New polyurethanes based on diphenylmethane diisocyanate and 1,4:3,6-dianhydrosorbitol, 1. Model kinetic studies and characterization of the hard segment

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SUMMARY:

1,4:3,6-Dianhydrosorbitol (DAS) seems to be an interesting reagent for the synthesis of polyurethanes. In the present work, the kinetics of the reaction of DAS with a monoisocyanate (*p*-tolyl isocyanate, p-TI) and with a diisocyanate (4,4'-diphenylmethane diisocyanate, MDI) were studied with the help of a chromatographic method (size exclusion chromatography, SEC). When the condensation reaction is performed in tetrahydrofuran (THF) solution, with dibutyltin dilaurate (SnDBDL) as catalyst, DAS exhibits two equireactive hydroxyl groups. The reaction rate can be well described by a second-order equation modified to include catalysis by the formed urethane functions. MDI and DAS were then condensed using two different experimental procedures (bulk and solution polycondensation in THF, in the presence of SnDBDL), and the characteristics of the resulting polyurethanes were compared. Bulk polycondensation led to an amorphous polymer, whereas the polyurethane prepared in solution was semi-crystalline. In both cases, we obtained a very high glass transition temperature (≈ 186°C). The synthesis of samples with various polymerization degrees gave a better understanding of the molecular weight distribution of segmented polyurethanes based on MDI and DAS.

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Introduction

Over the past few years, many studies have been made in the field of polymer synthesis in order to find substitution products for those derived from oil-based chemistry. Among other possible reactants, 1,4:3,6-dianhydrosorbitol (DAS), which has previously been used for its chemical[1)] and pharmaceutical properties, is an interesting candidate: it exhibits chemical and thermal stability[2)], has two hydroxyl groups and is available in industrial quantities from starch. In recent works, this monomer has found application in the synthesis of technical polymers. Thiem and Lüders[3,4)] were the first to report the study of the synthesis and characterization of polyesters deriving from terephthaloyl dichloride and DAS; these polyesters, as well as polyurethanes prepared some time after[5)], exhibited low molecular weights ($\overline{M_n}$ = 3 000). More recent works on polyesters[6,7)], polycarbonates, polyurethanes[7)] and polyamides[8)] mention higher molecular weights.

In this paper, we report the kinetic investigation of the reaction between a model monofunctional aromatic isocyanate, (*p*-tolyl isocyanate, p-TI) and the hydroxyl functions of DAS; the results have been applied to the preparation of polyurethane hard segments based on DAS and a classical aromatic diisocyanate, 4,4'-diphenylmethane diisocyanate (MDI)[a)]. Two polycondensation methods were compared: bulk and solution polycondensation in THF in the presence of little amounts of a catalyst (dibutyltin dilaurate, SnDBDL). The thermal properties of the resulting polymer have then been characterized and compared to those of classical hard segment moieties for segmented polyurethanes.

Experimental part

Materials

1,4:3,6-Dianhydrosorbitol (or isosorbide, DAS) was a gift from Roquette Frères. It was recrystallized from methyl ethyl ketone and then dried in vacuo (0.1 mbar). *p*-Tolyl isocyanate was purchased from Aldrich, whereas 4,4'-diphenylmethane diisocyanate (MDI) was a gift from Bayer AG; both isocyanates were used without further purification. Dibutyltin dilaurate (SnDBDL, Merck) was also used as received.

Kinetic studies

The reactions were carried out in a 500 mL round-bottom flask equipped with a magnetic stirrer and a reflux condenser, under inert atmosphere. DAS (0.05 mol) together with the isocyanate (*p*-TI, 0.05 or 0.1 mol or MDI, 0.05 mol) were dissolved in tetrahydrofuran (THF, 200 mL). The reactor was then placed in a thermoregulated oil bath; after the solution had reached the desired reaction temperature (50°C), the catalyst SnDBDL (0.15 wt.-% with respect to the whole weight of reagents) was added and the corresponding time was taken as the start of the reaction. Samples were pipetted at measured intervals and the *p*-TI or MDI contents were determined by size exclusion chromatography (SEC) using a Waters chromatograph equipped with a 6000 A pump, U6K injector, and 4 microstyragel columns. The eluent was THF, and the peak areas were calculated using refractometric detection (*p*-TI) together with UV detection (λ = 254 nm, for systems based on MDI, since DAS and MDI have the same elution time but DAS does not absorb at this wavelength). Toluene (10 mL) in the case of *p*-TI, and diphenyl in the case of MDI were used as internal standards. The molecular weights were determined using a calibration curve established with polystyrene standards.

[a)] Systematic name: 4,4'-methylenebis(1,4-phenylene) diisocyanate.

Polyurethane synthesis

Bulk polycondensation

In a reactor equipped with a mechanical stirrer and a nitrogen inlet, MDI and DAS were introduced in a stoichiometric ratio. The flask was then placed in a thermoregulated oil bath (temp. = 80℃). When the mixture had reached an adequate viscosity, it was degassed under vacuum with continuous stirring. After 10 min the reacting mixture was poured onto a plate mould which was finally pressed at 200°C (100 bars) for 24 h. The resulting polymer was transparent.

Solution polycondensation

The procedure was the same as that of kinetic studies. Various [NCO]/[OH] ratios were used (7/6, 5/4, 3/2 and 1/1). The reaction was carried out at 50°C in THF with SnDBDL as catalyst. Partial precipitation was often observed. After 3 h, the polymer was precipitated in methanol, filtered and dried under vacuum (0.1 mbar). The resulting polymers are white powders.

Polyurethane characterization

Thermal properties

Melting and glass transition temperatures were determined by differential scanning calorimetry (DSC). Analyses were run on a Mettler TA 3000 apparatus under argon, using a heating rate of 7.5 K/min.

Nuclear magnetic resonance

'H NMR spectra were collected on a Bruker AC 200 apparatus (200 MHz) on deuterated DMSO solutions at 50°C.

Results and discussion

Model kinetic studies

The structure of DAS is shown in Fig. 1[9)]. Its stereochemistry has been described several times[9-12)]; the OH-2 group is in the *exo* position, whereas OH-5 is in the *endo* position on the bicyclic ring system. As both are secondary hydroxyl groups and thus not very reactive towards isocyanates, we chose aromatic isocyanates because of their greater reactivity compared to aliphatic or cycloaliphatic isocyanates.

In the case of DAS, two factors can affect the hydroxyl group reactivity. On the one hand, an intramolecular hydrogen bond between the *endo* hydroxyl group on C5 and the ring-oxygen atom between C1 and C4 can enhance the nucleophilic character of the OH-5 function in comparison with the *exo* hydroxyl group on C2. On the other hand, the steric hindrance decreases the reactivity of the OH-5 group. Because of these different steric surroundings, and although numerous works regarding the reaction between alcohols and isocyanates had already been published, the reactivity of DAS towards a model monofunctional aromatic isocyanate (*p*-TI) was first investigated. The respective reactivities of OH-2 and -5 can actually be very different depending on the co-reactant and on the reaction conditions[10,12-17)].

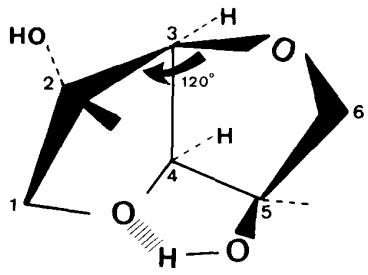
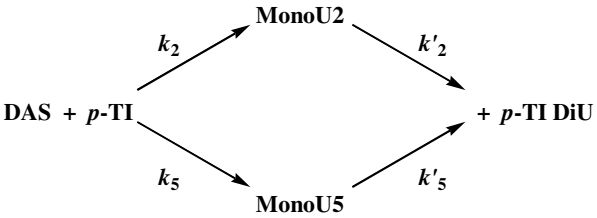


Fig. 1. Spatial structure of DAS (from ref. [9])

The reaction between DAS and p-TI can be described by the following scheme:

Scheme 1: Formation of the diurethane DiU with monourethanes MonoU2 (first reacted hydroxyl group = OH-2) and MonoU5 as intermediates



If the reaction of the first hydroxyl group on the DAS molecule does not modify the reactivity of the second one (i.e. if there is no substitution effect), then $k'_2 = k_5$ and $k'_5 = k_2$. If in addition both functions are equireactive, then $k_2 = k_5$.

Fig. 2 depicts the evolution with time of the SEC chromatograms obtained during the reaction of DAS with *p*-TI (NCO/OH = 1). This technique did not allow to separate the intermediates MonoU2 and 5.

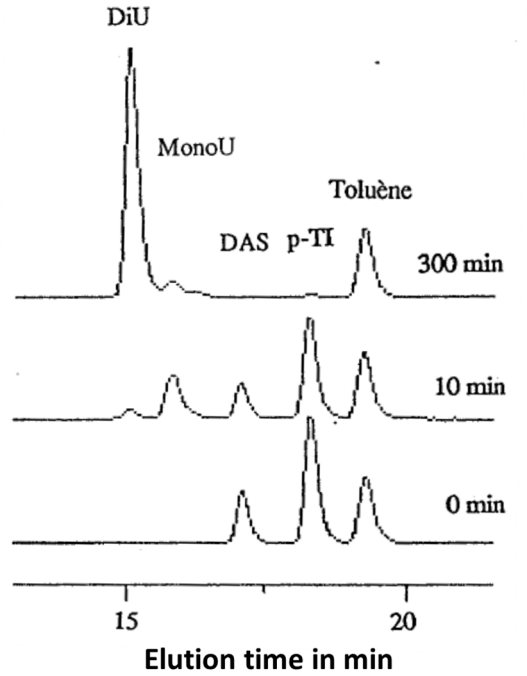


Fig. 2. Various SEC chromatograms obtained during the reaction of DAS with *p*-TI (THF solution, temp. = *50°C,* catalyst = dibutyltin dilaurate) (refractometric detection)

The disappearance of the monomers can be expressed in the following way:

$$X_t = \frac{[\mathrm{DAS}]_t}{[\mathrm{DAS}]_0} \quad ; \quad A_t = \frac{[p\mathrm{-TI}]_t}{[p\mathrm{-TI}]_0}$$

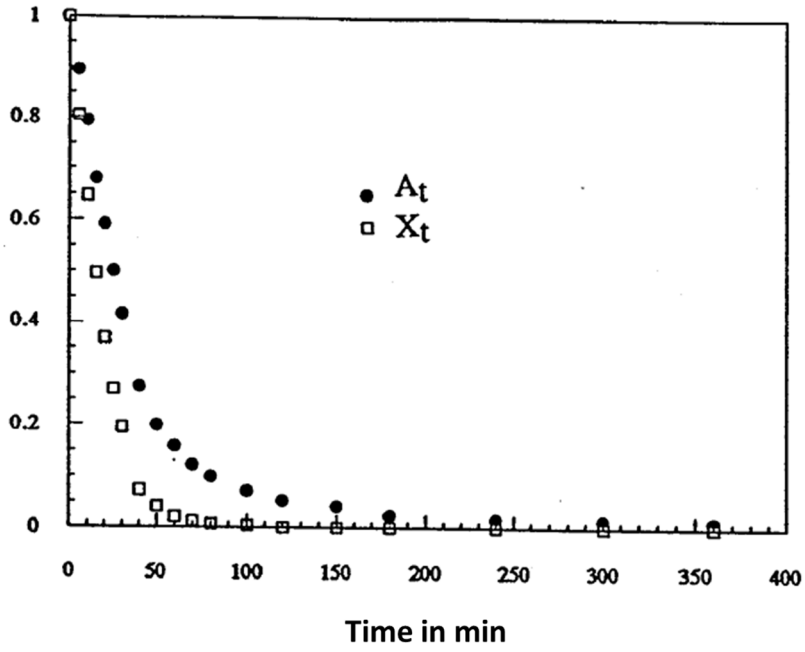


Fig. 3. Decrease in the concentration of DAS and pTI with time at 50°C (THF solution, catalyst = SnDBDL); (●) : $A_t = \frac{[p\mathrm{-TI}]_t}{[p\mathrm{-TI}]_0}$; (□) : $X_t = \frac{[\mathrm{DAS}]_t}{[\mathrm{DAS}]_0}$

where [DAS] and [*p*-TI] stand for the concentrations of the corresponding monomers (dihydroxyl compound and monoisocyanate) expressed in mol/kg; *X* and *A* can be calculated from the areas of the peaks in the SEC chromatograms. Fig. 3 shows the variation of X_t and A_t with time at 50°C in THF; total conversion is reached after about 5 h.

As *p*-TI is a monofunctional monomer, $A_t = \frac{[p\mathrm{-TI}]_t}{[p\mathrm{-TI}]_0} = \frac{[\mathrm{NCO}]_t}{[\mathrm{NCO}]_0}$. As for hydroxyl functions, the probability of finding one non-reacted monomer molecule can be expressed by *P* = *X*. If there is no substitution effect, then *P* is equal to the probability of finding both one non-reacted OH-2 (p_2) and one non-reacted OH-5 (p_5) groups at a time t and can be expressed as:

$$P = p_2 \bullet p_5 = x_{2t} \bullet x_{5t} \text{ with } x_{it} = \frac{[\text{OH-i}]_t}{[\text{OH-i}]_0} \quad ;$$

$$x_t = \frac{[\mathrm{OH}]_t}{[\mathrm{OH}]_0} = \frac{[\text{OH-2}]_t + [\text{OH-5}]_t}{[\text{OH-2}]_0 + [\text{OH-5}]_0} = \frac{1}{2}(x_{2t} + x_{5t})$$

If OH-2 and OH-5 are equireactive, then *P* is more simply equal to the probability of finding two non-reacted hydroxyl functions at a time t, thus to the squared probability of finding one non-reacted hydroxyl function (*p*):

$$P = p^2 = x_t^2 \quad \text{with } x_t = \frac{[\mathrm{OH}]_t}{[\mathrm{OH}]_0} \quad \text{and thus} \quad x_t = \sqrt{X_t}$$

As $[NCO]_0/[OH]_0 = 1$, and if we suppose that only the reactions depicted in *Scheme 1* are involved, then at any time $[OH]_t = [NCO]_t$ and $A_t = x_t$. Fig. 4 compares the decrease in A_t and $\sqrt{X_t}$ with increasing reaction time; the curves are very close to each other, which suggests that in these particular conditions (THF solution, with organotin catalyst) both hydroxyl functions of DAS are actually equireactive.

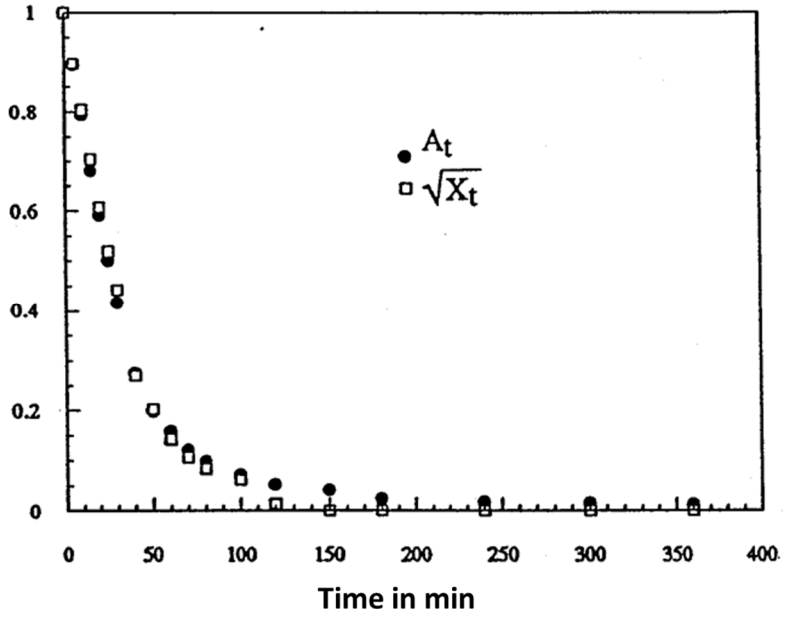


Fig. 4. Comparison between the amount of remaining isocyanate (●) $A_t = \frac{[p-\mathrm{TI}]_t}{[p-\mathrm{TI}]_0}$ and (□) $\sqrt{X_t}$ ($X_t = \frac{[DAS]_t}{[DAS]_0}$) ; (THF solution, temp. = 50°C, catalyst = SnDBDL)

The unexpected equireactivity of the two hydroxyl groups of DAS can be confirmed by ^{1}H NMR spectroscopy. Indeed, this method allows to distinguish DAS, MonoU2, MonoU5 and DiU. Using adequate conditions, an evaluation of the NMR spectrum of a representative reacting mixture allows a quantitative determination of the formed products.

Assuming that DAS (1 mol) is reacted with p-TI *(r* mol), the probability of finding a DAS molecule is still given by:

$$P_{\mathrm{DAS}} = p_2 \bullet p_5 = x_{2t} \bullet x_{5t} = \frac{[\mathrm{OH\text{-}2}]_t}{[\mathrm{OH\text{-}2}]_0} \cdot \frac{[\mathrm{OH\text{-}5}]_t}{[\mathrm{OH\text{-}5}]_0}$$

The probability of finding a MonoU2 molecule is the probability of finding both a non-reacted OH-5 group (p_5) and a reacted OH-2 group ($1 - p_2$)*:*

$$P_{\mathrm{MonoU2}} = p_5 \bullet (1 - p_2) = \frac{[\mathrm{OH\text{-}5}]_t}{[\mathrm{OH\text{-}5}]_0} \cdot \left(1 - \frac{[\mathrm{OH\text{-}2}]_t}{[\mathrm{OH\text{-}2}]_0}\right)$$

and likewise

$$P_{\mathrm{MonoU5}} = p_2 \bullet (1 - p_5) = \frac{[\mathrm{OH\text{-}2}]_t}{[\mathrm{OH\text{-}2}]_0} \cdot \left(1 - \frac{[\mathrm{OH\text{-}5}]_t}{[\mathrm{OH\text{-}5}]_0}\right)$$

Finally the probability of finding a DiU molecule can be written as:

$$P_{\text{DiU}} = \left(1 - \frac{[\text{OH-2}]_t}{[\text{OH-2}]_0}\right) \cdot \left(1 - \frac{[\text{OH-5}]_t}{[\text{OH-5}]_0}\right)$$

In the case of equireactive OH-2 and OH-5 groups, $[\text{OH-2}]_t$ remains equal to $[\text{OH-5}]_t$ all the time. Moreover, $[\text{OH-2}]_t = [\text{OH-2}]_0 \bullet (1 - \frac{r}{2})$, and consequently for equireactive OH groups:

$$P_{\text{DAS}} = \left(1 - \frac{r}{2}\right)^2$$

$$P_{\text{MonoU2}} = P_{\text{MonoU5}} = \frac{r}{2} \cdot \left(1 - \frac{r}{2}\right)$$

$$P_{\text{DiU}} = \left(\frac{r}{2}\right)^2 = \frac{r^2}{4}$$

In our case $r = 1$, hence $P_{\text{DAS}} = P_{\text{MonoU2}} = P_{\text{MonoU5}} = P_{\text{DiU}} = 0.25$. Equal amounts of DAS, MonoU2, MonoU5 and DiU should thus be found by ^{1}H NMR spectroscopy if both OH groups are actually equireactive.

Fig. *5* depicts the useful part of the ^{1}H NMR spectrum of the product of the reaction of 1 mole of DAS with 1 mole of *p*-TI.

As the signals associated with H_3 and H_4 are well separated from the others, they were used for quantitative analysis. The H_3 and H_4 of DAS and DiU could be assigned without ambiguity with the help of DAS and diurethane spectra. As it can be seen in the spectra, substitution shifts the peaks downfield. The respective assignments of H_3 and H_4 were inferred from the fact that H_3 must be represented by a doublet and H_4 by a triplet. In addition, considering the substitution effects, H_4 (MonoU5) must be more deshielded than H_4 (MonoU2) whereas H_3 (MonoU5) must be less deshielded than H_3 (MonoU2).

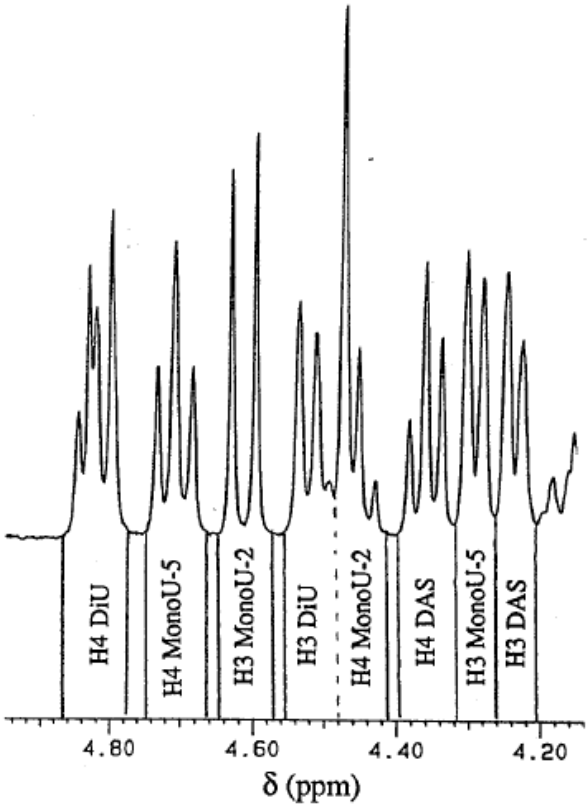


Fig. *5.* ^{1}H NMR spectrum (DMSO-d_6, 200 MHz), of the reacting mixture DAS (1 mole)/*p*-TI (1 mole)

Tab. 1. ^{1}H NMR analysis of the reaction between DAS and *p*-TI (*r* = 1) in catalyzed THF solution (50°C); chemical shifts, assignments and integration of the peaks associated with protons H_3 and H_4

Chemical shifts δ in ppm	Assignments	Integration
4.82	H_4 DiU	7.6
4.52 – 4.44	H_3 DiU + H_4 MonoU2	11.1
4.61	H_3 MonoU2	4.8
4.70	H_4 MonoU5	5.75
4.29	H_3 MonoU5	5.5
4.36	H_4 DAS	4.95
4.23	H_3 DAS	5.2

The signals given by the four products were rather well separated and thus the areas of the various peaks could be compared in Tab. 1.

Although the triplet given by H_4 (DiU) is not well defined, the other peak areas are quite similar; therefore, this NMR analysis leads to the same conclusion as SEC, i.e. that under our conditions (THF solution; catalyst: SnDBDL; 50°C), the hydroxyl groups of DAS are definitely equireactive.

According to the different steric and electronic considerations stated above, this result is rather unexpected. Numerous works regarding DAS esterification actually mention different reactivities for the two hydroxyl groups[10,12-17]. Depending on the reaction conditions, an inversion of the order of reactivity can even be observed. One can thus imagine that appropriate experimental conditions could allow to equilibrate both reactivities: the intramolecular hydrogen bond would activate the OH-5 by increasing the nucleophilicity of its oxygen atom; on the contrary, the Bu_2Sn^{2+} ion, which usually catalyzes the reaction between OH and NCO functions via the formation of a mixt complex, would be almost totally hindered when linked to the OH-5, because of the two oxygen atoms in the vicinity. As shown in Fig. 6, the coordination of the isocyanate function would not be possible in this case, and thus the organotin catalyst would mostly favor the reaction between OH-2 and NCO functions.

In the literature, steric effects in the ternary complexes alcohol-metal-isocyanate have already been proved to induce differences in the catalyst efficiency, due to the geometry of the complex or to the position of the hydroxyl groups[18,19].

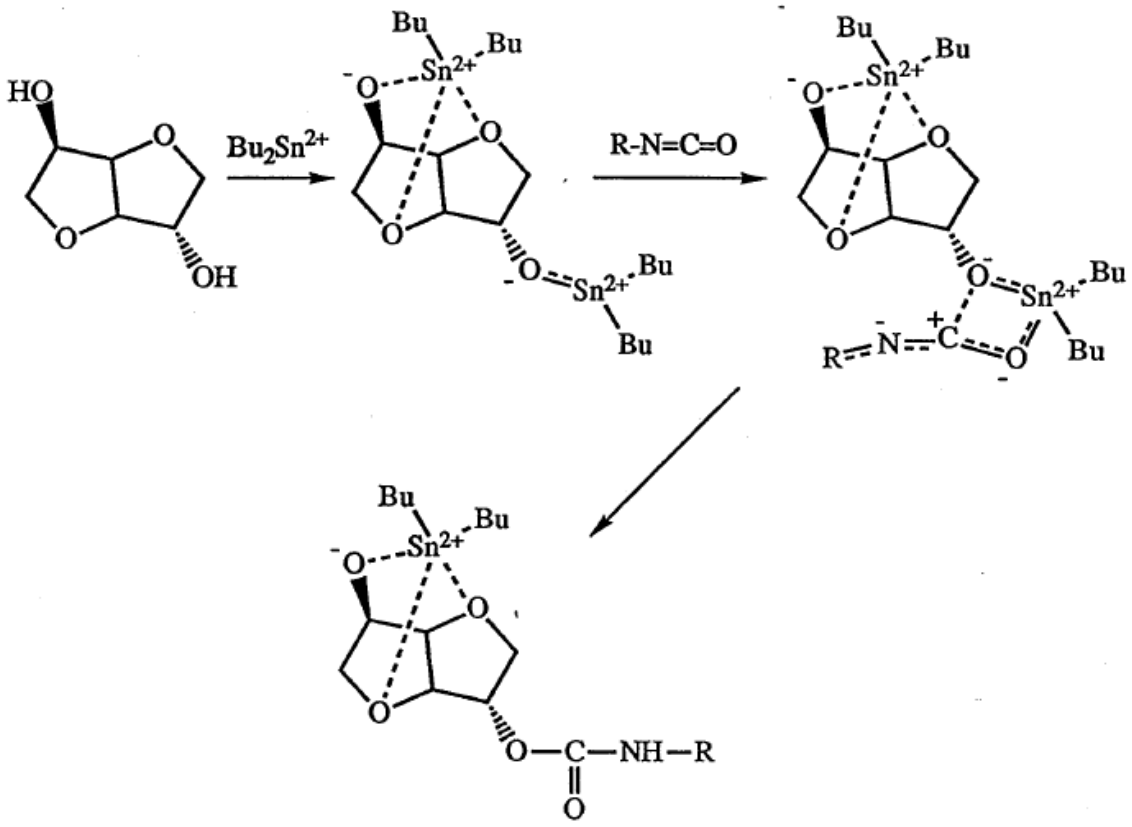


Fig. 6. Possible structure of the DAS-Bu_2Sn^{2+}-isocyanate complex

Kinetic investigation of the polyurethane synthesis

Since isosorbide displays equireactive hydroxyl groups in our experimental conditions (THF solution, SnDBDL catalysis), the kinetic study of the reaction between DAS and 4,4'-diphenylmethane diisocyanate (MDI) becomes easier. For these studies, a 1/1 [NCO]/[OH] ratio was used.

Fig. 7 shows the evolution of the SEC chromatograms with time. The presence of a small peak at a lower elution time indicates that part of the monomers had already reacted at our conventional starting time. Thanks to a standard straight line, we estimated that at this time 8.8% monomer had reacted.

The disappearance of the monomers is depicted in Fig. 8. Both reactants are consumed at the same rate.

Numerous works mention a substitution effect for MDI[20a,b]. The isocyanate groups are sensitive to steric hindrance; and once the first isocyanate function has reacted, the second one is reported to be twice to more than three times less reactive, depending on the alcohol, the catalyst and the temperature.

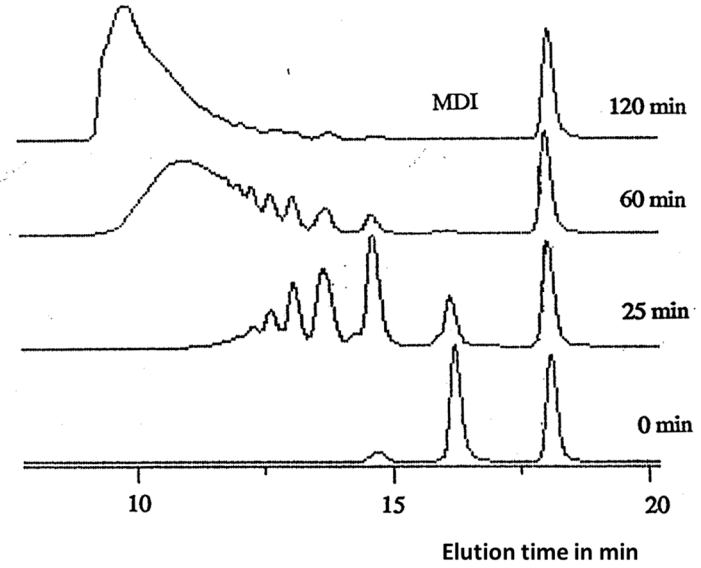


Fig. 7. Evolution of the SEC chromatograms with time during the polycondensation of DAS with MDI (THF solution, temp. = 50°C, catalyst = SnDBDL) (UV detection, λ = 254 nm)

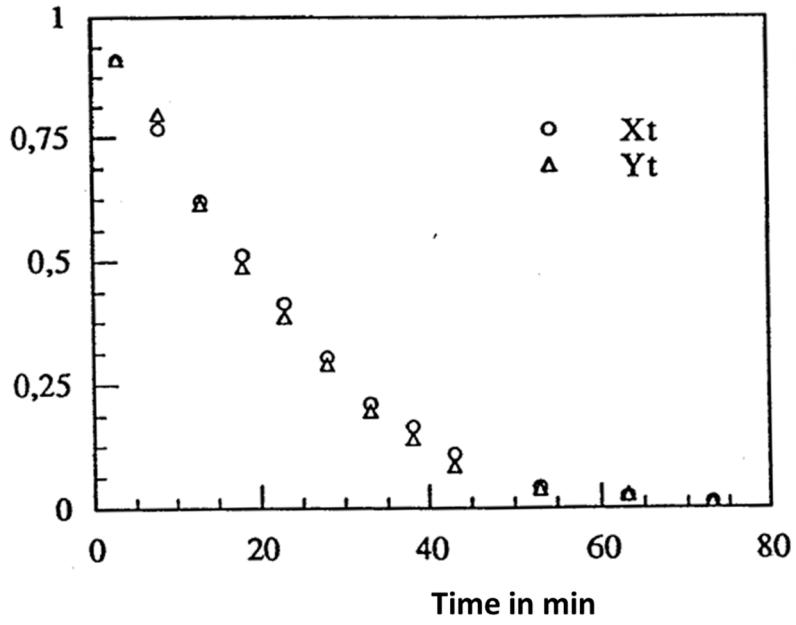


Fig. 8. Decrease in the amount of remaining monomers during the polycondensation of DAS with MDI (THF solution, temp. = 50°C, catalyst = SnDBDL); (○) $X_t = \frac{[DAS]_t}{[DAS]_0}$ and (△) $Y_t = \frac{[MDI]_t}{[MDI]_0}$

The elementary model for the alcohol-isocyanate reaction in the presence of a catalyst was described by Baker[21] as a second-order reaction:

$$-\frac{d[NCO]}{dt} = -\frac{d[OH]}{dt} = k_0 \bullet [NCO] \bullet [OH] + k_c \bullet [cat] \bullet [NCO] \bullet [OH] \quad (1)$$

$$= k \bullet [NCO] \bullet [OH]$$

where $k = k_0 + k_c \bullet [cat]$. Since in our case at any time $[OH]_t = [NCO]_t$, the second order rate constant k can easily be estimated by plotting $1/(1 - \alpha_t) = 1/x_t$ as a function of t:

$$\frac{1}{1-\alpha_t} = \frac{1}{x_t} = k \bullet [OH]_0 \bullet t + 1$$

(α_t is the urethane conversion)

Fig. 9 shows the second-order plot for the reaction between *p*-TI and DAS; the corresponding curve associated with the MDI/DAS system is totally similar. The reaction between DAS and *p*-TI follows second-order kinetics up to x = 58%, and that of DAS with MDI up to x = 70%. Then, the experimental curves exhibit a positive deviation with respect to the second-order straight lines.

Many reactions obey second order kinetics up to a high conversion where a positive or negative incurvation of the experimental data with respect to the theoretical straight line occurs. According to Ephraim[22], the formation of a complex between alcohol and solvent would be responsible for this phenomenon. For example, it is well known that there are most of time interaction s between ethers and alcohols (here between THF and DAS).

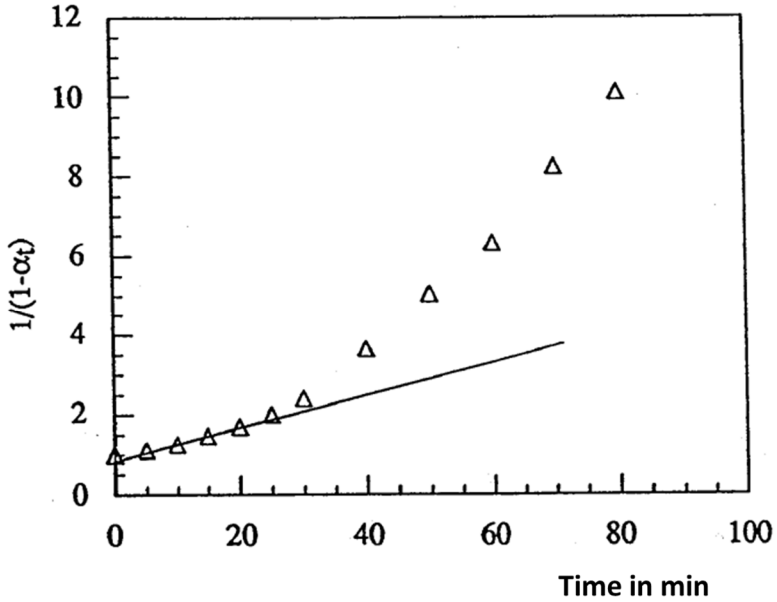


Fig. 9. Application of a second-order kinetic model to the reaction of DAS with p-TI (THF solution, temp. = 50°C, catalyst = SnDBDL); α_t = urethane conversion

However, in order to account more precisely for these deviations, the reaction between alcohols and isocyanates was also studied by Sato[23], who suggested the following kinetic equation:

$$-\frac{d[NCO]}{dt} = k_1 \bullet [NCO] \bullet [OH]2 + k_2 \bullet [U] \bullet [NCO] \bullet [OH] + k_3 \bullet [cat] \bullet [NCO] \bullet [OH]$$

where [U] stands for the concentration of formed urethane and k_1, k_2 and k_3 are the rate constants for the condensation catalyzed by alcohol functions, urethane functions and the catalyst, respectively. In this model, the effects of OH and urethane groups are consequently not neglected any longer.

Eq. 2 can be written in the form:

$$\frac{d\alpha}{dt} = K_1 \bullet (1-\alpha)^2 + K_2 \bullet \alpha(1-\alpha)^2$$

with $K_1 = k_1 \bullet A_0^2 + k_3 \bullet [cat] \bullet A_0$ and $K_2 = (k_2 - k_1)A_0^2$ ($A_0 = [OH]_0 = [NCO]_0$)

K_1 and K_2 can be calculated using Runge-Kutta's method. The results obtained using Eqs. 1 and 3 are expressed in Tab. 2.

Tab. 2. Rate constants for second-order (k, Eq. 1) and third-order kinetics (K_1 and K_2, Eq. 3) for the reaction between isosorbide and *p*-tolyl isocyanate or 4,4'-diphenylmethane diisocyanate

Reactive system	k / min^{-1} (Eq. 1)	K_1 / min^{-1} (Eq. 3)	K_2 / min^{-1} (Eq. 3)
DAS/*p*-TI	$4.16 \cdot 10^{-2}$	$1.12 \cdot 10^{-2}$	$13.53 \cdot 10^{-2}$
DAS/MDI	$1.96 \cdot 10^{-2}$	$0.28 \cdot 10^{-2}$	$13.99 \cdot 10^{-2}$

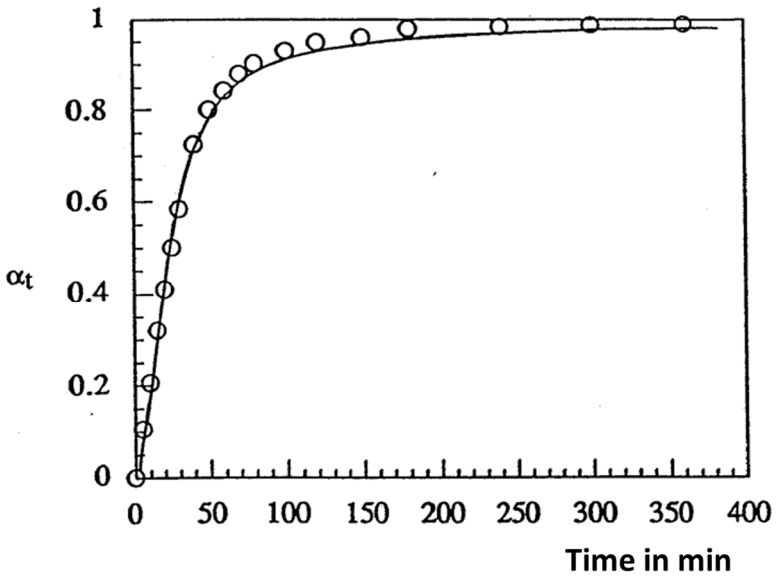


Fig. 10. Simulated (using Sato's equation) (———) and experimental (○) urethane conversion α_t versus time curves for the reaction of DAS with *p*-TI (THF solution, temp. = 50°C, catalyst = SnDBDL)

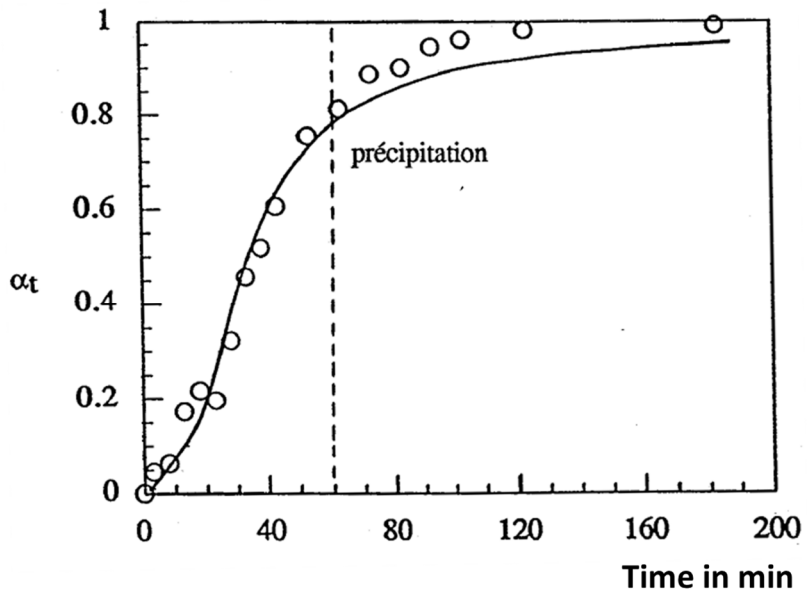


Fig. 11. Simulated (using Sato's equation) (———) and experimental (○) urethane conversion α_t versus time curves for the reaction of DAS with MDI (THF solution, temp. = 50°C, catalyst = SnDBDL)

Fig. 10 shows the experimental and simulated (using Sato's equation) curves for the reaction between DAS and pTI. A reasonable fit of the reaction profile could be achieved with the model. It was established above that this system follows second-order kinetics and then shows a positive deviation, and therefore we can postulate that this deviation is due to the catalytic effect of the formed urethane since the hydroxyl concentration decreases with increasing time.

The corresponding experimental and calculated curves for the reaction of DAS with MDI are shown in Fig. 11. The model fits the experimental curve only up to t = 60 min; afterwards a positive deviation is once again observed. This time happens to be the moment when precipitation of the DAS/MDI polymer in the reactive medium was first observed. It has been demonstrated in the literature that precipitation affects the rate of reactions since it controls the rate of mass transfer of the reactants. Pearson[24] showed that the heterogeneous rate constants in interfacial isocyanate/alcohol polycondensations were higher than those obtained for the homogeneous conditions, although the mechanism was apparently the same; he suggested that the reactant molecules could in some way be more favorably presented at the reaction interface under heterogeneous conditions.

Characterization of polyurethane hard segments based on DAS

- Chemical structure

Fig. 12 shows the ^{1}H NMR spectrum of the polyurethane obtained in solution and recovered by precipitation in methanol. The various chemical shifts and their corresponding assignments are reported in Tab. 3. Due to the dissymmetrical structure of 1,4 : 3,6-dianhydro-2,5 D-sorbitol units, the spectrum is rather complicated. The different chemical shifts have nevertheless all been attributed with the help of previous works about DAS[1,11,12]. The anisotropy of the carbonyl oxy groups induces a

change in the chemical shifts of the protons of DAS once it has been substituted. Small peaks in the H_3 - H_4 region (indicated by asterisks) can be associated with DAS chain ends.

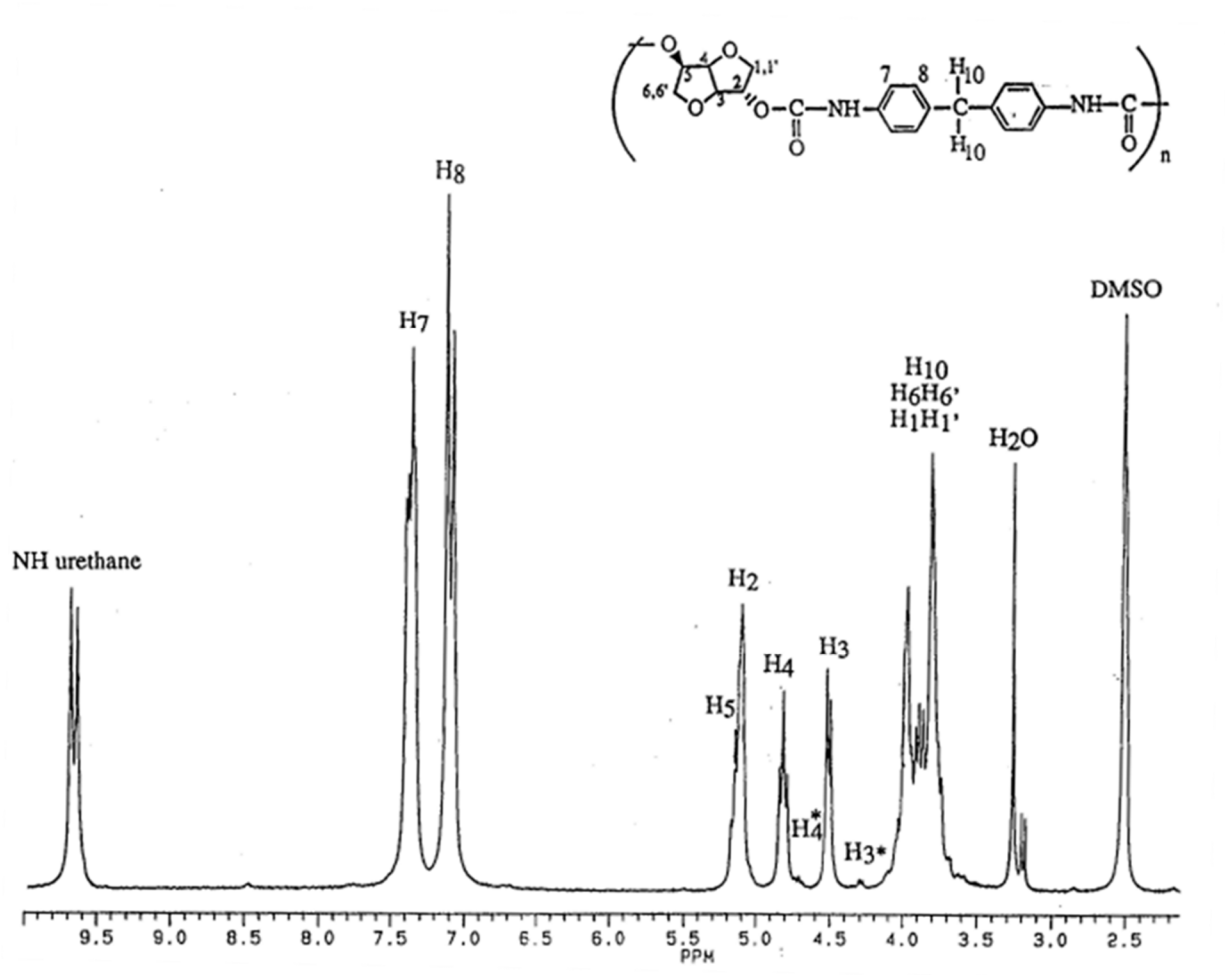


Fig. 12. ^{1}H NMR spectrum (DMSO-d_6, 200 MHz) of the hard segment based on DAS and MDI ($[NCO]_0/[OH]_0$ = 1, solution polycondensation)

- Molecular weight analysis

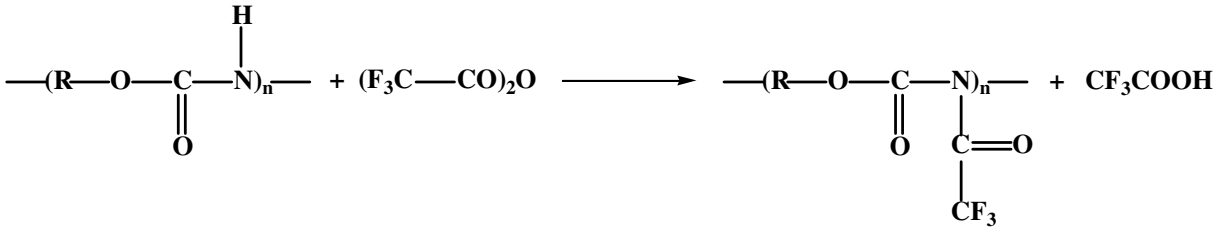
The polyurethane based on MDI and isosorbide is essentially not soluble in THF, a common solvent and eluent for SEC analysis. However, a chemical modification by trifluoroacetic anhydride can be used to improve its solubility. This technique was often applied to semi-crystalline polymers such as polyamides[25,26] and more recently to polyurethanes[27]. Jacobi et al.[25] reported that the reaction was quantitative and reproducible for polyamides, whereas we have shown[27,28] that it was only partial for polyurethanes.

Tab. 3. ^{1}H NMR chemical shifts and their respective assignments for the (MDI-DAS)$_n$ polyurethane synthesized in solution

Chemical shifts δ in ppm	Assignment
2.50	DMSO
3.20	H_2O
3.80 – 4.00	H_1, H'_1, H_6, H'_6 and H_{10}
4.28	H_3* (chain ends)
4.70	H_4* (chain ends)
4.80	H_4
5.10	H_2, H_5
7.11	H_8, H'_8
7.37	H_7, H'_7
9.68	NH (urethane)

The modification was run in a 1% polyurethane solution or suspension in THF, with excess trifluoroacetic anhydride. In the case of polyurethanes, it can be written as:

Scheme 2: Modification of urethane functions with trifluoroacetic anhydride



According to Darud[27], the kinetics and the reaction yield depend on the chemical structure of the polyurethane and on the nature of the solvent. Here the resulting N-trifluoroacetylated polymer is totally soluble in THF. Moreover, this chemical modification was proved to systematically induce a decrease in the apparent molecular weights determined by SEC measurements, as compared to that of the corresponding soluble fractions.

Tab. 4 shows the number-($\overline{M_n}$) and weight-($\overline{M_w}$) average molecular weights obtained for the polyurethanes obtained by bulk (modified polymer) and solution polycondensation.

The higher polydispersity index obtained in solution is probably due to the precipitation during the reaction. Apart from this, no striking difference appears between the two kinds of experimental procedure.

Tab. 4. Number- and weight average molecular weights of (MDI-DAS)$_n$ polyurethanes as determined by SEC analysis (polystyrene standards)

Experimental conditions	$\overline{M_n}$	$\overline{M_w}$	I_p[a)]
bulk	13 000	31 000	2.4
solution	15 000	41 000	2.7

[a)] Molecular weight distribution.

- Thermal properties

The DSC curves obtained with the $(MDI\text{-}DAS)_n$ hard segment are represented in Fig. 13. According to the synthesis procedure, the morphology is totally different.

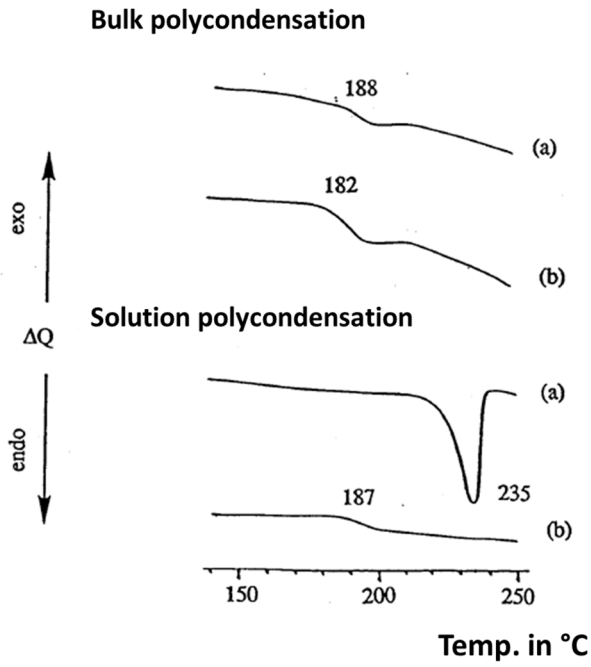


Fig. 13. DSC curves: first scan (a) and second scan (after a quench) (b) of the $(DAS\text{-}MDI)_n$ hard segment prepared in bulk or in THF solution

The polyurethane prepared in solution is highly crystalline at the beginning. It presents a melting endotherm at 235°C on the first DSC curve. However, recrystallization is not observed; the polymer looks amorphous in the second scan. This may result from the proximity of the glass transition (187°C) and melting temperatures. Similar behaviors were observed by Fu et al.[29] on polyurethanes based on 2,4-toluene diisocyanate and 1,4-butanediol; a quench from above glass transition to low temperature at a rate of 10 K/min is sufficient to prevent the polyurethane from crystallizing.

On the contrary, the polyurethane prepared in bulk appears entirely amorphous, even at the first scan. This suggests that as it is commonly observed, crystallization probably occurs during the precipitation of the polymer synthesized in solution, but that it is difficult to obtain crystallization for the bulk sample after a long thermal treatment at 200°C. Quite surprisingly, the T_g of the bulk sample decreases from 188 to 182°C after the first DSC scan. This would indicate some degradation or at least rearrangement of the polymer chains. Such phenomena were observed in the literature for this particular polymer starting from about 230°C, with a maximum degradation rate at 340°C[7] (but in this case the sample, prepared by solution polycondensation in dimethyl sulfoxide, had a much lower glass transition temperature, T_g = 102°C. This latter value is rather surprising since the molecular weights of the sample seem to be close to ours).

In our case, the T_g of this MDI-DAS polymer is remarkably high, probably due to the rigid structure of DAS: it can be compared to the much lower value found for a similar hard segment based on MDI and a softer diol of the same length such as 1,4-butanediol (T_g= 107°C[28], see below). A comparison between rigid polyurethanes obtained with DAS and with various common diols[28] is given in Tab. 5.

Tab. 5. Comparison of the polyurethane hard segment based on MDI and isosorbide with other common hard segments based on commercial diols (from ref. [28]). All polymers were synthesized in solution

Chemical structure	$\overline{M_n}$	$\overline{M_w}$	I_p	T_g/°C	ΔC_p/(J.g^{-1}.K^{-1})	T_m/°C
(MDI-DAS)$_n$	15 000 [a]	41 000 [a]	2.7	187 [b]	0.32	235
(MDI-BDO)$_n$ [c]	24 300 [a]	41 300 [a]	1.7	107 [b]	0.39	198-225-240
(MDI-HQEE)$_n$ [c]	insoluble	insoluble		98 [b]	0.40	215-245
(MDI-CHDM)$_n$ [c]	48 200	91 600	1.9	134 [b]	0.30	190-210
(MDI-NPG)$_n$ [c]	11 600	22 100	1.9	94	0.34	amorphous

[a] Soluble in THF only after chemical modification by trifluoroacetic anhydride.

[b] T_g values obtained after two DSC scans, after an initial scan followed by quenching.

[c] BDO : 1,4-butanediol; HQEE : β,β'-dihydroxyethylhydroquinone; CHDM : 1,4-*cis*/*trans*-dihydroxymethylcyclohexane; NPG : 2,2-dimethyl-1,3-propanediol (neopentyl glycol).

From a general point of view, the glass transition temperature of the polymer obtained with DAS is strikingly above the values associated with all the others. This makes it a particularly interesting candidate for the chain extension of segmented polyurethanes, since the thermal stability of their hard segments would be greatly improved compared to classical systems. Moreover, its melting temperature is not too high (235°C) and this polymer should thus remain processable at reasonable temperatures.

Synthesis of hard segments of differential lengths

Several polyurethanes were synthesized using various NCO/OH ratios (7/6, 5/4, 3/2 and 1/1). Fig. 14 displays typical SEC chromatograms of the samples, before and after their precipitation in methanol. By this technique, the excess MDI is removed from the polyurethane. The chromatograms show that the hard segments prepared in this way are blends of macromolecules of different length. This result is confirmed by the DSC curves depicted in Fig. 15; the different melting endotherms come from the discontinuous distribution of chain length in the sample.

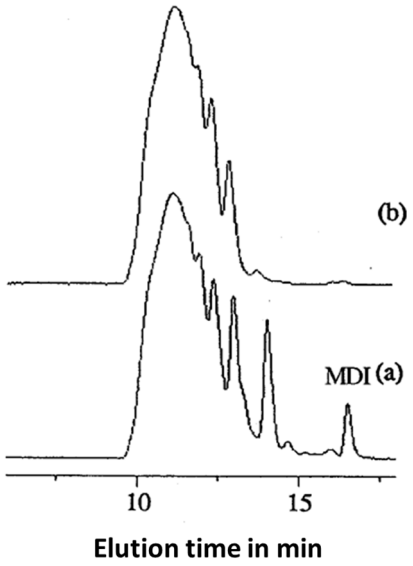


Fig. 14. SEC chromatograms of the crude (a) and precipitated (b) $(MDI\text{-}DAS)_n$ polyurethane prepared in THF solution ($[NCO]_0/[OH]_0 = 3/2$) (refractometric detection)

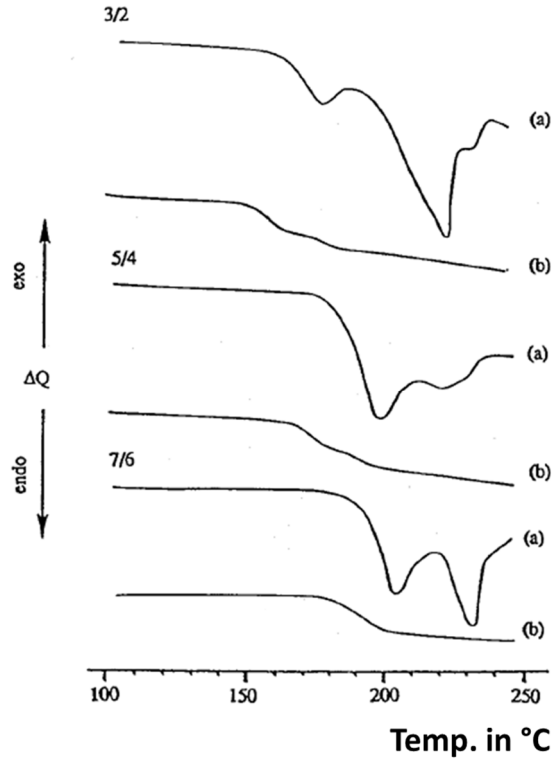


Fig. 15. DSC curves of the MDI-DAS hard segments obtained with various excess amounts of MDI: $[NCO]_0/[OH]_0 = 3/2, 5/4, 7/6$; first scan (a) and second scan (after a quench) (b)

All the molecular weights and T_g values of the various samples are gathered in Tab. 6.

Tab. 6. Characterization of the hard segments obtained from the polycondensation of DAS with various amounts of MDI

NCO/OH	$\overline{M_n}$	$\overline{M_w}$	I_p	T_g/°C
3/2	3 100	4 300	1.4	154
5/4	4 800	10 300	2.1	170
7/6	7 100	13 500	1.9	183
1/1	15 000	41 000	2.7	187

T_g can be plotted versus the inverse of the number-average molecular weight (Fig. 16). A straight line is obtained, which can be described by a relationship analogous to the Fox-Flory relation[30]:

$$T_g = T_{g\infty} - \frac{K}{\overline{M_n}}$$

where $T_{g\infty}$ is the T_g of a hard segment of infinite molecular weight and K is a constant. Here we find experimentally K = 13.1 . 10^4 K and $T_{g\infty}$ = 190°C. This would mean that our solution synthesis with stoichiometric NCO/OH ratio almost allows to reach the maximum T_g.

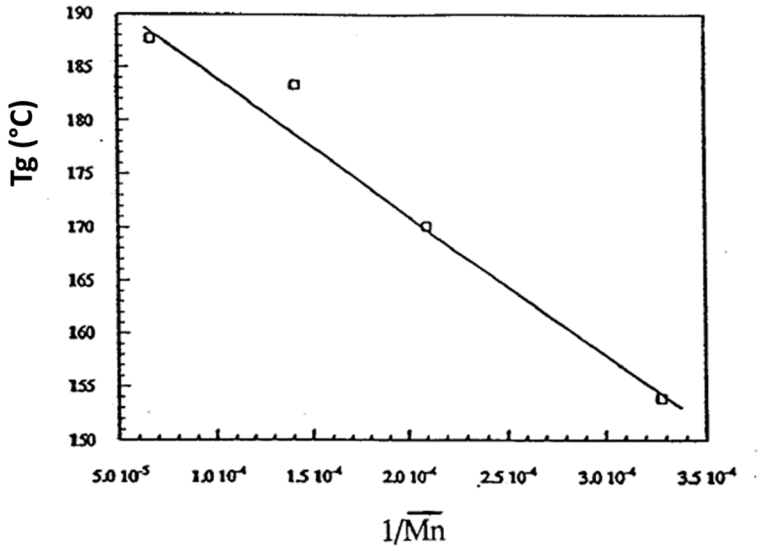


Fig. 16. Fox-Flory plot of T_g versus $1/\overline{M_n}$ for MDI-DAS hard segments of different length

Conclusion

The equireactivity towards isocyanate functions of the two hydroxyl groups of 1,4 : 3,6-dianhydrosorbitol (DAS) in the presence of a catalyst (dibutyltin dilaurate) was established in a model kinetic study with a monofunctional aromatic isocyanate. The results were then applied to the kinetic study of the polycondensation of DAS with 4,4'-diphenylmethane diisocyanate (MDI). The kinetics can be described by a second order equation, modified to take into account catalysis by the formed urethane functions (Sato's equation).

The structure of the (MDI-DAS) polymer was fully characterized by ^{1}H NMR spectroscopy. No particular side reaction was found, except a slight hydrolysis of some isocyanate functions which probably occurred during the recovery of the polymer.

When the reactants were used in stoichiometric ratio (NCO/OH = 1), the average molecular weights of the resulting polyurethane were reasonably high. The value obtained for its T_g was remarkably high: we obtained 187"C, i.e. very close to the value of $T_{g\infty}$ that can be deduced from the measurements on oligomers of different length *($T_{g\infty}$* = 190°C). These results make the (MDI-DAS) hard segment an interesting compound for the preparation of high performance segmented polyurethanes.

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