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Polymer 46 (2005) 15–25

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Hydrogenated hydroxy-functionalized polyisoprene (H-HTPI) and isocyanurate of isophorone diisocyanates (I-IPDI): reaction kinetics study using FTIR spectroscopy

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Received 20 May 2004; received in revised form 27 September 2004; accepted 27 October 2004
Available online 18 November 2004

Abstract

The reaction between a hydrogenated hydroxyl-functionalized polyisoprene (H-HTPI) and isophorone diisocyanate isocyanurate (I-IPDI) is followed by using direct FTIR spectroscopy. The reaction kinetics is studied using a simple model taking into consideration the I-IPDI structure. The rates of individual isocyanate groups are described by a second order equation. Influence of dibutyltin dilaurate (DBTL) concentration and temperature on selectivity, defined as the ratio between the rate constant of secondary isocyanate group and the rate constant of the primary isocyanate group, is investigated. It is observed that selectivity decreases when temperature or DBTL concentration increases. Eyring parameters are determined for the catalyzed [$\Delta H^{*}=77/35$ (kJ mol^{-1}), $\Delta S^{*}=12/-100$ (J mol^{-1} K^{-1})] and uncatalyzed reactions [$\Delta H^{*}=48/43$ (kJ mol^{-1}), $\Delta S^{*}=-179/-167$ (J mol^{-1} K^{-1})] primary and secondary isocyanate groups being differentiated.

Keywords: Polyurethane; Isocyanurate; Reaction kinetic

1. Introduction

Radically prepared low molecular weight hydroxyl-capped polybutadiene (HTPB) and polyisoprene (HTPI) lead, after catalytic hydrogenation, to inert polyols, having a hydroxyl functionality greater than 2, which can be used to prepare high molecular weight polyurethanes [1–3]. The inertness of these soft segments contributes to enhance the solvent resistance, hydrolytic, oxidative, thermal and mechanical properties of the resulting segmented polyurethanes compared to the corresponding unsaturated homologues [1,4–7]. This excellent combination of properties renders these materials of interest for car manufacture and electrical insulation applications [2].

In this work, hydrogenated hydroxy-terminated polyisoprene (H-HTPI)-based polyurethane networks were synthesized by reacting H-HTPI with isophorone diisocyanate isocyanurate (I-IPDI) in stoechiometric conditions. As other isocyanurates, I-IPDI is a mixture of polyisocyanates whose main component is the triisocyanate isocyanurate (at least 70%) [8,9]. According to the functionalities of the reactants, PU networks will be obtained. The kinetic study of the reaction, carried out in bulk, by using FTIR spectroscopy in situ, will therefore be complex. Moreover, likely to IPDI, I-IPDI has two main different isocyanate groups (primary and secondary) which should also have distinct reactivities. A two order kinetic law taking into consideration the I-IPDI structure was therefore used to follow the reaction mechanism. Influence of reaction temperature and catalyst concentration was also investigated. The kinetic constants, isocyanate group selectivity, activation energies and enthalpies were estimated.

2. Experimental

2.1. Materials

H-HTPI (EPOL® Atofina, $\bar{M}n = 2700$, $I_{OH}=0.92$ mequiv

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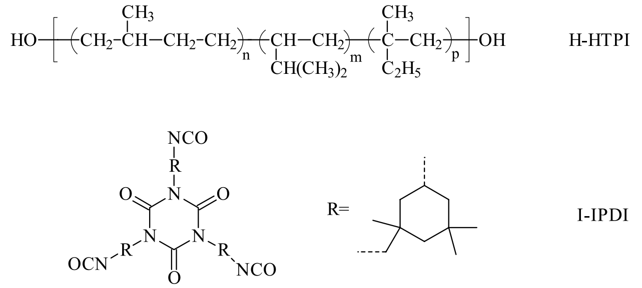
doi:10.1016/j.polymer.2004.10.080



Scheme 1. Chemical structure representation of hydrogenated hydroxyl-functionalized poly(isoprene) (H-HTPI) and isocyanurate of isophorone diisocyanate (I-IPDI).

g^{-1}, $\bar{f}_{wOH} = 2.34$) and I-IPDI (IPDI isocyanurate) (VESTANAT® 1890/100, Degussa-Hüls, $\bar{M}n = 825$, 16% NCO (w/w), $\bar{f}_{wNCO} = 3.43$) were kindly supplied (Scheme 1). Dibutyltin dilaurate (DBTL), cyclohexylisocyanate, *n*-heptanol (Aldrich) and freshly distilled tetrahydrofuran (THF) were used.

2.2. FTIR spectroscopy measurements

Thirty grams of H-HTPI were introduced in a 250 ml round bottom flask equipped with a mechanical stirrer (300 rpm), a switchable inlet for nitrogen and a vacuum connector. H-HTPI was degassed for 1 h under vacuum (10^{-2} mmHg) at room temperature and then put under nitrogen atmosphere. DBTL was added in the desired amount and 7.3 g of isocyanurate (stoichiometry), previously dissolved in THF (50% w/w). After 2 min stirring an aliquot of the mixture was spread out on an IRTRAN window placed in a thermo-controlled chamber pre-heated at the desired temperature in the FTIR spectrometer. The fast evaporation of THF present in the mixture was followed by FTIR and a 2 min drying time (for which no more THF bands were observed) was adopted. By this way a thin film was obtained and its thickness was considered constant along time. Moreover the thickness of the film was so as to have a starting spectra with a –NCO absorption band < 1.0 so as to be in the linear part of the Beer–Lambert relationship between –NCO concentration and the observed absorptions. This method was already successfully used by other authors to follow macrodiol-isocyanate reaction kinetics [10–15]. IR spectroscopies were carried out using a Perkin Elmer spectrum 2000 FTIR in transmission mode. A calibration curve prepared from standard samples, which contain known amounts of I-IPDI and H-HTPI in THF, is shown Fig. 1. The linear relationship between –NCO concentration and its absorption band at 2260 cm^{-1} is confirmed as well as the accuracy of the method used. Moreover, FTIR was chosen because the –NCO back-titration method with HCl [10], although giving the same results (not shown), is limited by the gelation process (∼56% conversion) since both starting materials have functionalities higher than 2. Lastly, the studied system is involved in coating application, thus FTIR was obviously considered as the most adequate technique to follow the kinetic reaction in the film.

Thus, knowing that a complete disappearance of the –NCO band is observed after 7 days, i.e. $(A_{2260})_{\infty} = 0$, the disappearance of isocyanate band at 2260 cm^{-1} allowed us to determine the conversion, $C(t)$:

$$C(t) = 1 - \frac{(A_{2260})_t}{(A_{2260})_0} \qquad (1)$$

with $(A_{2260})_t$, absorbance at time t; $(A_{2260})_0$, absorbance at $t = 0$.

The absorbance at $t = 0$ ($(A_{2260})_0$) is determined by extrapolation of the first data points as this value cannot be

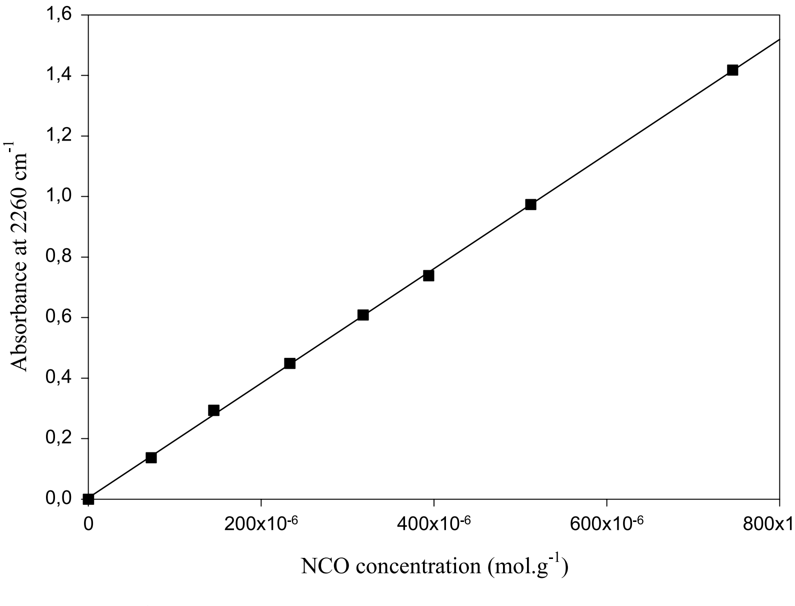


Fig. 1. Absorbance at 2260 cm^{-1} versus NCO concentration calibration curve in THF at room temperature using a 25 μm cell.

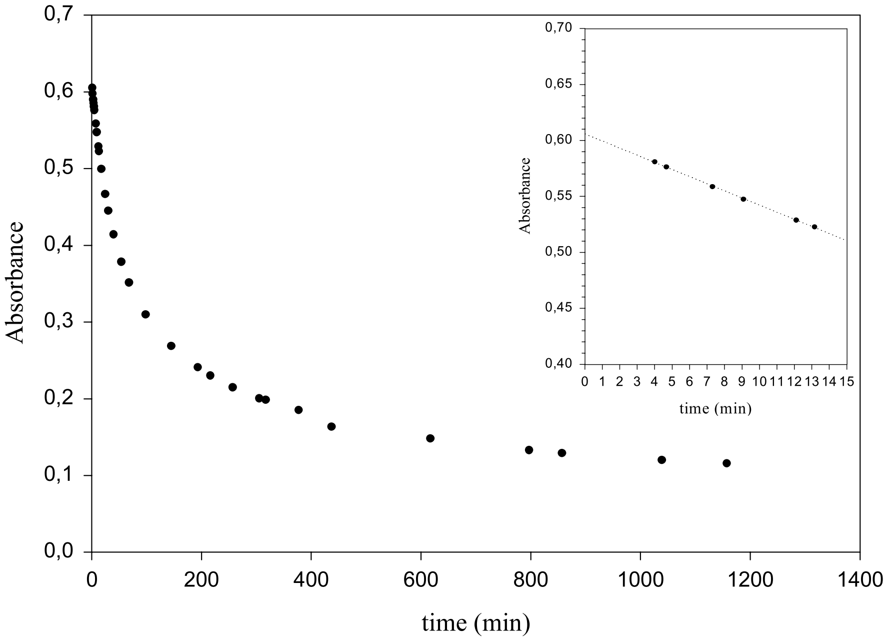
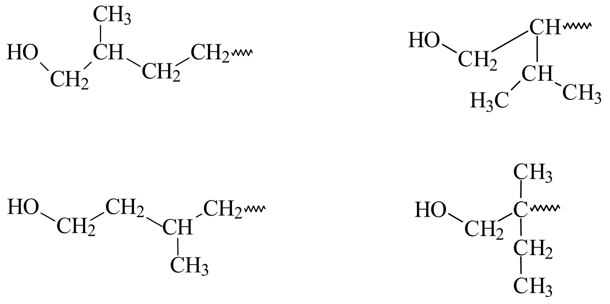


Fig. 2. Absorbance at 2260 cm^{-1} versus time for the stoichiometric reaction of H-HTPI and I-IPDI at 25 °C with DBTL as catalyst (1.86×10^{-3} mol l^{-1}). Determination of $(A_{2260})_0$ by extrapolation of the first points (15 min), $(A_{2260})_0=0.605$.

directly measured due to the applied mixing and drying times (Fig. 2).

2.3. Methodology

H-HTPI is first reacted with cyclohexylisocyanate to check the overall reactivity of the hydroxyl groups. By analogy with HTPB, it was assumed that a discontinuity in the second order plot (first order with respect to each of the reactant) would be attributed to a different reactivity of the primary alcohols present on H-HTPI chain ends and inversely [10,16]. Similarly, I-IPDI is first reacted with *n*-heptanol to check –NCO groups reactivities. According to these preliminary data a simple kinetic model was elaborated and the resolution of the differential equation was achieved by numerical resolution using the well-known Runge–Kutta mathematical method [17]. Thus, fitting of the calculated curve with the experimental data allows the determination of the kinetic constants. Influence of DBTL concentration and temperature on the kinetics reaction is studied.



Scheme 2. Primary alcohol groups present on H-HTPI chains according to previous NMR study [22].

2.4. Thermodynamic parameters

Thermodynamic parameters are determined using Arrhenius law (Eq. (3)) and Eyring relationship (Eq. (4)) is used to determine activation enthalpy (ΔH^*) and entropy (ΔS^*) by plotting

$$\ln\frac{k}{T}=f\left(\frac{1}{T}\right) \tag{2}$$

$$k=A\,\mathrm{e}^{-E_a/RT} \tag{3}$$

$$\ln\frac{k}{T}=\ln\frac{R}{Nh}+\frac{\Delta S*}{R}-\frac{\Delta H*}{RT} \tag{4}$$

where T is the temperature, $R=8.314$ J mol^{-1} K^{-1} the universal gas constant, A the frequency factor, E_a the activation energy, k the kinetic constant, $N=6.02\times10^{23}$ the Avogadro's constant and $h=6.62\times10^{-34}$ J s the Planck's constant.

3. Results and discussion

Reaction mechanism between hydrocarbon polyols and aromatic or aliphatic diisocyanates commonly follow second order kinetics [11,18–21]. The polyol used in this study, H-HTPI, is obtained by a radical route and subsequent hydrogenation [2]. H-HTPI precursor structure contains (88/6/6%) of 1,4-, 1,2- and 3,4-isoprene units,

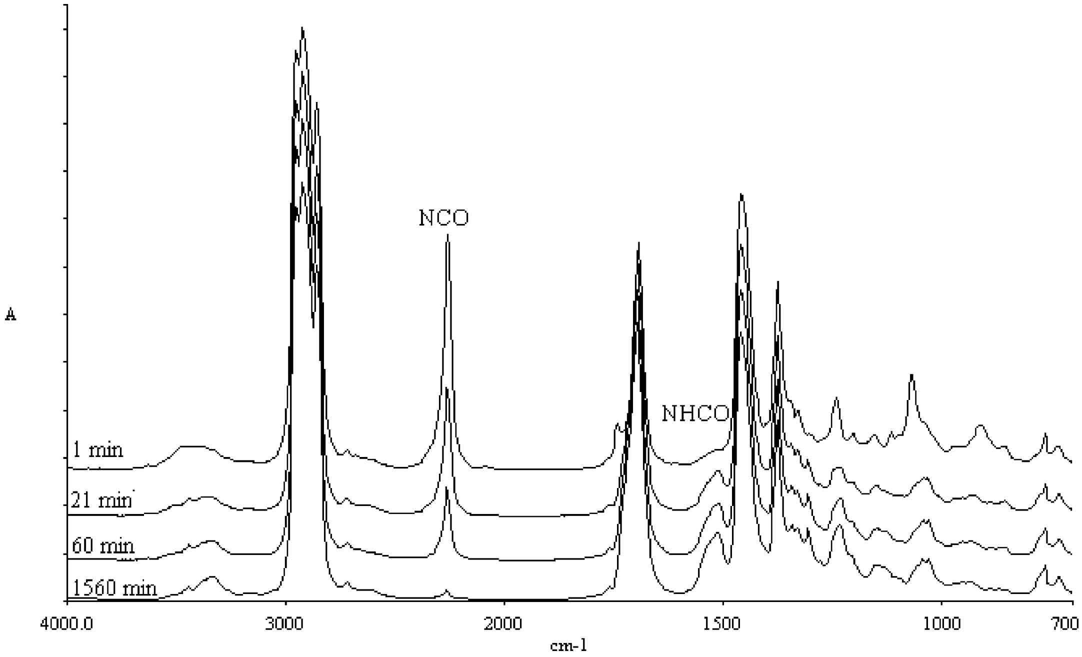


Fig. 3. FTIR spectra versus time of H-HTPI and cyclohexylisocyanate (stoichiometry) reaction in bulk at 25 °C with DBTL as catalyst (7.88×10^{-3} mol l^{-1}).

respectively [22], and leads after hydrogenation to a colorless oligomer with primary alcohol groups at their chain ends [3]. According to NMR studies, authors have only evidenced the presence of primary alcohols correlated to the different hydrogenated isoprene units (Scheme 2).

The overall reactivity of the different alcoholic groups was evaluated by following the disappearance of isocyanate functions for the reaction between H-HTPI and cyclohexylisocyanate ($[NCO]=[OH]=0.35$ mol l^{-1}), using DBTL as a catalyst (2.68×10^{-4} mol l^{-1}) at 25 °C by FTIR (Fig. 3). The conversion curve (Fig. 4) follows a classical second order rate law (Fig. 5), with an apparent rate constant $k=3.1\times10^{-2}$ l mol^{-1} min^{-1}.

Thus, the different H-HTPI hydroxyl functions can be considered as equireactive and independent. Similar results were observed when reacting hydroxy telechelic polybutadiene (HTPB) with different isocyanates [10,16].

An IPDI-based isocyanurate (I-IPDI) was chosen in this study because of technological reasons, leading to a chemically inert, light-stable, PU network with good mechanical properties.

Among diisocyanates, IPDI has the particularity to

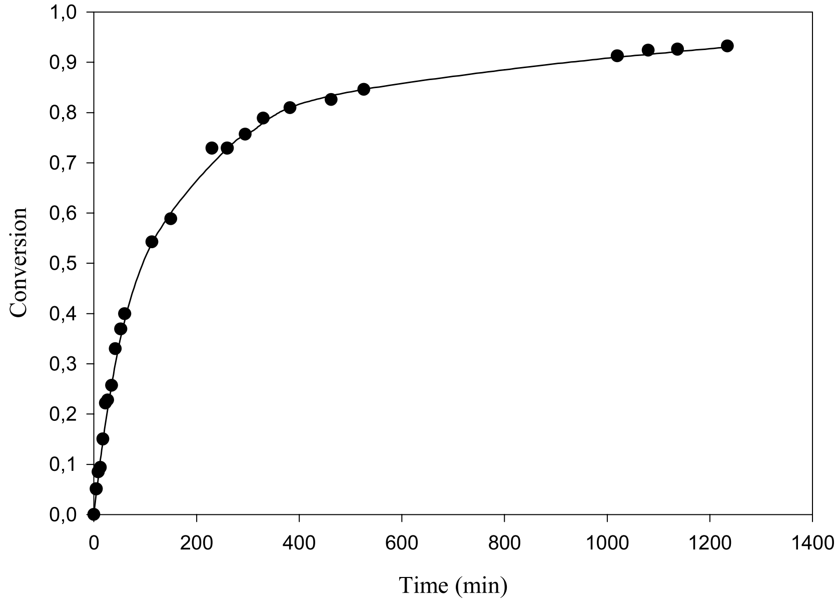


Fig. 4. Conversion versus time of H-HTPI and cyclohexylisocyanate (stoichiometry) reaction in bulk at 25 °C with DBTL as catalyst (2.68×10^{-4} mol l^{-1}).

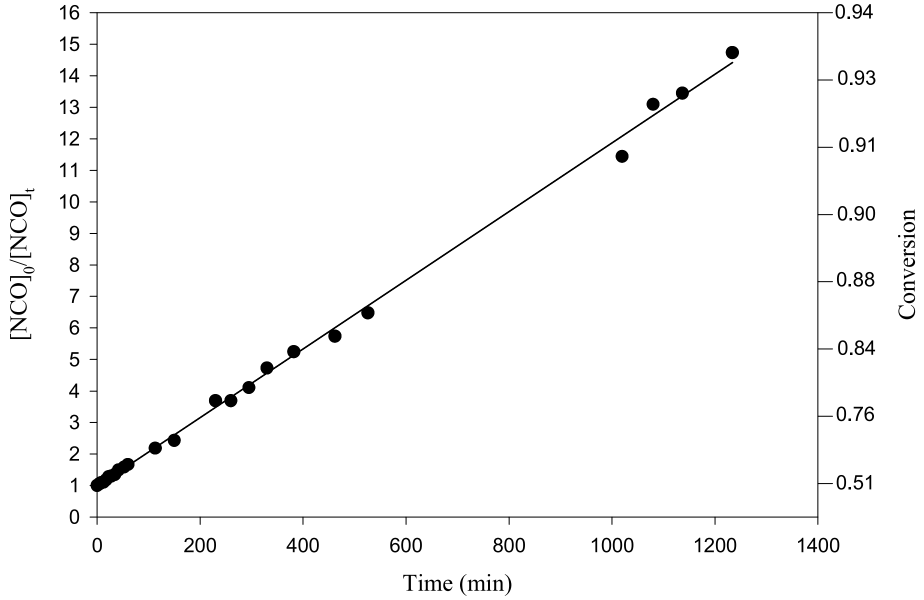


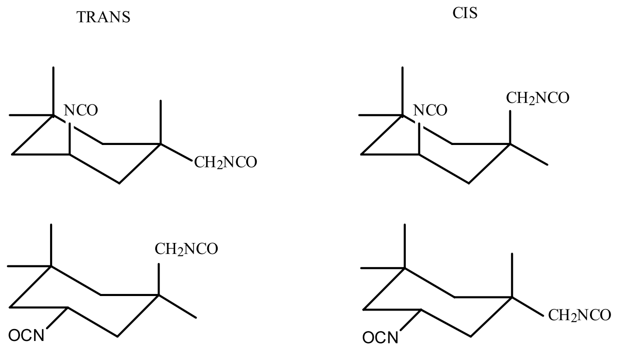
Fig. 5. Second order rate law for H-HTPI and cyclohexylisocyanate (stoichiometry) reaction in bulk at 25 °C with DBTL as catalyst (2.68×10^{-4} mol l^{-1}).

possess a primary aliphatic and a secondary cycloaliphatic isocyanate group, leading to four isomers from *cis* and *trans* conformation (Scheme 3).

An unequal reactivity between the primary and secondary NCO groups is usually reported. However depending on the reaction conditions the reactivity difference between the NCO groups were found to be in the range 0.2:1 to 12:1 (secondary:primary) [12,23–29]. In particular, Lomölder et al. [23] show that the catalyst nature had a dramatic effect on the selectivity of IPDI in the urethane reaction (1,4-diazabicyclo[2,2,2]octane (DABCO) 0.2:1, DBTL 11.5:1).

This selectivity may be the origin of contradictory observations when reacting IPDI with hydrocarbon polyols. In detailed studies, authors concluded that a simple second order equation could describe the HTPB–IPDI bulk reaction [11,12], while inversely others observed a discontinuity in the second order plot [18].

According to a previous structural study of I-IPDI, it was observed that primary and secondary isocyanate groups are present in a 33/67 ratio [9]. Prior to modeling PU network kinetics, reaction of I-IPDI with *n*-heptanol ([NCO]=[OH]=1.2 mol l^{-1}), using DBTL as a catalyst (2.68×10^{-3} mol l^{-1}), in THF at 25 °C, was investigated. A discontinuity in the second order plot was clearly evidenced for conversion rate higher than 67% by authors, meaning that a simple overall second order kinetic law was not appropriate to completely follow this reaction and therefore does not allow to determine an average rate constant.



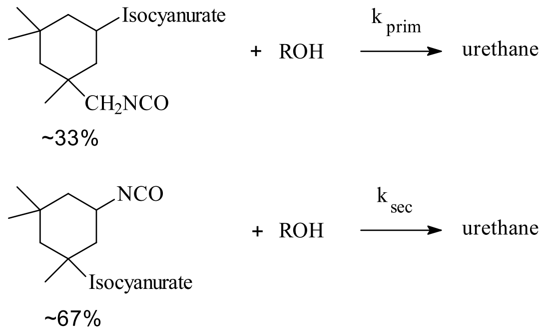
Scheme 3. IPDI conformational structures.

Thus, the isocyanate groups were differentiated and their content was taken into account (Scheme 4).

From the model presented in Scheme 4 it is assumed that both isocyanate groups react independently since these last are away from each other. Thus, it is considered that the reactivity of each NCO group is not changed after one of the –NCO group has reacted, as often considered for asymmetric diisocyanates [15,30].

3.1. Kinetic study

In this case, the general second order kinetic equation



Scheme 4. Model reaction scheme taking into account the different reactivities of the –NCO group present on I-IPDI. k_{prim} and k_{sec} are defined as the rate constants of the primary and secondary isocyanate groups, respectively, for the H-HTPI/I-IPDI reaction.

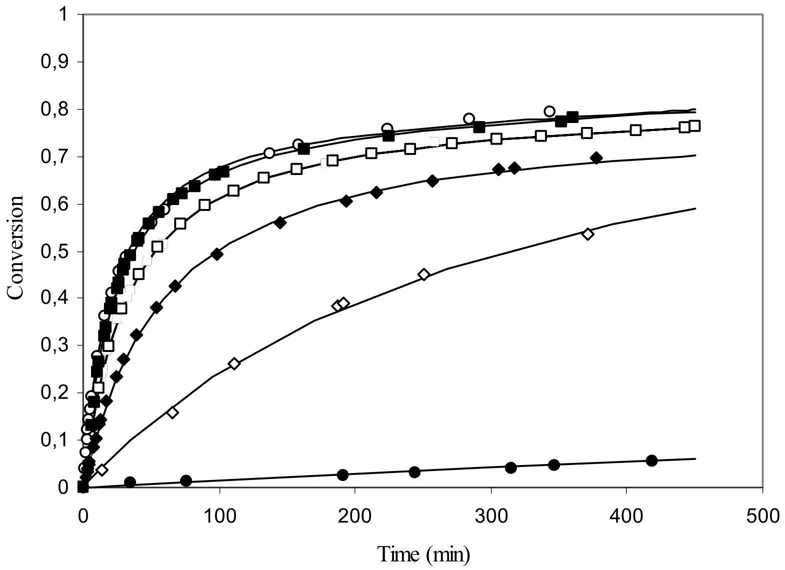


Fig. 6. I-IPDI and H-HTPI (stoichiometry) reaction in bulk at 25 °C. Influence of DBTL concentration on conversion rate. ●, 0; ◇, 1.9×10^{-4}; ◆, 1.86×10^{-3}; □, 2.29×10^{-3}; ■, 5.57×10^{-3}; ○, 7.88×10^{-3} mol l^{-1}.

differentiating the two –NCO groups is as follows:

$$-\frac{d[NCO]}{dt} = (k^0_{prim}[NCO]_{prim} + k^0_{sec}[NCO]_{sec})[OH] + (k^{cat}_{prim}[NCO]_{prim} + k^{cat}_{sec}[NCO]_{sec}) \times [OH][DBTL] \quad (5)$$

hence,

$$-\frac{d[NCO]}{dt} = (k_{prim}[NCO]_{prim} + k_{sec}[NCO]_{sec})[OH] \quad (6)$$

with

$$[NCO] = [NCO]_{prim} + [NCO]_{sec} \quad (7)$$

$$k_{prim} = k^0_{prim} + k^{cat}_{prim}[DBTL] \quad (8)$$

and

$$k_{sec} = k^0_{sec} + k^{cat}_{sec}[DBTL] \quad (9)$$

with

$$\frac{[NCO]^0_{sec}}{[NCO]^0_{prim}} = \frac{67}{33} \approx 2$$

where k_{prim} and k_{sec} are the apparent constants of the primary and secondary –NCO group, respectively, k^0_{prim}, k^0_{sec} and k^{cat}_{prim}, k^{cat}_{sec} the spontaneous and catalyzed rate constants, respectively.

The kinetic model (5) was carried out using Runge–Kutta numerical resolution and allowed the determination of the kinetic constants. The calculated selectivity was found similar to HTPB–IPDI bulk reactions with DBTL as a catalyst [23,27]:

$$S = \frac{k_{sec}}{k_{prim}} = \frac{0.353}{0.056} = 6.3 \quad (10)$$

The higher reactivity of the secondary isocyanate towards the primary isocyanate established here was similarly observed for IPDI/primary alcohol systems [19,26,31]. Moreover, if IPDI was reacted with secondary alcohols, it was even observed that the secondary isocyanate group was completely reacted at the beginning of the process while the primary isocyanate gradually reacted [32]. For IPDI, and by analogy for I-IPDI, this higher reactivity of the secondary isocyanate function was attributed to the larger electronic density of the latter –NCO group.

Thus, these preliminary studies indicate that in I-IPDI. The two isocyanate functions can be considered as independent and a simulation of the H-HTPI/I-IPDI reaction with Eq. (5) is possible taking into consideration the content and selectivity of the two isocyanate groups.

3.2. Influence of catalyst concentration

There is controversy on the influence of DBTL concentration on the urethane kinetic reaction. Authors found that the rate constant is not linearly dependent on catalyst concentration and in some case even independent of catalyst concentration ($>1.5\times10^{-3}$ mol l^{-1}) [33,34]. Conversely, linear relations were obtained for low DBTL concentrations ($<1.5\times10^{-3}$ mol l^{-1}) by others [34–36]. In our case, it is first noteworthy that the theoretical conversions, calculated with only two rate constants, perfectly fit the experimental points, even after gelation (Fig. 6), which appears between 58 and 59% conversion [37]. Secondly, k_{prim} and k_{sec} values, determined from Fig. 6 fittings, should have been considered as varying linearly up

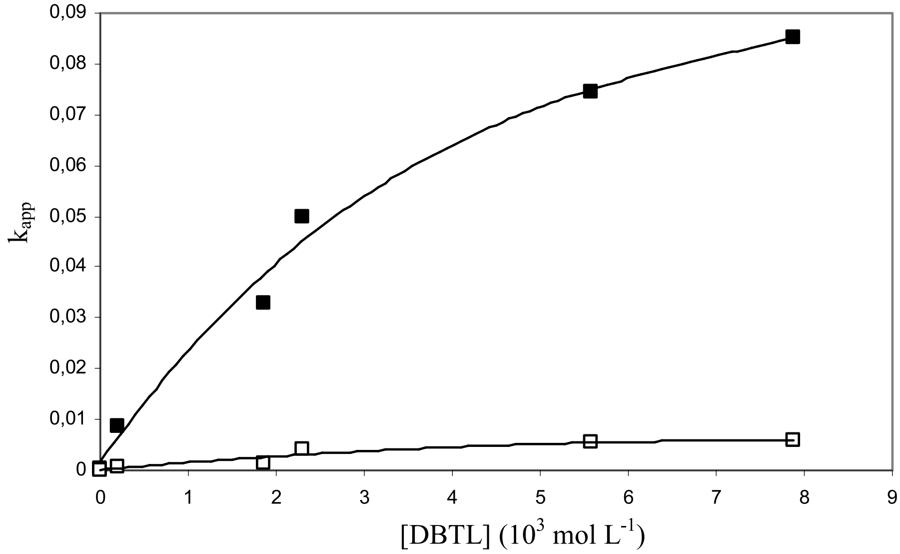


Fig. 7. Kinetic constants of the reaction on primary (□, k_{prim}) and secondary (■, k_{sec}) NCO groups versus catalyst concentration for I-IPDI and H-HTPI (stoichiometry) reaction in bulk at 25 °C.

Table 1
Kinetic constants without or with DBTL at different temperatures according to the model taking into consideration primary and secondary NCO reactivity and content

T (°C)	k^0_{prim} (10^{-4} l mol^{-1} min^{-1})	k^0_{sec} (10^{-4} l mol^{-1} min^{-1})	k^{cat}_{prim} (l^2 mol^{-2} min^{-1})	k^{cat}_{sec} (l^2 mol^{-2} min^{-1})
26	0.1	3	–	–
30	–	–	0.94	20.7
38	0.4	11	4.4	82.1
47	1.4	35	–	–
56	–	–	12.6	123.6
66	6.0	120	37.8	126.1
88	55	800	–	–

to [DBTL]$=2\times10^{-3}$ mol l^{-1}, but in the overall studied range (0–8×10^{-3} mol l^{-1}), a curve is observed (Fig. 7). From these results we may consider that the rate constant linear dependence on catalyst concentration, up to a limit DBTL concentration, i.e. 2×10^{-3} mol l^{-1}, is attributed to the absence of catalyst aggregation. Above this last, DBTL

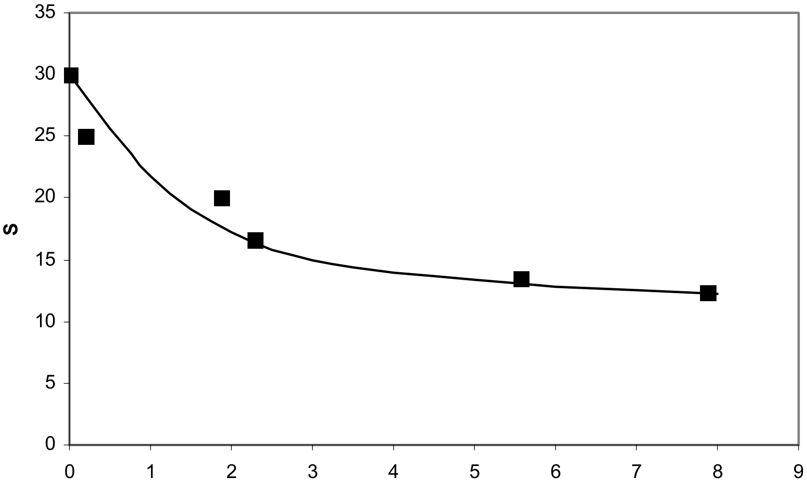


Fig. 8. Influence of DBTL concentration on selectivity S (k_{sec}/k_{prim}).

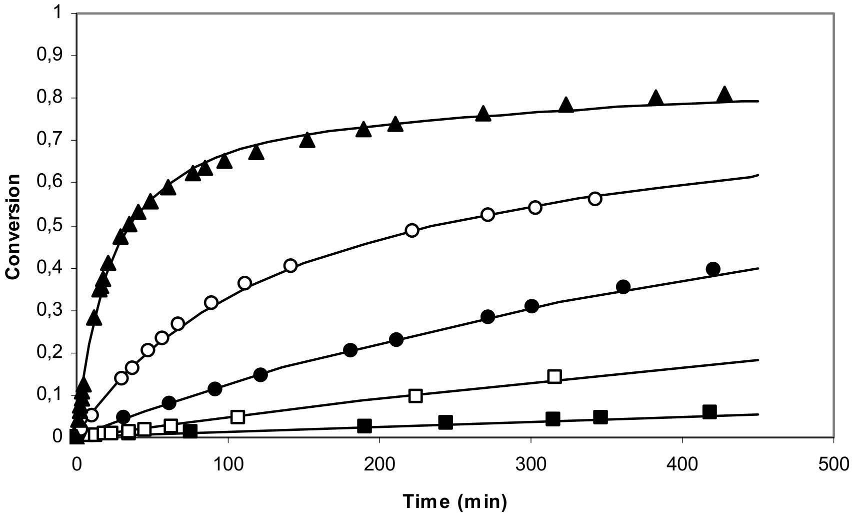


Fig. 9. I-IPDI and H-HTPI (stoichiometry) uncatalyzed reaction in bulk. Influence of temperature on conversion rate (■, 26 °C; □, 38 °C; ●, 47 °C; ○, 66 °C; ▲, 88 °C). Experimental points and theoretical curves using a two rate constant model (k_{prim} and k_{sec}).

concentration is high enough to lead to the formation of complexes or aggregates thus affecting the kinetics of the reaction [33,34]. With another dibutyltin derivative, Tondeur et al. [38] also observed a particular dependence of the reaction kinetic on the rate of catalyst concentration. This last was attributed to a self-blocking of the catalyst in non-productive aggregates with rising catalyst content.

Moreover, it is interesting to note that the selectivity $S = k_{\text{sec}}/k_{\text{prim}}$ decreases and tends towards a plateau as DBTL content increases (Fig. 8). This result was also observed by Lomölder et al. [23] on IPDI, and similar results were obtained on tolylene diisocyanate (TDI) for which ortho- and para-NCO groups reactivities get closer in the presence of catalyst [39].

3.3. Influence of temperature

Temperature influence on uncatalyzed and catalyzed H-HTPI/I-IPDI reactions was studied (Figs. 9 and 10). Theoretical and experimental conversions are thoroughly in agreement, and it is observed that k_{prim} and k_{sec} classically increase with raising temperature. k^0_{prim}, k^0_{sec}, $k^{\text{cat}}_{\text{prim}}$, $k^{\text{cat}}_{\text{sec}}$ were determined and summarized in Table 1.

The phenomenon of decreasing selectivity with increasing temperature was also observed here. Selectivity varied inversely with temperature and decreased linearly in the studied range (Fig. 11).

This observation, i.e. temperature enhancement of the primary NCO reactivity rather than the secondary one, was related by others when reacting IPDI with different alcohols in the temperature range 20–100 °C [23]. Similarly, the significant influence of temperature on selectivity was quoted for TDI molecule [39]. It was reported that at 25 °C the NCO group in the para position is 8 to 10 times as reactive as that in the ortho position, but at 100 °C both NCO have similar reactivities. Moreover, it is observed here

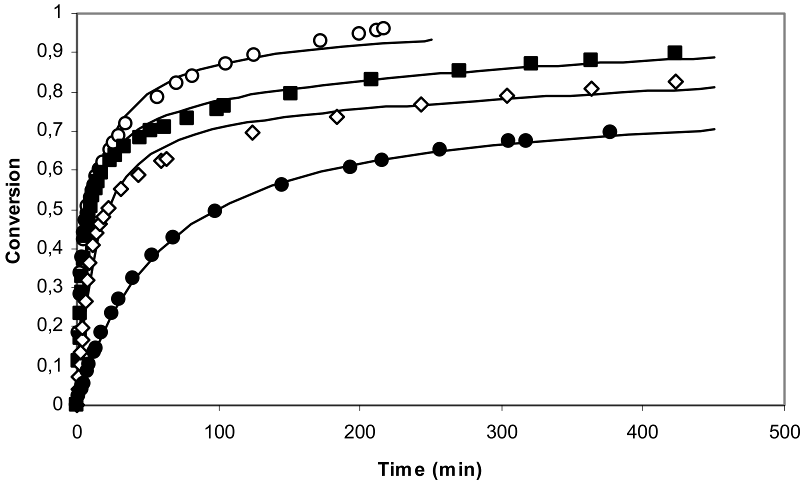


Fig. 10. I-IPDI and H-HTPI (stoichiometry) reaction in bulk with DBTL (2.68×10^{-4} mol l^{-1}). Influence of temperature on conversion rate (●, 30 °C; ◇, 38 °C; ■, 56 °C; ○, 66 °C). Experimental points and theoretical curves using a two rate constant model (k_{prim} and k_{sec}).

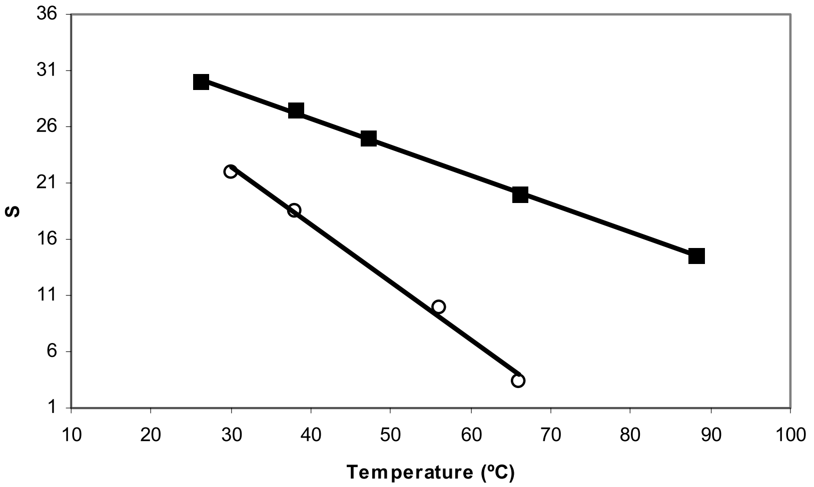


Fig. 11. Influence of temperature on selectivity S (k_{sec}/k_{prim}) for the catalyzed (○) and uncatalyzed (■) I-IPDI and H-HTPI (stoichiometry) reaction in bulk.

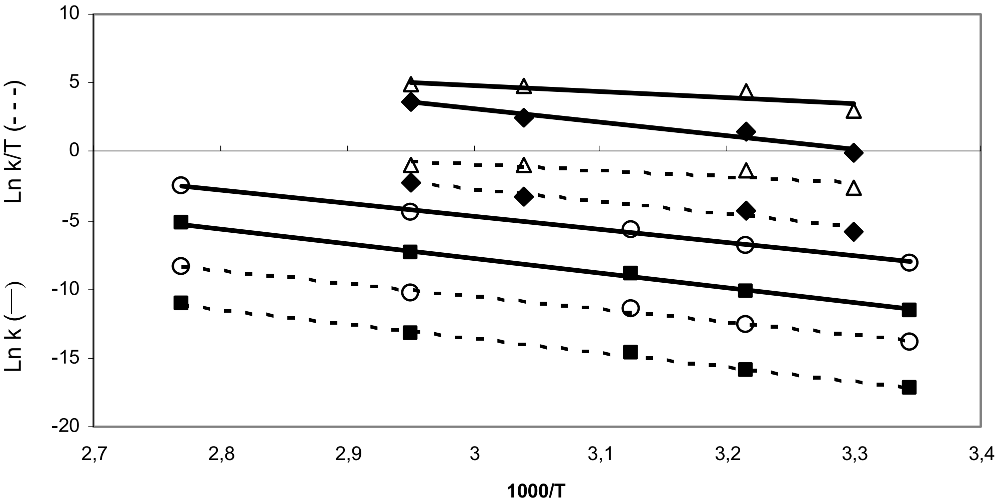


Fig. 12. Arrhenius (—) and Eyring (- - -) plots for I-IPDI and H-HTPI (stoichiometry) reaction in bulk without catalyst (■, k^0_{prim}; ○, k^0_{sec}) and with [DBTL] = 2.68×10^{-4} mol l^{-1} (◆, k^{cat}_{prim}; △, k^{cat}_{sec}).

that temperature influence on selectivity was emphasized when DBTL is present.

Thermodynamic parameters were determined by applying Arrhenius law. Pre-exponential factors (A^0 and A^{cat}) and activation energies (E^0 and E^{cat}) of the uncatalyzed and DBTL catalyzed reactions are reported on Table 2 and Fig. 12.

Activation energy of the secondary NCO group was found lower than the primary one and both values decreased when catalyst was present, this phenomenon being emphasized for the secondary NCO group.

Compared to other model system involving small molecules in the urethane formation, the resulting Ea found in this study are higher indicating a slower rate of the reaction when reacting a macrodiol with an isocyanurate.

Activation enthalpy (ΔH^*) and entropy (ΔS^*) are two thermodynamic parameters that can be used to understand the reaction mechanism [40]. Eyring relationship (Eq. (9)) was used to determine them and results are presented in Fig. 12 and Table 3.

Activation enthalpies are roughly the same for the primary and secondary NCO groups in the uncatalyzed reaction (~45 kJ mol^{-1}). Theoretically lower values are expected for the catalyzed reaction. However, the decrease

Table 2
Pre-exponential factors (A^0, A^{cat}) and activation energies (E^0_a, E^{cat}_a) for the catalyzed and uncatalyzed I-IPDI/H-HTPI (stoichiometry) reaction

	E^0 (kJ mol^{-1})	E^{cat} (kJ mol^{-1})	A^0 (l mol^{-1} min^{-1})	A^{cat} (l^2 mol^{-2} min^{-1})
Primary NCO	90.0	80.0	5.1×10^{10}	7.1×10^{13}
Secondary NCO	79.3	38.0	2.3×10^{10}	1.1×10^{8}

Table 3
Activation enthalpies and entropies values according to the Eyring equation

System	ΔH^* (kJ mol^{-1})	ΔS^* (J mol^{-1} K^{-1})	Reference
HTPB + PrNCO (solution, DBTL)	54	−38	[35]
HTPB + PhNCO (solution, no catalyst)	53	84	[42]
HTPB + PhNCO (bulk, no catalyst)	37	113	[42]
HTPB + HMDI (solution, no catalyst)	33	88	[43]
HTPB + HMDI (bulk, DBTL)	62	128	[44]
HTPB + HMDI (solution, DBTL)	34	201	[44]
HTPB + IPDI (bulk, no catalyst)	41	−198	[11]
HTPB + TDI (solution, DBTL)	30	−213	[41]
H-HTPI + I-IPDI (bulk, no catalyst)	87/76[a]	−49/−55[a]	This work
H-HTPI + I-IPDI (bulk, DBTL)	77/35[a]	12/−100[a]	This work

PrNCO, propylisocyanate; PhNCO, phenylisocyanate; HMDI, hexamethylene diisocyanate; TDI, toluene diisocyanate; IPDI, isophorone diisocyanate; HTPB, hydroxy telechelic polybutadiene; H-HTPI, hydrogenated hydroxy telechelic polyisoprene; I-IPDI, isocyanurate of isophorone diisocyanate; DBTL, dibutyltin dilaurate.

[a] Primary/secondary.

in energy level of transition state is much more highlighted for the secondary NCO group.

Overall, high values for the activation enthalpies were found, meaning that strong associations between the hydroxyl groups are present [11,41]. These could be considered similar to those present in HTPB-isocyanate systems, according to ΔH^* values (Table 3).

A negative value for the activation entropy was found for the uncatalyzed reaction attesting an associative mechanism in the transition state [10,11]. For the catalyzed reaction ΔS^* was higher, indicating an associative mechanism involving the DBTL catalyst in urethane–tin complexes [23].

4. Conclusion

The kinetics of the condensation reaction between I-IPDI and H-HTPI in the bulk state was followed using FTIR spectroscopy. By analogy to IPDI, I-IPDI has, at least, two kinds of isocyanate groups (primary and secondary) which have distinct reactivities. The kinetics of each group followed a second order rate equation. I-IPDI/H-HTPI reaction is well described, by an overall model taking only into consideration the distinct reactivities and contents of the primary and secondary NCO groups, even at high conversion rates (after gelation). As DBTL concentration increases selectivity decreases and tends towards a plateau. Influence of temperature was inversely proportional to selectivity.

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