B) (112.0 mmol, Degussa) were conducted using equivalent diisocyanate and polyol content, so NCO/OH ratio equal to 1, with the commercial catalyst DBTDL and acetylacetonates systems: Fe(acac)$_3$, Cu(acac)$_2$, Cr(acac)$_3$, and Sn(acac)$_2$ in ∼ 0.1% by weight (5 mmol of catalyst).

Characterization

The products of catalytic reactions were characterized by infrared spectroscopy using a Perkin Elmer Instruments Spectrum One FTIR Spectrometer, in
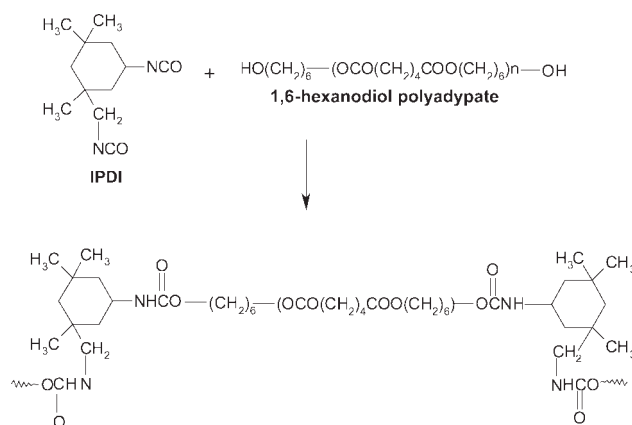

Figure 2 Scheme of reaction between isophorone diisocyanate (IPDI) and 1,6-hexanodiol polyadipate (polyesters A and B).
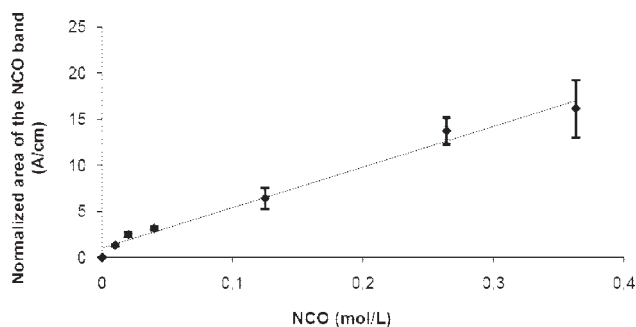
Figure 3 Calibration curve of normalized area of the NCO group versus NCO concentration.

the range of 4000 to 400 cm^{-1}. The samples were analyzed with the attenuated total reflectance (ATR) accessory.

The products molar mass were determined by gel permeation chromatography in a chromatograph equipped with an isocratic pump-1515 (eluent: toluene, flow: 1 mL/min) detector of refraction index-2414 of Waters Instruments with Styragel column. The analysis was conducted using polymeric solution in tetrahydrofuran.

Kinetic study

The kinetic reactions were evaluated determining the residual content of NCO group by FTIR as mentioned earlier. It is possible to determinate the NCO concentration by the normalized area of the characteristic band of the NCO group (2300–2200 cm^{-1}) verifying the decrease of band in time, based on the Lambert-Beer Law.[1,24]

The kinetic data were determined by the approximation referenced by Li et al.,[1] eqs. (1)–(3).

$$n = 1, \quad \ln(1 - p) = -k_0 t + C \quad (1)$$

$$n = 2, \quad \frac{1}{1 - p} = k_0 t + C \quad (2)$$

$$n = 3, \quad \frac{1}{(1 - p)^2} = k_0 t + C \quad (3)$$

where p is the isocyanate conversion, k_0 is the kinetic constant, t is the time value, and C is the NCO concentration.
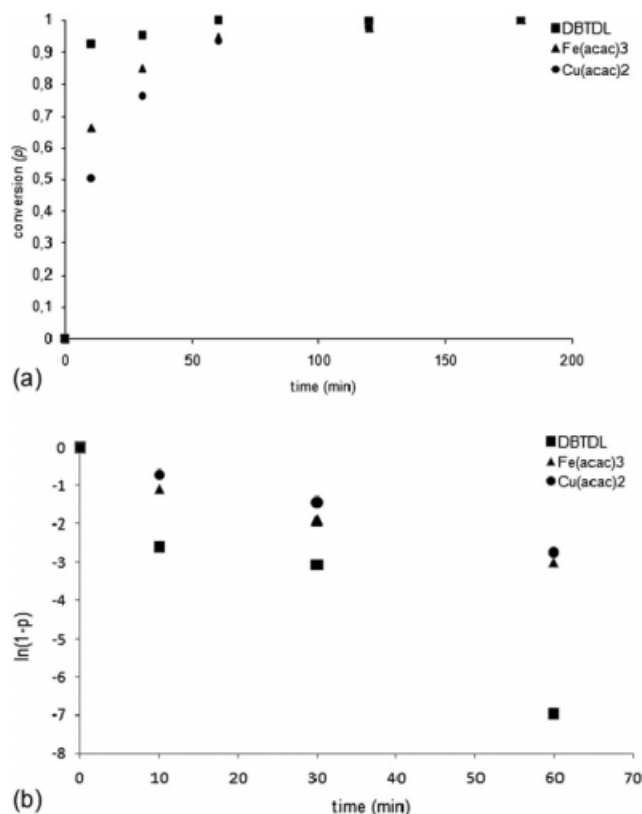

Figure 4 Kinetics data of reactions between IPDI and PPG/DEG: (a) Conversion versus time (minutes), (b) Curve ln $(1 - p)$ versus time (minutes).

Applying the conversion data in the equations above, it is possible to find the adequate kinetic model and determine the kinetic constant.[1]

The accuracy of the used method was confirmed by a calibration curve that demonstrated the linear relationship between NCO concentration and absorption band.[25] This curve was prepared using IPDI solutions with known concentration (Figure 3).

RESULTS AND DISCUSSION

Reactions between IPDI and PPG/DEG were conducted in a rate of NCO/OH of 1/10, with an OH excess, so a pseudo-first order reaction is expected, due to the speed of the reaction which depends only on the limiting reagent, in this case diisocyanate. With the conversion data of NCO group it will be possible to determine the kinetic model [eqs. (1)–(3)] of the reaction and calculate the kinetic constants.

TABLE I
Obtained Data in Reactions with Polyethers

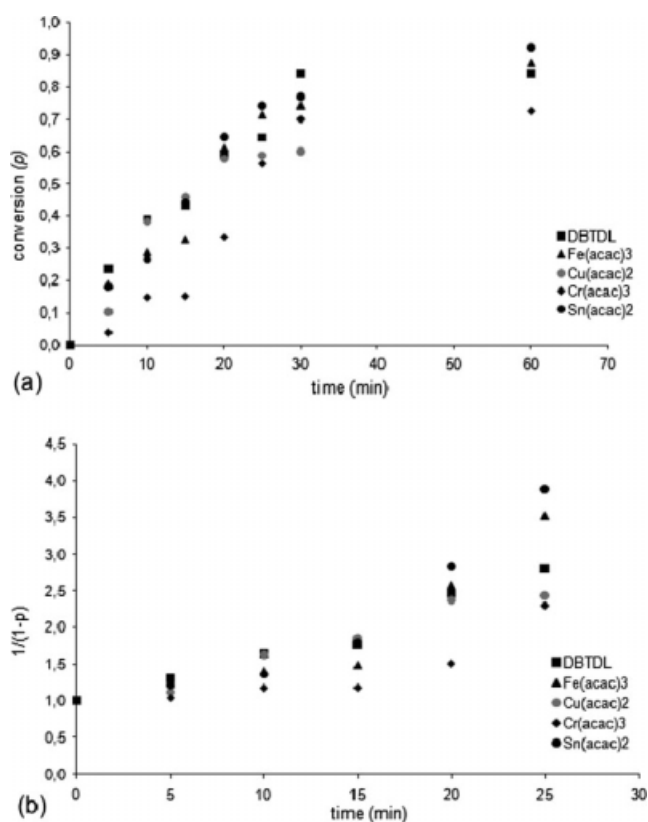| Polyol	Catalyst	K (min^{-1})	M_n (g/mol)	M_w (g/mol)	M_w/M_n	NCO/OH
PPG/DEG	DBTDL	0.11	1,415	1,568	1.10	1/10
	Fe(acac)$_3$	0.05	1,422	1,549	1.08	
	Cu(acac)$_2$	0.05	1,289	1,525	1.18	

Figure 5 Kinetics data of reactions between IPDI and polyester A: (a) Conversion versus time (minutes), (b) Curve $1/(1-p)$ versus time (minutes).

Figure 4 shows the diisocyanate conversion and kinetic determination graphics. The kinetic graphic and the kinetic constants confirm the first-order reaction (Table I) showing a greater reaction speed when DBTDL ($k = 11 \times 10^{-2}$) was used as a catalyst compared to Fe and Cu acetylacetonates ($k = 5 \times 10^{-2}$ min^{-1} for both). This result is in agreement with the literature,[26] DBTDL is known as being more effective in the polyurethane formation reaction and Fe(acac)$_3$ is more effective in synthesis of mono and di-urethanes compounds.[27,28]

Reactions conducted between IPDI and polyester A were performed in NCO/OH equivalent ratio.

According to the literature, a second-order kinetic is expected for these reactions, because reagents equally compete.[1,12,29] As described previously, based on the conversion data of the NCO group, the kinetics of this reaction was determined (Fig. 5). Two distinct behaviors were observed for these reactions, until 30 min the kinetic behavior was of second order, as expected, and after this interval a deviation of this kinetic order was verified. Similar deviations were reported in reactions with hexamethylene diisocyanate, diphenylmethane diisocyanate, and toluene diisocyanate.[30,31] These deviations were described in terms of reaction characteristics, as the difference in reactivity between the two NCO groups presents in the same molecule and the occurrence of parallel reactions between an urethane group formed and a NCO group not reacted. It was accepted that the difference of reactivity between the asymmetric NCO groups is a possibility for the observed deviations, as IPDI has a NCO group bonded directly to the aliphatic cycle and another that is bonded to a methyl group of this cycle. After 30 min of reaction it was not possible to determine the kinetics order. The kinetic constants (Table II) for these reactions were determined until this interval of (second-order behavior) time in which a great content of NCO was reacted. The kinetic constants for Fe(acac)$_3$, DBTDL, Sn(acac)$_2$, and Cu(acac)$_2$ were similar (6 to 9×10^{-2} mol^{-1} min^{-1}), showing that other catalysts could be effective in the polyurethanes formation reactions using an equivalent ratio of NCO/OH.

Reactions between IPDI and polyester B were also conducted on equivalent rate of NCO/OH and it was observed the 2nd order of reaction until thirty minutes and the same deviations after this interval. The kinetic data are presented in Figure 6 and demonstrate similar behavior to the group of reactions carried with polyester A.

The molecular mass obtained for prepolymers in reactions with PPG/DEG polyols (Table I) are relatively similar ($M_w \sim 1550$ g/mol). The reactions were performed keeping all parameters constant,

TABLE II
Obtained Data in Reactions with Polyesters

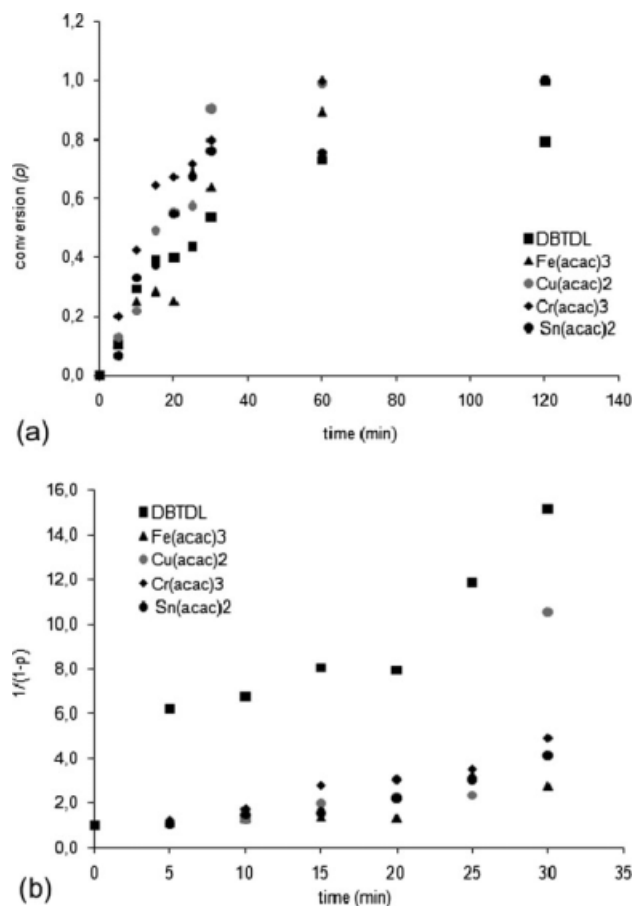| Polyol	Catalyst	K (mol^{-1} min^{-1})	M_n (g/mol)	M_w (g/mol)	M_w/M_n	NCO/OH
Polyester A	DBTDL	0.07	9,229	13,058	1.41	1/1
	Fe(acac)$_3$	0.09	6,491	10,010	1.54	
	Cu(acac)$_2$	0.06	3,984	6,956	1.74	
	Cr(acac)$_3$	0.04	8,089	10,284	1.27	
	Sn(acac)$_2$	0.07	4,841	7,740	1.59	
Polyester B	DBTDL	0.05	3,203	3,809	1.18	1/1
	Fe(acac)$_3$	0.05	5,193	6,923	1.33	
	Cu(acac)$_2$	0.05	5,349	6,100	1.14	
	Cr(acac)$_3$	0.10	8,680	9,312	1.07	
	Sn(acac)$_2$	0.06	4,353	6,276	1.44	

Figure 6 Kinetics data of reactions between IPDI and polyester B: (a) Conversion versus time (minutes), (b) Curve $1/(1-p)$ versus time (minutes).

varying only the catalytic system; this behavior indicates that there was no influence of the catalyst on the molecular mass of the obtained prepolymer.

For the reactions with polyester A and B (Table II), a variation in the molecular mass was verified according to the catalyst (e.g., Polyester A M_w $\sim$ 13,000–7700 g/mol). The molecular mass of these products were relatively higher than those obtained in the reaction between IPDI and PPG/DEG. This behavior shows that the alcohol carbon chain and the catalyst nature have influence on the molecular mass.

The synthesized prepolymers were characterized by IR spectroscopy and the attributions of the bands were compared with the values of the characteristics bands for the existing groups in the molecule, according to literature.[23,32] Figure 7 shows the typical IR spectrum of the polyurethanes prepolymers formed with the PPG and 1,6-hexanodiol polyadipate polyols.

In the prepolymer spectrum obtained using polyether PPG, a band is observed at 1090 cm^{-1}, which is attributed to the C—O—C group stretch characteristic of ether [Fig. 7(a)]. This band is not observed in the spectrum (b), which is derived from a polyester prepolymer. In Figure 7(a,b), bands are observed at 2271 and 2265 cm^{-1}, respectively, for the stretch of the NCO group. Comparing the two spectra it appears that the band of the figure (b) is notably bigger than the figure (a), which is in agreement with the NCO/OH ratios used in the synthesis of prepolymers. An excess of PPG was used in the reaction with IPDI, so it is expected the total consumption of the NCO content, in the reaction with
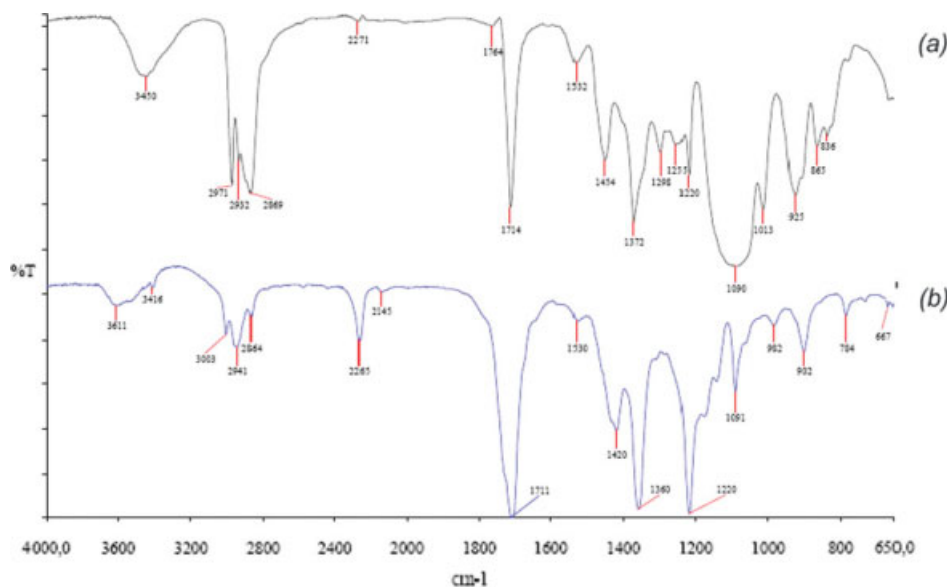

Figure 7 Spectrum of FTIR of prepolymers PU synthesized with (a) polyether PPG, (b) polyester 1,6-hexanodiol polyadipate (ATR). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

1,6-hexanodiol polyadipates an equivalent ratio of NCO and OH was used, once the presence of this band is justified by a residual content of NCO not reacted with polyol.

CONCLUSIONS

Among the metallic complex evaluated in the catalytic reactions of prepolymers formation, two situations were observed: in the reaction with polyol excess the more effective system was the commercial DBTDL and the iron (III) acetylacetonate system, while in the reaction with equivalent content of isocyanate and polyol better results were obtained using DBTDL, tin (II) acetylacetonate, and chromium (III) acetylacetonate. The kinetic study showed that the reactions carried out with a polyol excess have kinetics of pseudo-first order as expected, since only one of the reagents governs the reaction, the limiting reagent.

Moreover, reactions with NCO and OH equivalent content presented kinetics of second order until the first 30 min of reaction, and after this period a deviation of this kinetics order was shown. Through this study it was found that it is possible to use acetylacetonates systems in the polyurethane synthesis, as an alternative to commercial system.

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