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Low molar mass polybutadiene made crosslinkable by the introduction of silane moities via urethane linkage: 1. Synthesis and kinetic study

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Polybutadiene crosslinkable under moisture was synthesised by modification of hydroxy telechelic functions of low molecular weight polybutadiene with isocyanato propyl triethoxy silane. At 50°C and with dibutyl tin dilaurate (DBTL) as catalyst, silane moities were introduced quantitatively at the rate of 1.2, 2 and 2.4 per polymer chain. Two analytical methods (*FT*i.r. spectroscopy and volumetric titration) were used to follow isocyanate consumption. Two kinetic treatments were investigated (2nd and 3rd order) and influence of catalyst concentration and temperature were studied. A 2nd order kinetic seems to be better fitted for our experimental results. Nevertheless, in each case, Arrhenius law suggests an entropically controlled reaction with probably ethoxy silane groups participating in a transition state in the presence of DBTL. © 1997 Elsevier Science Ltd.

(Keywords: polybutadiene; silane; modification)

INTRODUCTION

The low molar mass polybutadiene used in this work (Poly Bd R45 HT®)[1] is a commercial hydroxy telechelic polymer (HTPB) synthesised by radical polymerisation route. Its main characteristics are an average molar mass $\overline{M_n} = 2800$ and an average hydroxy functionality $\overline{f_{OH}} = 2.4$. Microstructure studies, (using ^1H and ^{13}C n.m.r. spectra) indicate 22% of 1,2 units (vinyl units) and 78% of 1,4 units (23.7% cis and 54.3% trans)[2–4]. Industrially, HTPB is used as polyol for the synthesis of polyurethane network, generally by reaction with a diisocyanate. Many commercial uses of this polymer stem from its low glass transition temperature (Tg~−75°C), good mechanical properties and strong resistance to chemical attacks. HTPB is generally used in the preparation of adhesives, mastics, sealing gaskets, elastomers, encapsulants... in many fields such as automobile, paint, surface coating, building-trade, electronic, medicine[1,5,6]. In this work, our aim is to modify HTPB in order to obtain a crosslinkable polymer by a route without isocyanate reactants. Functionalisation of HTPB by alkoxy silane moities was chosen and, the resulting polymer will be crosslinked by hydrolysis. This modification can be carried out either by reaction of the hydroxy groups or by addition on HTPB double bonds. In this paper, we only report the results obtained by using hydroxy-isocyanate reaction leading to urethane linkage.

EXPERIMENTAL

Materials

Polybutadiene (Poly Bd R45 HT®) was kindly supplied by Elf Atochem. Isocyanato propyl triethoxysilane (IPTS) (Interchim) and dibutyl tin dilaurate (DBTL) (Aldrich) were used without further purification.

Synthesis

0.01 mole (30 g) of HTPB is introduced to a 250 ml round bottom flask equipped with a mechanical stirrer (300 rpm), a switchable inlet for nitrogen and a vacuum connector. HTPB is first degased for 15 hr by a graduated vacuum up to 10^{-1}–10^{-2} mm Hg at 60°C. Then, the reactor is raised to the required temperature under nitrogen. The catalyst (DBTL) is added in variable amounts (see text) and the mixture is stirred for 5 min; 0.012, 0.021 or 0.025 mole of IPTS (respectively 3, 5.2 or 6.2 g) is introduced carefully as rapidly as possible. The reaction is allowed to proceed until entire disappearance of isocyanate functions.

Measurements

The different syntheses were followed by two analytical methods:

- volumetric titration: free isocyanate functions were classically treated by an excess of dicyclohexylamine and back-titrated with HCl standard solution by using self-acting apparatus (Titroline Schott).
- *FT*i.r. spectroscopy: i.r. spectroscopies were carried out with a Nicolet 510 M IR/FT. Samples are set apart from the reactive mixture during reaction time and spread out on IRTRAN window. The variable thickness of the films implies the use of a reference band in the spectrum to calculate the reaction conversion (C) according to Beer–Lambert law. This reference band at 960 cm^{-1}, which undergoes no modification during the reaction, corresponds to CH vibration of HTPB 1,4 trans double bond. Thus, the disappearance of isocyanate band at

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$2270\,cm^{-1}$ allows us to determine conversion *versus* time:

$$C = 1 - \frac{R_t}{R_0} = 1 - \frac{\left(\dfrac{A_{2270\,cm^{-1}}}{A_{960\,cm^{-1}}}\right)_t}{\left(\dfrac{A_{2270\,cm^{-1}}}{A_{960\,cm^{-1}}}\right)_0} \qquad (1)$$

where A is the absorbance and subscript 0 corresponds to initial time.

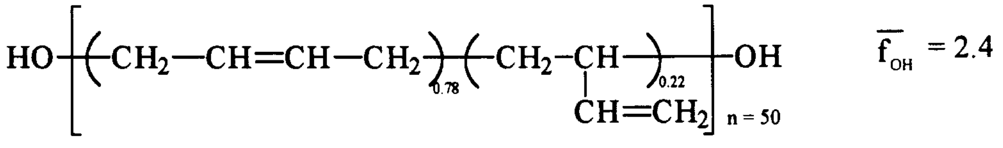
RESULTS AND DISCUSSION

Schematic structure of HTPB is shown below (*Scheme 1*).

Hydroxy functions of HTPB can react with monoisocyanate compounds to lead to newly functionalised polymers. In order to obtain hydrolysable crosslinking, we have chosen to introduce ethoxy silane moities onto HTPB via urethane linkage, with IPTS as reactant, according to the following scheme (*Scheme 2*) where n is the number of triethoxysilane groups per chain.

The reactions were carried out, with or without catalyst (DBTL), at 50°C to prevent secondary reactions. Without catalyst, IPTS has a weak reactivity and the reaction is not quantitative even after 36 hr (e.g. *Figure 1* for PBU2Si). We can follow the concomitant disappearance of NCO band at $2270\,cm^{-1}$ and the appearance of NHCO band at $1760\,cm^{-1}$.

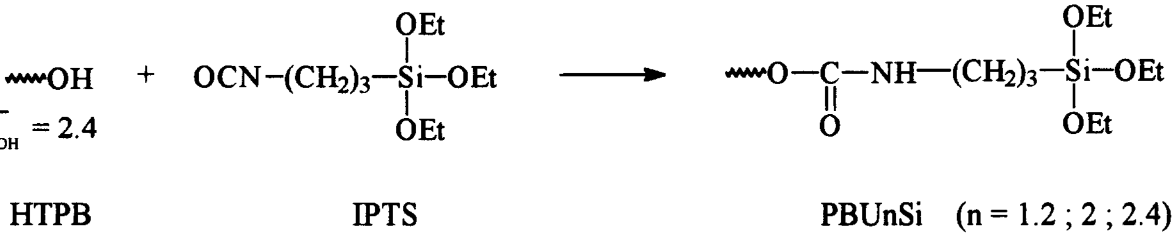
It is noteworthy that for practical reasons (duration of introduction of the reactants, homogenisation of the mixture, setting apart of a sample, preparation of thin film on i.r. window and carrying out of spectrum) the first



$$HO\left[\left(CH_2{-}CH{=}CH{-}CH_2\right)_{0.78}\left(CH_2{-}\underset{\displaystyle CH{=}CH_2}{CH}\right)_{0.22}\right]_{n=50}OH \qquad \overline{f}_{OH} = 2.4$$

HTPB

Scheme 1



$$\sim\!OH + OCN{-}(CH_2)_3{-}Si(OEt)_3 \longrightarrow \sim\!O{-}\underset{\displaystyle O}{\overset{\|}{C}}{-}NH{-}(CH_2)_3{-}Si(OEt)_3$$

Scheme 2

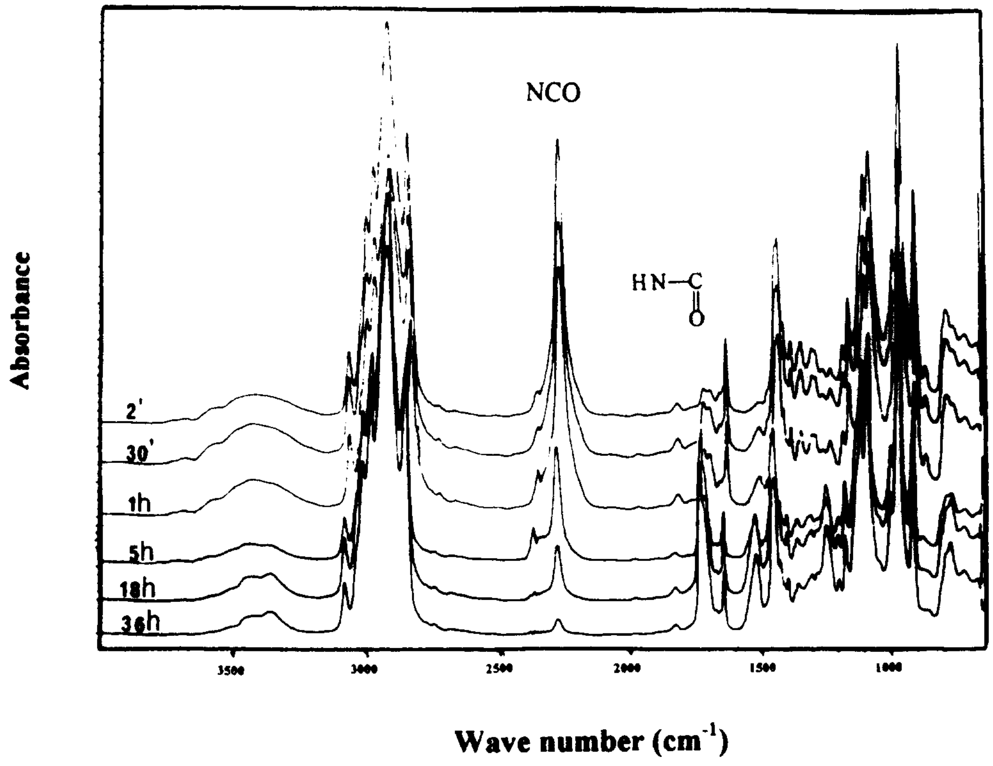


Figure 1 *FT*i.r. spectra *versus* time for PBU2Si/IPTS reaction at 50°C without catalyst

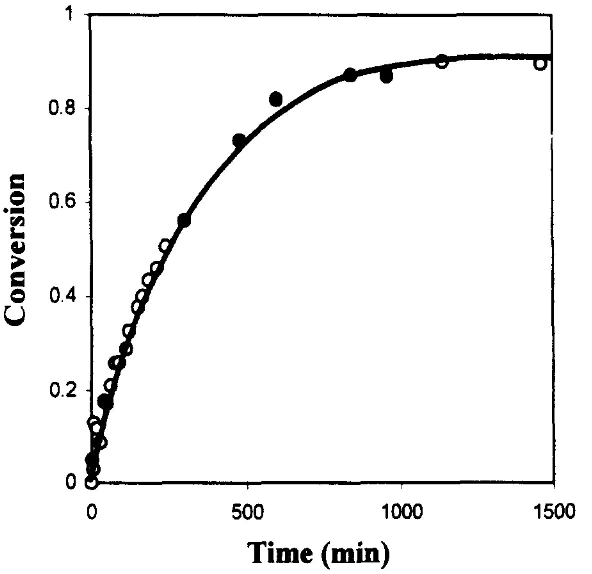


Figure 2 *FT*i.r. (●) and titration (○) conversion curves for PBU2Si/IPTS reaction at 50°C without catalyst

spectrum does not correspond to initial time and the ratio R_0 (equation (1)) is unknown. Nevertheless, when we compare the two conversion curves obtained by titration or by i.r. analysis (e.g. *Figure 2* for PBU2Si), we can observe that there is a good agreement with a value of $R_0 = 1$.

In the presence of catalyst ($[DBTL] = 11.8\ 10^{-4}\ \mathrm{mol{\cdot}kg^{-1}}$) the reaction is greatly accelerated with a quasi-quantitative yield after 45 min, 1 and 2 hr for n = 1.2, 2 and 2.4, respectively (e.g. *Figure 3* for PBU2Si). By using the above-mentioned value of R_0, volumetric titration and i.r. methods give the same results for conversion *versus* time (e.g. *Figure 4* for PBU2Si).

The resulting samples of modified polybutadiene are transparent and display a slight yellow coloration when DBTL is used. Viscosity is the same as initial HTPB whatever the modification rate is. PBUnSi are stable at room temperature but it is more advisable to preserve them in hermetically sealed containers to prevent moisture hydrolysis.

Kinetic study

For PBU2Si, we studied the influence of catalyst concentration and temperature on conversion. Two kinetic treatments were used to investigate whether the reaction obeys 2nd or 3rd order kinetics[7–20].

2nd order kinetics

In this case, the general kinetic equation is as follows:

$$-\frac{d[NCO]}{dt} = -\frac{d[OH]}{dt}$$

$$= k_0[NCO][OH] + k_{cat}[DBTL][NCO][OH]$$

hence,

$$-\frac{d[NCO]}{dt} = -\frac{d[OH]}{dt} = k[NCO][OH]$$

with

$$k = k_0 + k_{cat}[DBTL] \tag{2}$$

where k is the apparent rate constant and k_0 and k_{cat} are the spontaneous and catalysed rate constants, respectively. In our conditions, $[OH]_0$ is higher than $[NCO]_0$ and the analytical solution gives:

$$\frac{1}{[OH]_0 - [NCO]_0} \mathrm{Ln} \frac{[NCO]_0[OH]_t}{[NCO]_t[OH]_0} = k\,t \tag{3}$$

Influence of catalyst concentration. In *Figure 5*, we

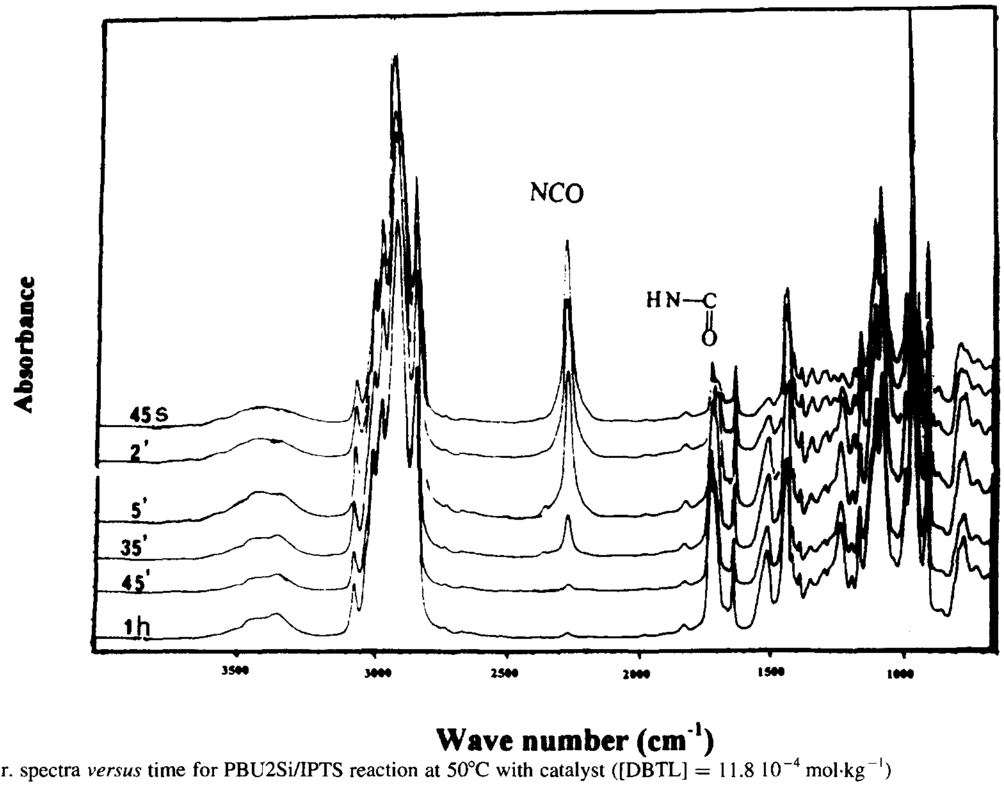


Figure 3 *FT*i.r. spectra *versus* time for PBU2Si/IPTS reaction at 50°C with catalyst ($[DBTL] = 11.8\ 10^{-4}\ \mathrm{mol{\cdot}kg^{-1}}$)

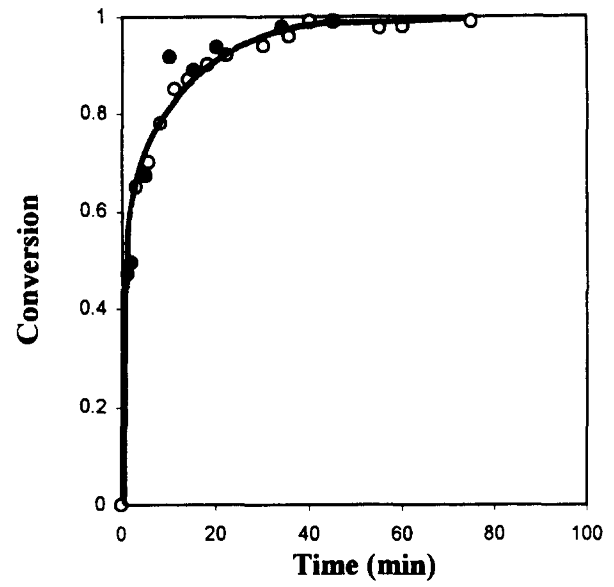


Figure 4 *FTi.r.* (●) and titration (○) conversion curves for PBU2Si/IPTS reaction at 50°C with catalyst ([DBTL] = 11.8 10^{-4} mol·kg^{-1})

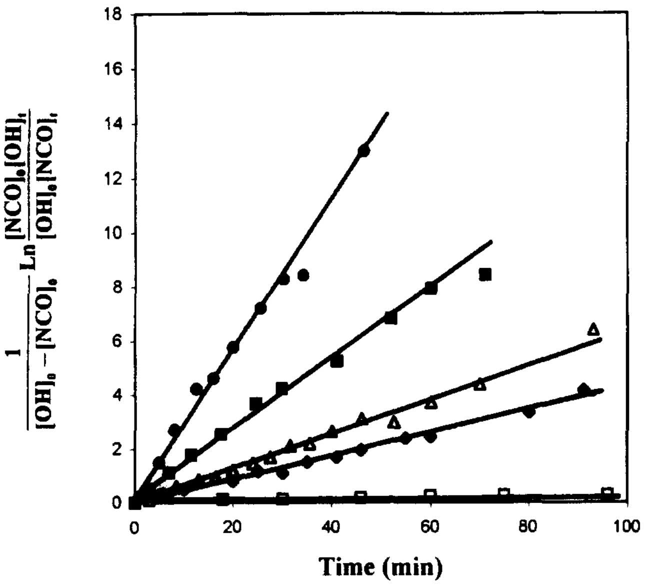


Figure 5 Second order kinetics for PBU2Si/IPTS reaction at 40°C *versus* catalyst concentration ([DBTL].10^4 mol·kg^{-1}: (□) 0; (♦) 1.5; (△) 2.9; (■) 5.9; (●) 11.8)

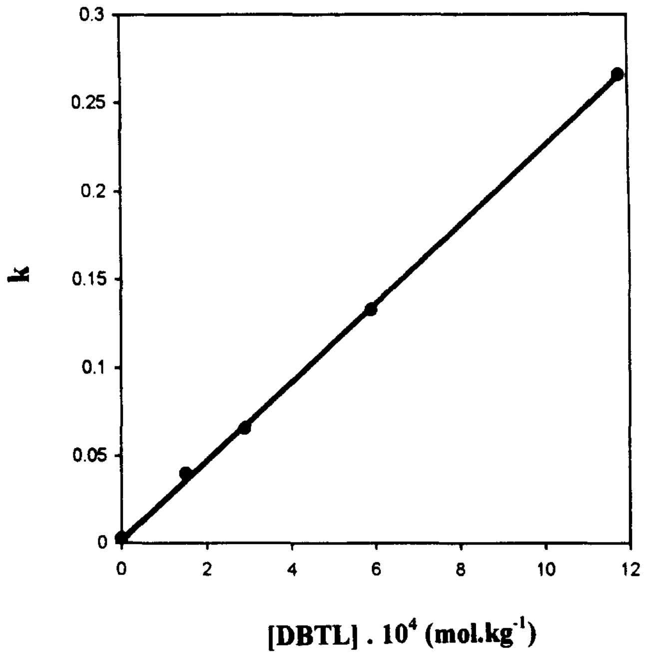


Figure 6 Kinetic constant k *versus* catalyst concentration for PBU2Si/IPTS reaction at 40°C

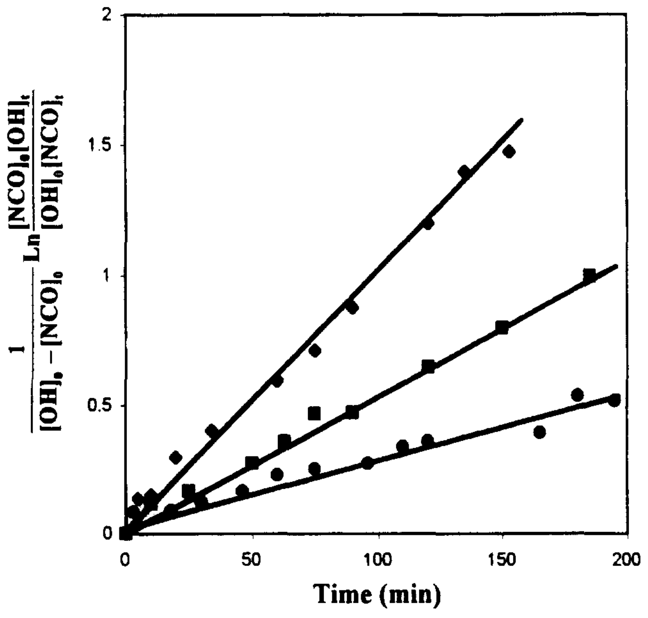


Figure 7 Second order kinetics for PBU2Si/IPTS reaction without catalyst *versus* temperature: (●) 40°C; (■) 50°C; (♦) 60°C.

reported the results obtained at 40°C for catalyst concentrations in the range 0–11.8 10^{-4} mol·kg^{-1}. Whatever the catalyst concentration is, we obtain a straight line up to 0.90–0.95% conversion, which perfectly fits 2nd order kinetics.

There is a discrepancy between these results and those of Pham[18] concerning the reaction of propyl and phenyl isocyanates on similar polybutadienes of non-equivalent microstructure. In this case, a deviation is observed from 2nd order kinetics for yields above 60–70% both in bulk and in solution. This deviation is explained by urethane autocatalysis phenomenon.

Another matter for discussion is the influence of DBTL concentration on the alcohol–isocyanate reaction rate constant which has been greatly studied and is much debated. For some authors[19,20], the rate constant k would not linearly depend on catalyst concentration and would raise to a limit when DBTL concentration is high due to formation of complexes or aggregates. Moreover, in some cases, k would be independent of catalyst in a certain range of concentration and would stay equal to spontaneous reaction rate constant k_0. Nevertheless, linear dependence is verified again when catalyst aggregation is prevented. This is observed when catalyst is linked at the end of macromolecular chain, even when the latter is short. For polybutadiene oligomers, a linear relation is obtained by Pham[18] for DBTL concentration below 2.7 10^{-4} mol·l^{-1}. In our case, k values, obtained from the slope of the different straight lines in *Figure 5*, *versus* DBTL concentration (*Figure 6*) allow us to determine k_0 and k_{cat} according to

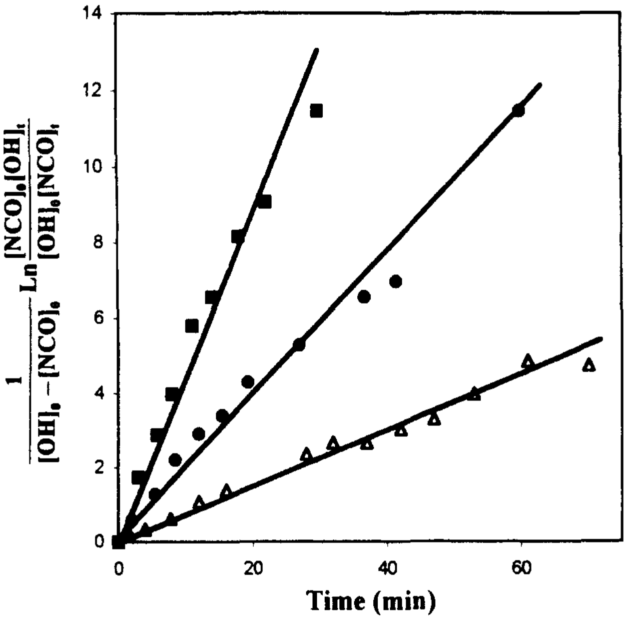


Figure 8 Second order kinetics for PBU2Si/IPTS reaction with catalyst ([DBTL] = 11.8 10^{-4} mol·kg^{-1}) *versus* temperature: (△) 30°C; (●) 40°C; (■) 50°C

relation (3):

$$k_0 = 2.8\ 10^{-3}\ mol^{-1}\ kg\ min^{-1} \text{ and}$$

$$k_{cat} = 200\ mol^{-2}\ kg^{-2}\ min^{-1}$$

A good linearity is obtained in the range of studied concentrations.

Influence of temperature. Influence of temperature on reactions was studied with or without DBTL respectively at 30, 40, 50°C and 40, 50, 60°C. The results are reported in *Figure 7* and *Figure 8* according to (3).

Whatever the temperature is, with or without catalyst, 2nd order kinetics is well verified up to high conversions (90–95%). k_0 is calculated from the slopes in *Figure 7* and k_{cat} from the slopes in *Figure 8* by using relation (2) with [DBTL] = 11.8 10^{-4} mol·kg^{-1}. These values are reported in *Table 1*.

Table 1 Second order rate constants

T (°C)	$k_0.10^3$ (mol^{-1} kg min^{-1})	$k.10^3$ (mol^{-1} kg min^{-1})	k_{cat} (mol^{-2} kg^2 min^{-2})
30	1.4[a]	81	68
40	2.8	227	190
50	5.5	454	380
60	9.8	—	—

[a] Determined from Arrhenius plot.

Thermodynamic parameters. From *Table 1*, we applied Arrhenius law (*Figure 9*) and computed preexponential factors (A_0 and A_{cat}) and activation energies (E_0 and E_{cat}).

$E_0 = 53$ kJ mol^{-1} $\quad$ $E_{cat} = 72$ kJ mol^{-1}

$A_0 = 3.10^6$ mol^{-1} kg min^{-1}

$A_{cat} = 1.8\ 10^{14}$ mol^{-2} kg^2 min^{-1}

It may be surprising that activation energy of catalysed reaction is slightly higher than uncatalysed reaction. Our interpretation is a complexation between DBTL and silane groups because DBTL is also the catalyst used for the hydrolysis of alkoxy silanes. In fact, the most important kinetic parameter for the reaction is the preexponential factor (entropy parameter) which sharply increases in the presence of DBTL.

These results can be compared to those obtained by Pham[18] on similar polybutadiene with propyl isocyanate (PI) and phenyl isocyanate (PhI), without catalyst:

$E_{PI} = 20$ kJ mol^{-1} $\quad$ $E_{PhI} = 36.5$ kJ mol^{-1}

$A_{PI} = 12$ mol^{-1} kg min^{-1}

$A_{PhI} = 1.3\ 10^5$ mol^{-1} kg min^{-1}

Phenyl isocyanate, which is the more reactive, has the higher activation energy but also a preexponential factor 10^4 times higher.

3nd order kinetics

An additional term due to urethane autocatalysis appears

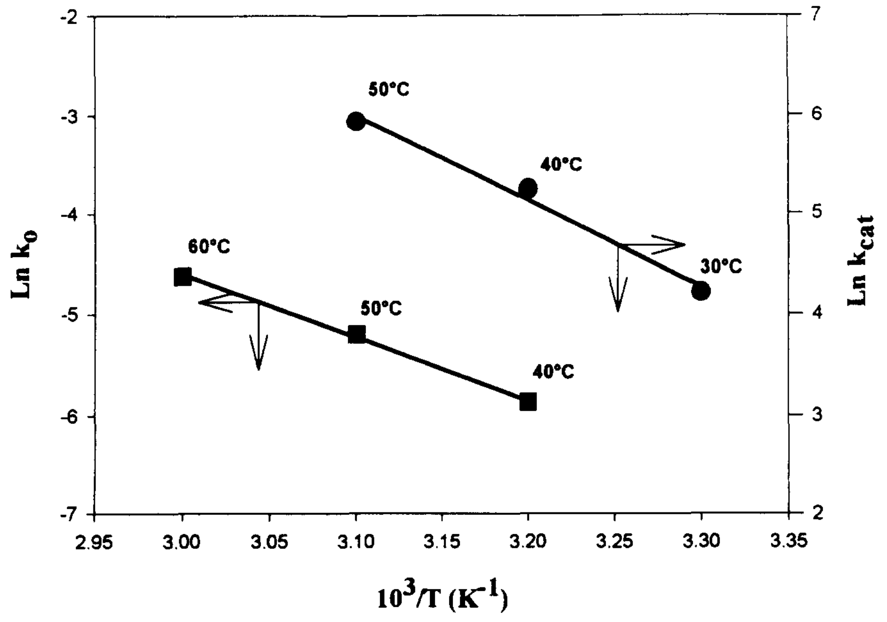


Figure 9 Second order kinetics: Arrhenius plots for PBU2Si/IPTS reaction without (k_0) and with (k_{cat}) catalyst ([DBTL] = 11.8 10^{-4} mol·kg^{-1})

Table 2 Third order rate constants of catalysed reaction

$[DBTL].10^4$ (mol kg^{-1})	1.5	2.9	5.9	11.8
k_{cat} (mol^{-2} kg^{-2} min^{-1})	260	177	208	201

Table 3 Third order rate constant k_u of autocatalysed reaction

Exp.	$[DBTL].10^4$ (mol kg^{-1})	k_u (mol^{-2} kg^{-2} min^{-1})
1	0.0	0–0.005
2	1.5	0.02–0.03
3	2.9	0–0.02
4	5.9	0–0.03
5	11.8	0–0.02

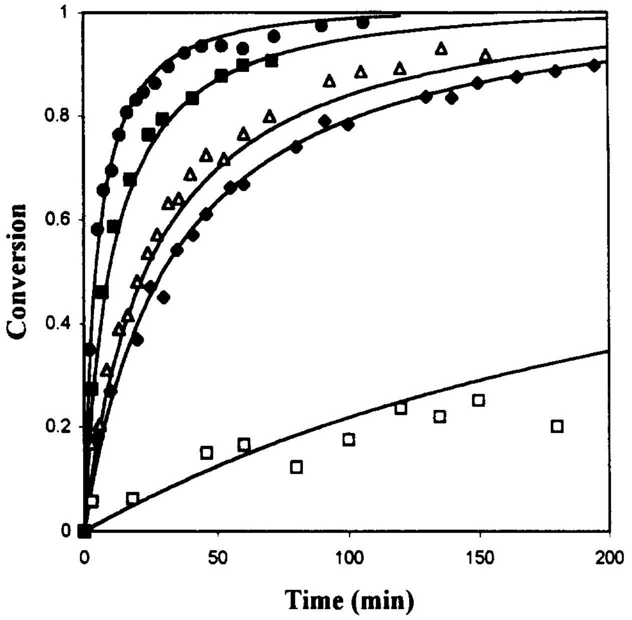


Figure 10 Third order kinetics for PBU2Si/IPTS reaction at 40°C *versus* catalyst concentration ($[DBTL].10^4$ mol·kg^{-1}: (□) 0; (♦) 1.5; (△) 2.9; (■) 5.9; (●) 11.8) and simulated curves (——————)

in the general kinetic equation:

$$-\frac{d[NCO]}{dt}=-\frac{d[OH]}{dt}$$

$$=k_0[NCO][OH]^2+k_{cat}[DBTL][NCO][OH]$$

$$+k_u[U][NCO][OH] \qquad (4)$$

k_0 is measured from reaction without catalyst by using initial slope of conversion curve (initial rate V_0), when urethane concentration is low:hence,

$$V_0=k_0[NCO]_0[OH]_0^2 \; k_0=\frac{V_0}{[NCO]_0[OH]_0^2}$$

k_{cat} is calculated for the same initial concentration $[NCO]_0$ and $[OH]_0$ and always at the beginning of the reaction to neglect urethane concentration. Initial rate of conversion curve for catalysed reaction (V_0^{cat}) is given by:

$$V_0^{cat}=V_0+k_{cat}[DBTL][NCO]_0[OH]_0$$

$$k_{cat}=\frac{V_0^{cat}-V_0}{[DBTL][NCO]_0[OH]_0}$$

Finally, k_u is determined by numerical method because analytical integration of general kinetic relation (4) is too complex.

Setting $[NCO]_0=a$; $[OH]_0=b$; $[DBTL]=c$; $[U]=x$; (4) becomes,

$$\frac{dx}{dt}=k_0(a-x)(b-x)^2+k_{cat}c(a-x)(b-x)$$

$$+k_ux(a-x)(b-x)=f(x)$$

assuming $(dx/dt)=(\Delta x/\Delta t)$ for Δt sufficiently small, thus:

$$\frac{\Delta x}{\Delta t}=\frac{x_{i+1}-x_i}{\Delta t}=f(x_i)$$

or,

$$x_{i+1}=f(x_i)\Delta t+x_i \text{ with } x_0=0 \text{ (initial state)}$$

Thus, one can calculate the different x_i and then deduce

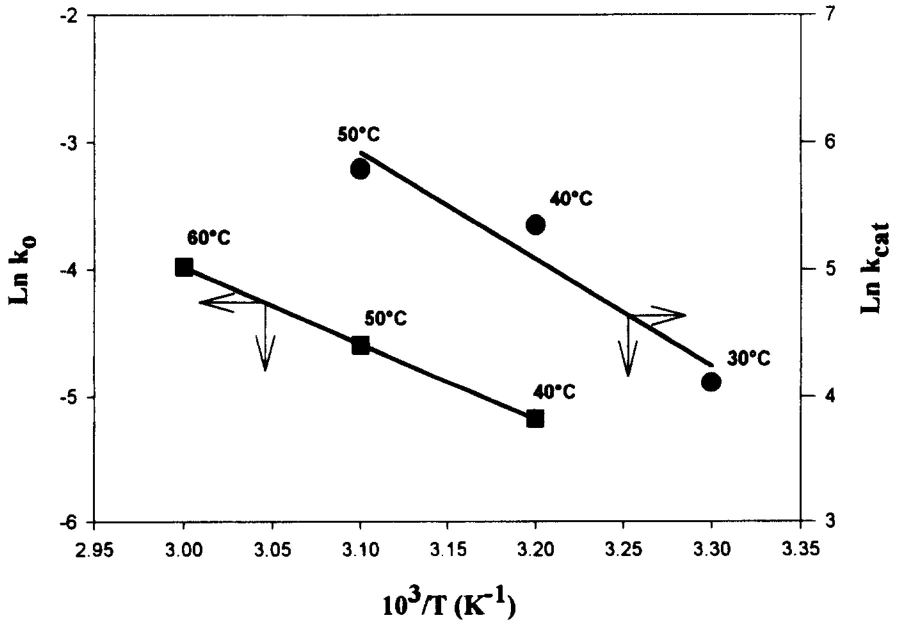


Figure 11 Third order kinetics: Arrhenius plots for PBU2Si/IPTS reaction without (k_0) and with (k_{cat}) catalyst ($[DBTL]=11.8\ 10^{-4}$ mol·kg^{-1})

Table 4 213Third order rate constants without or with catalyst at different temperatures

T (°C)	k_0 (mol^{-2} kg^{-2} min^{-1})	k_u^b (mol^{-2} kg^{-2} min^{-1})	k_{cat}^c (mol^{-2} kg^{-2} min^{-1})	k_u^d (mol^{-2} kg^{-2} min^{-1})
30	0.0025[a]	—	61	0–0.01
40	0.0056	0–0.005	210	0–0.1
50	0.0101	0–0.001	330	0–0.15
60	0.0185	0–0.002	—	—

[a] Calculated from Arrhenius plot.
[b] Without catalyst.
[c] [DBTL] = 11.8 10^{-4} mol·kg^{-1}.
[d] With catalyst.

the conversion at $t_{i+1} = (i + 1)\ \Delta t$:

$$\text{conversion} = \frac{\sum_{j=0}^{i+1} x_j}{a}$$

where a = $[NCO]_0$ is the lowest concentration in our experimental conditions.

Influence of catalyst concentration. This study was carried out at 40°C. From the uncatalysed reaction, we obtained $k_0 = 5.6\ 10^{-3}$ mol·kg^{-1}. Concerning k_{cat}, experimental values are reported in *Table 2*. It is noteworthy that there is a lack of accuracy in the determination of the slopes although the gap between the lowest or the highest values of each slope is narrow.

An average value of $k_{cat} = 210\ mol^{-2}\ kg^{-2}\ min^{-1}$ (close to second order one) was chosen for numerical computation. The limiting values of k_u to obtain the best simulated curves are reported in *Table 3*. Nevertheless, optimisation of k_u leads to different values according to DBTL concentration whereas there is a single value of k_u for a given temperature. Thus, *Table 3* shows that:

- there is no accuracy in the determination of k_u and moreover, in four experiments, it seems that it is not necessary to take this constant into account.
- the results obtained for experiments 1 and 2 are not compatible.
- even if there is a lack of accuracy, we have chosen $k_u = 0.01\ mol^{-2}\ kg^{-2}\ min^{-1}$, which is the best average value. Nevertheless, in *Figure 10*, we can observe a reasonable agreement between experimental points and simulated curves.

Influence of temperature. For each temperature, rate constants are computed as mentioned above. The resulting values are reported in *Table 4*. Experiments without catalyst are relatively accurate but no real variation is observed with increasing temperature. As above, urethane catalysis is not convincing.

Thermodynamic parameters. From Arrhenius plot (*Figure 11*), preexponential factors (A_0 and A_{cat}) and activation energies (E_0 and E_{cat}) lead to the same conclusions as mentioned for second order kinetics:

$$E_0 = 53\ \text{kJ mol}^{-1} \qquad E_{cat} = 63\ \text{kJ mol}^{-1}$$

$$A_0 = 3\ 10^6\ \text{mol}^{-2}\ \text{kg}^2\ \text{min}^{-1}$$

$$A_{cat} = 5\ 10^{12}\ \text{mol}^{-2}\ \text{kg}^2\ \text{min}^{-1}$$

CONCLUSION

Alkoxy silane moities were quantitatively linked on hydroxy telechelic polybutadiene by using isocyanate compounds. In the presence of DBTL as catalyst and at 50°C, the reaction is fast whatever the modification rate is. Kinetic study shows on the one hand that the reaction is entropically controlled and on the other hand that a second order kinetic may explain experimental observations without taking into account an autocatalysis phenomenon.

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