

¹H Nuclear Magnetic Resonance Study of Polyurethane Prepolymers from Toluene Diisocyanate and Polypropylene Glycol

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ABSTRACT: Polyurethane prepolymers prepared from toluene 2,4-diisocyanate, toluene 2,6-diisocyanate, and polypropylene glycol with a ratio between the isocyanate and hydroxyl groups equal to 2 were analyzed by ¹H nuclear magnetic resonance (NMR) spectroscopy in acetone-d₆. Different temperatures and concentrations were used. Toluene 2,4-dimethylurethane and toluene 2,6-dimethylurethane were synthesized and used as model compounds to assign prepolymer signals. Measurements of spin-lattice relaxation time T_1 by "inversion recovery" experiments were carried out on toluene 2,4-diisocyanate, toluene 2,6-

diisocyanate, toluene 2,4-dimethylurethane, toluene 2,6-dimethylurethane, and polyurethane prepolymers. Differences in T_1 times were used to interpret prepolymer spectra, by means of the strong observed effect on protons due to the presence of adjacent isocyanate groups. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 347–357, 2003

Key words: polyurethane prepolymers; toluene diisocyanate; polypropylene glycol; ¹H-NMR spectroscopy; proton spin-lattice relaxation time

INTRODUCTION

Linear, isocyanate terminated, polyurethane prepolymers prepared from nonequivalent amounts of toluene diisocyanate over polyether glycol are widely used as precursors of the correspondent polymers. Chain-extending reactions with low molecular weight compounds containing different amounts of active hydrogens enable both linear and crosslinked polyurethane to be obtained.

The complete prepolymer characterization by spectroscopic analysis and the knowledge of average molecular weight are very important factors in final polyurethane property prediction.

In recent years many authors have studied polyurethanes in solution by ¹H,¹³C, and ¹⁵N nuclear magnetic resonance (NMR) spectroscopy.^{1–13} Nevertheless, there are few papers reporting on the NMR study of isocyanate terminated polyurethane oligomers^{4,14} and in particular the ones prepared from an excess quantity of commercial toluene diisocyanate (TDI) over polyether glycol. This is probably due to the complexity of the system aroused by the two posi-

tional isomers, toluene 2,4-diisocyanate (2,4-TDI) and toluene 2,6-diisocyanate (2,6-TDI), present in commercial product (usually in the ratio 80:20).

In this work we focused our attention on spectral ¹H-NMR characterization in solution of prepolymers prepared from toluene 2,4-diisocyanate and from toluene 2,6-diisocyanate using polypropylene glycol with a ratio of isocyanate to hydroxyl groups equal to 2. Acetone-d₆ was used in order to improve the spectral resolution in the aromatic region due to sharp signals generated by urethane linkages in this polar solvent, and different prepolymer concentrations were utilized to exclude possible resonance due to the presence of hydrogen bonds between urethane groups. Toluene 2,4-dimethylurethane and toluene 2,6-dimethylurethane were prepared and characterized in the same conditions as model compounds. We also report some considerations on the electronic behavior of two isocyanate groups simultaneously present on aromatic ring, taking into account the chemical shift of aromatic protons. Proton spin-lattice relaxation times T_1 were measured by "inversion recovery" experiments and differences were utilized to interpret ¹H-NMR spectra.

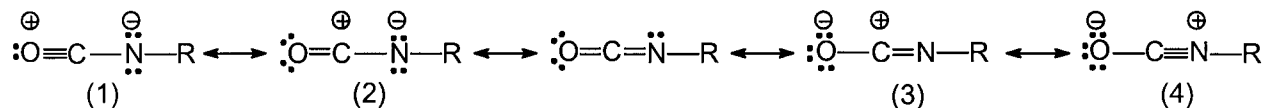
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EXPERIMENTAL

Reagents and solvents

Polypropylene glycol (Voranol 1200 Dow Chemicals, $\langle M_n \rangle = 1230$)¹⁵ was dried by heating at 80°C under



Scheme 1

vacuum for 24 h (amount of residual H_2O about 130 $\mu\text{g}/\text{mL}$, measured by the Karl Fischer method). Solvents were dried over molecular sieves. Toluene 2,4-diisocyanate (Aldrich, 98%) and toluene 2,6-diisocyanate (Fluka, 97%) were used as received.

Sample preparation

Polyurethane prepolymers were prepared using a reagent ratio $[\text{NCO}]/[\text{OH}] = 2$. Reactions were carried out under nitrogen atmosphere, using dried glassware and by means of mechanical stirring. Toluene diisocyanate was added to polypropylene glycol at room temperature and the mixture was heated at 85°C under stirring. Heating was interrupted when half of the NCO groups was consumed (titration with dibutylamine).¹⁶ Toluene dimethylurethane was prepared by the slow addition, at room temperature, of an excess of methanol to a solution of toluene diisocyanate in dry toluene, under magnetic stirring and nitrogen atmosphere. The reaction was carried out overnight. Excess methanol and solvent were removed under vacuum.

NMR experiments

^1H -NMR spectra were recorded on a Bruker AC-300 instrument operating at 300 MHz and at variable temperatures (30 – 50°C). Solutions were prepared under nitrogen atmosphere dissolving the samples in acetone- d_6 (Merck, content $\text{H}_2\text{O} + \text{D}_2\text{O}$: max. 0.02%) in NMR tubes having PTFE/silicone septum caps; about 3% w/v concentrations for prepolymers were used. Toluene diisocyanate and prepolymers spectra were recorded with a time relaxation delay (RD) equal to 60 s.

Inversion-recovery experiments were recorded using successive $[180^\circ - \tau - 90^\circ]$ pulse trains with a delay between each train equal to 120 s for toluene diisocyanate and prepolymers, and equal to 50 s for toluene dimethylurethane. Eight scans for each time τ were used.

To calculate T_1 the following equation¹⁷ was used: $T_1 = \tau_{\text{null}}/0.693$, where τ_{null} is annulment time for the signal generated by the examined proton.

Because of the weakness of urethane hydrogen bonds, in order to obtain reproducible and well-resolved spectra, it was very important to record at a constant temperature.

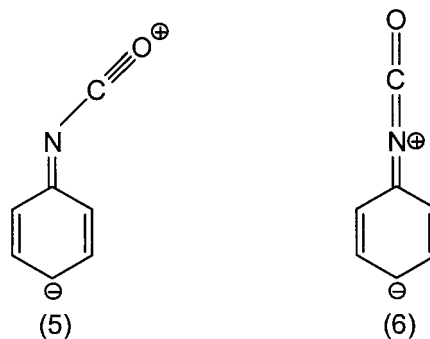
RESULTS AND DISCUSSION

Monomers and model compounds

Isocyanate and urethane electronic effects

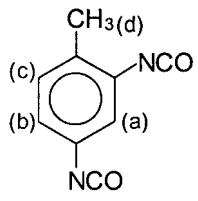
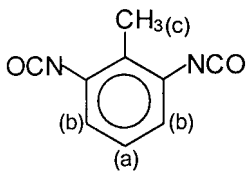
Literature data for monosubstituted benzenes^{19–22} describe the isocyanate group as a rather strong inductive electron acceptor, due to the nitrogen atom electronegativity and as a very weak resonance donor; phenyl isocyanate conjugation energy is reported close to zero. Hammett constants are the following: $\sigma_{\text{para}} = 0.24$ – 0.38 , $\sigma_{\text{meta}} = 0.30$ – 0.43 , $\sigma_{\text{R}} = -0.17$ – -0.40 , which indicate that the isocyanate group is an overall electron-withdrawing substituent. Possible R–NCO mesomeric forms due to internal conjugation²¹ are reported in Scheme 1: some experimental evidence led to the conclusion that structures (1) and (2), having a negative charge on the nitrogen atom, are predominant while the contribution due to form (4), having a positive charge on the nitrogen atom, can be considered negligible. The insignificant mesomeric effect +M in aryl isocyanate can be interpreted on the basis of the poor electron-donating effect from mesomeric structures (1) and (2), possible by the overlapping between the π electronic ring system and the π system of the NCO group (Scheme 2, structure 5). In fact, for phenyl isocyanate it was shown²⁰ that the preferred overlapping is between π electrons of the ring system and the electronic doublet on the nitrogen atom sp^2 orbital (Scheme 2, structure 6).

Moreover, it is well known that the isocyanate group electronic properties are very sensitive to the system to which this group is bonded and can be reversed from donation to acceptance (donor–acceptor character); in *para*-substituted phenyl isocyanate, NCO can interact strongly with the other group.²⁰



Scheme 2

TABLE I
2,4-TDI and 2,6-TDI: ¹H-NMR Chemical Shifts and Relaxation Times *T*₁, Measured at *T* = 30°C in Acetone-*d*₆

		Chemical Shift (ppm)	Time <i>T</i> ₁ (s)
	H _d	2.31	5.8
	H _b	7.01	20.2
	H _a	7.09	46.2
	H _c	7.27	13.6
	H _c	2.32	9.5
	H _b	7.13	28.1
	H _a	7.23	17.3

Therefore, the isocyanate group electronic effect on the aromatic ring in the presence of more than an NCO group is not simply to foresee by any rule.

Because a well-known measure for the charge on a carbon atom is the chemical shift δ of the proton bonded to it (high δ corresponds to low electronic density and vice versa) and taking as reference the chemical shift values for toluene ($H_{ortho} = 7.06$ ppm; $H_{meta} = 7.14$ ppm; $H_{para} = 7.04$ ppm),¹⁸ we evaluated the electronic effects on the aromatic ring of isocyanate and urethane groups in toluene 2,4- and 2,6-diisocyanate and in toluene 2,4- and 2,6-dimethylurethane by chemical shift analysis (Tables I and II).

A shielding effect in the *ortho* and *para* position and a deshielding effect in the *meta* position to NCO substituents were observed. This experimental observation can be interpreted on the basis of a charge density increase in *ortho* and *para* positions to isocyanate groups and a decrease in *meta* position, due to the presence of a mesomeric electron-donating effect (+M) prevailing over an inductive electron-withdrawing effect (-I). This trend was not predictable on the basis of electronic effects reported for phenyl isocyanate (strong -I, very weak +M) and additivity rules.

For the urethane —NHCOO—CH₃ groups a deshielding effect in the *ortho* positions and no significant effect in *meta* and *para* positions were observed. This trend can be interpreted on the basis of a decrease of charge density in *ortho* positions to urethane groups, due to the presence of a strong inductive electron-withdrawing effect (-I) and to a negligible mesomeric electron-donating effect (+M), in accordance with the nitrogen electronegativity and to the possible internal conjugation in the —NHCOO— group.

Temperature effect on urethane protons

Table II shows the chemical shifts recorded at 30 and 50°C for the biurethane model compounds. It can be observed the NH upfield shift with temperature increases, due to the progressive breaking of the strong hydrogen bonds with the polar acetone-*d*₆ solvent.

Relaxation time

The aromatic protons of the two toluene diisocyanate isomers show very long spin-lattice relaxation times,

TABLE II
Toluene 2,4-Dimethylurethane and Toluene 2,6-Dimethylurethane: ¹H-NMR Chemical Shifts at Variable Temperature and Relaxation Times *T*₁, Measured at *T* = 30°C in Acetone-*d*₆

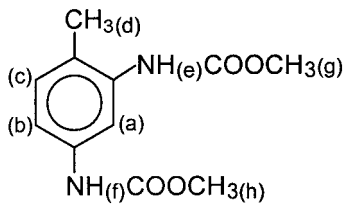
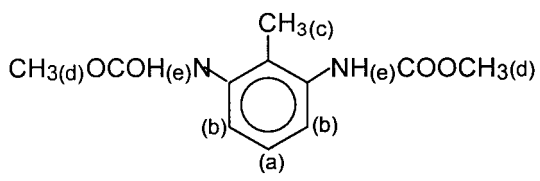
		Chemical Shift (ppm)		Time <i>T</i> ₁ (s)	
		<i>T</i> = 30°C	<i>T</i> = 50°C		
	H _d	2.23	Unchanged	2.0	
	H _g	3.68	Unchanged	4.0	
	H _h	3.69	Unchanged	4.0	
	H _c	7.09	Unchanged	4.9	
	H _b	7.30	Unchanged	5.9	
	H _e	7.74	7.60	4.9	
	H _a	7.78	Unchanged	7.9	
	H _f	8.52	8.36	3.5	
		H _c	2.20	Unchanged	3.2
		H _d	3.69	Unchanged	4.6
H _a		7.14	Unchanged	5.8	
H _b		7.36	Unchanged	8.3	
H _e		7.86	7.70	5.5	

TABLE III
Polypropylene Glycol (Voranol 1200): $^1\text{H-NMR}$ Chemical Shifts, Measured at $T = 30^\circ\text{C}$ in Acetone- d_6

		Chemical Shift (ppm)
$\text{HO} \left[\begin{array}{c} \text{CH}_3(m) \\ \\ \text{CH} - \text{CH}_2 - \text{O} \\ \quad \\ (k) \quad (l) \end{array} \right]_n \text{H}$	H_m	1.13
	$\text{H}_{k,l}$	3.0–4.0

not usual for organic molecules (Table I); the 2,4-isomer presents the following scale: $T_{1 \text{H}_a} > T_{1 \text{H}_b} > T_{1 \text{H}_c}$, where the longest T_1 belongs to the proton H_a placed between the two NCO groups, the shortest to H_c having no adjacent NCO and the intermediate to H_b having one adjacent NCO. The same observation is valid for the 2,6-isomer: $T_{1 \text{H}_b} > T_{1 \text{H}_a}$ due to the proximity of the isocyanate groups. These experimental data indicate the considerable effect of isocyanate groups on the adjoining proton relaxation times, probably due to the scarcity of effective dipolar intramolecular interactions (dipole–dipole) necessary for the relaxation mechanisms (in this case possible only with nuclei having little abundant spin active ^{15}N , ^{13}C , ^{17}O). Even taking into account the methyl groups it is possible to observe that the protons placed between the two NCO groups in the 2,6-isomer have a longer relaxation time than in the 2,4-isomer. In this case, nevertheless, it should be pointed out that for the methyl group relaxation could also take place by means of the mechanism called “spin rotation,”¹⁷ and so T_1 time might be dependent on the more or less hindered rotation of the methyl groups in the two isomers.

The relaxation times of the two toluene dimethylurethane isomers reported in Table II indicate that, compared to isocyanate groups, urethane groups give more effective dipolar interactions with the adjoining aromatic protons and, consequently, a shorter spin–lattice relaxation time. The relation between relaxation times remains the same: $T_{1 \text{H}_a} > T_{1 \text{H}_b} > T_{1 \text{H}_c} > T_{1 \text{H}_d}$ for the 2,4 isomer and $T_{1 \text{H}_b} > T_{1 \text{H}_a}$ for the 2,6-isomer. The longest time T_1 belongs to H_a placed between the two urethane groups in the toluene 2,4-dimethylurethane molecule and so in an unfavorable position for producing intramolecular dipolar interaction and, as a consequence, for producing an effective relaxation mechanism.

These differences in T_1 times were used to attribute aromatic chemical shifts for the species present in isocyanate terminated polyurethane prepolymers.

Polypropylene glycol

Table III shows chemical shifts recorded at 30°C for polypropylene glycol; as it is well known, hydroxy groups in polypropylene glycol are mainly secondary.

Prepolymer from toluene 2,4-diisocyanate and polypropylene glycol

A polyurethane prepolymer synthesis from toluene 2,4-diisocyanate and polypropylene glycol, with a molar ratio equal to 2 between isocyanate groups and hydroxy groups and in the absence of side reactions, involves the formation of four aromatic systems (Table IV): unreacted 2,4-TDI, two chain ends corresponding to structures (1) and (2), and a bireacted, internal, and belonging to the chain repeating unit, structure (3). Regarding the polyether chain [structure (5)], it is necessary to consider separately the oxy-propylene units bonded directly to the urethane groups due to the deshielding effect of the urethane carbonyl groups.

Figure 1 shows the $^1\text{H-NMR}$ prepolymer spectrum in acetone- d_6 , recorded at 30°C with a relaxation delay time (RD) equal to 60 s. Portions of the spectrum relative to the polyether chain, aromatic methyl groups, urethane, and aromatic protons are analyzed separately.

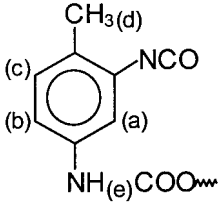
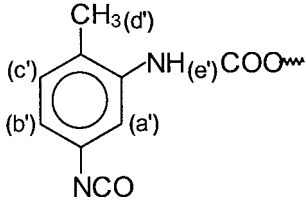
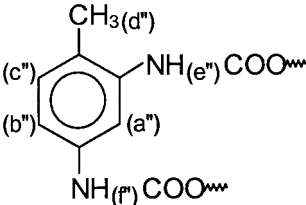
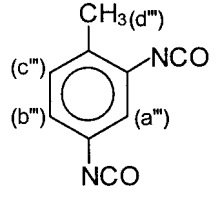
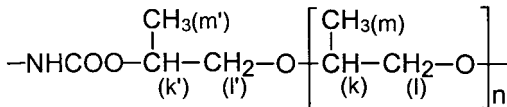
The polyether chain

Looking at the spectra reported in Figure 1, signals at 1.12 ppm (d) and 1.25 ppm (d) are due to the methyl protons belonging respectively to the internal portion of the polyether chain (more abundant) and to the terminal units involved in the urethane linkages; the complex group of signals in the 3.2–3.9 ppm range is due to the methine belonging to the internal units and to the methylene protons; the signal at 4.98 ppm (m) is due to the methine protons involved in the urethane linkages. Effective proton dipolar interactions explains the short spin–lattice relaxation times [Table IV, structure (5)].

Aromatic methyl groups

Figure 1 shows the spectrum expansion between 2.2 and 2.4 ppm: four singlets are present (2.25, 2.28, 2.30, 2.31 ppm; Table IV), the one at 2.28 ppm being much intenser than the other three, which are comparable in intensity. Attributions were given by comparing them with toluene 2,4-diisocyanate and toluene 2,4-dimethylurethane chemical shifts (Table I and II) and on the basis of intensity ratios: signals at 2.31 and 2.25 ppm were assigned, respectively, to structure (4) (2,4-TDI residue; $\Delta\delta = 0$ ppm relating to the spectra of pure compound) and to biurethane species (3) ($\Delta\delta = 0.02$ ppm relating to spectra of model compound toluene 2,4-dimethylurethane); the more intense signal at 2.28 ppm was assigned to methyl protons belonging to the more abundant species (1) (chain ends formed by the more reactive NCO in the *para* position to the methyl group)^{23,24}; the signal at 2.30 ppm was attributed, by exclusion, to methyl protons belonging

TABLE IV
Structures Formed from Reaction of Excess Toluene 2,4-Diisocyanate with Polypropylene Glycol: ¹H-NMR
Chemical Shifts and T₁ Times, Measured at T = 30°C in Acetone-d₆

		Chemical Shift (ppm)	T ₁ Time (s)
 <p>(1)</p>	H _d	2.28	1.3
	H _c	7.17	2.7
	H _b	7.31	2.6
	H _a	7.48	6.9
	H _e	8.59	1.7
 <p>(2)</p>	H _{d'}	2.30	1.7
	H _{b'}	6.87	8.7
	H _{c'}	7.19	3.6
	H _{a'}	7.60	14.8
	H _{e'}	7.83	~2*
 <p>(3)</p>	H _{d''}	2.25	0.7
	H _{c''}	7.09	1.3
	H _{b''}	7.33	1.4
	H _{e''}	7.68	1.1
	H _{a''}	7.83	~2*
	H _{f''}	8.46	0.9
 <p>(4)</p>	H _{d'''}	2.31	5.0
	H _{b'''}	7.01	20.2
	H _{a'''}	7.09	43.3
	H _{c'''}	7.27	13.0
 <p>(5)</p>	H _m	1.12	1.1
	H _{m'}	1.25	0.9
	H _{l,k,l'}	3.2-3.9	1.3
	H _{k'}	4.98	2.0

* No simple determination due to overlapping.

to the species (2) (less abundant chain ends due to NCO minor reactivity in *ortho* position to the methyl group).

Nevertheless, the differences between the chemical shifts are very small (the difference between signals at lowest and highest fields is only 0.06 ppm), and if the attribution of the more abundant species (1) appeared

unequivocal, the attribution of the remaining three could be considered doubtful.

These attributions were confirmed by studies on spin-lattice relaxation times T₁ (Table IV) considering the effect due to the presence of isocyanate groups and considering negligible the effect due to the different mobility at the chain ends (more mobility, longer T₁).

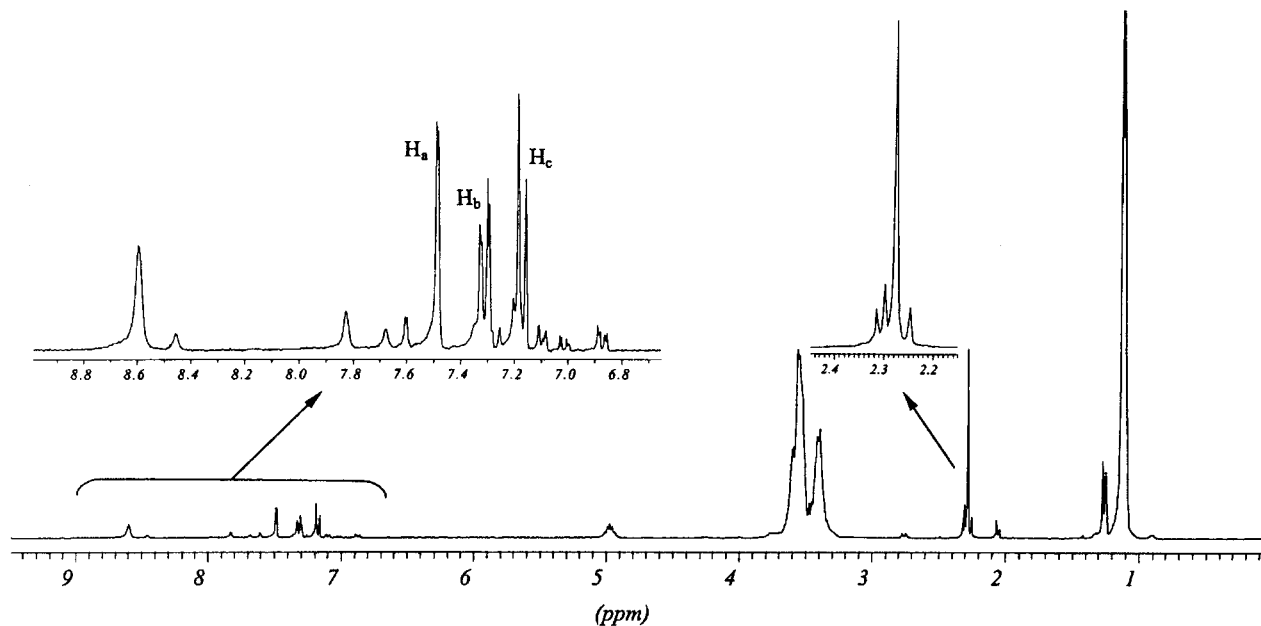


Figure 1 $^1\text{H-NMR}$ of the prepolymer obtained from 2,4-TDI and polypropylene glycol with $[\text{NCO}]/[\text{OH}] = 2$ at $T = 30^\circ\text{C}$ in acetone- d_6 , recorded with delay time $\text{RD} = 60$ s.

Signal at 2.31 ppm attributed to the toluene 2,4-diisocyanate (4) residue in the reaction mixture showed, as expected, the longest relaxation time (5.0 s), a value comparable to that of the methyl group recorded for pure 2,4-TDI (5.8 s); the signal at 2.25 ppm attributed to the biurethane species (3) showed, as expected, the shortest relaxation time (0.7 s; this value is shorter than the value measured for the methyl protons of toluene 2,4-dimethylurethane, probably due to a lesser molecular mobility); signals at 2.28 and 2.30 ppm, attributed to the chain ends (1) and (2), showed intermediate relaxation times (respectively: 1.3 and 1.7 s), as expected due to a NCO group presence and, therefore, to an intermediate relaxing capacity through dipolar interactions.

Urethane protons, concentration, and temperature effects

In order to exclude signals arising because of the presence of inter- and intramolecular hydrogen bonds between the urethane groups,^{5,6} spectra with high (17% w/v) and low (0.5% w/v) prepolymer concentrations were recorded in the same conditions: variations in the number of signals, their position, and integration ratios were not observed. Therefore formation of hydrogen bonds between urethane groups can be excluded for solutions in acetone- d_6 with a concentration lower than 17% w/v and it may be supposed that they occur mainly between NH and solvent.

Figure 1 shows the expansion in the region between 6.6 and 9.0 ppm (spectrum recorded at 30°C). Signals deriving from four urethanic protons are expected in

this area: H_e , $\text{H}_{e'}$, $\text{H}_{e''}$, and H_p belonging respectively to species (1), (2), and (3) (Table IV).

As protons involved in hydrogen bonds are deshielded with a strength decreasing with a rise in temperature due to bonds breaking, it was possible to single out urethane mobile protons from the complex set of signals present in the aromatic region: $^1\text{H-NMR}$ spectra recorded at different temperatures (Fig. 2) showed, as expected, four signals moving to higher fields with temperature increase.

Signals were attributed at 30°C (Table IV) on the basis of chemical shifts determined for the toluene

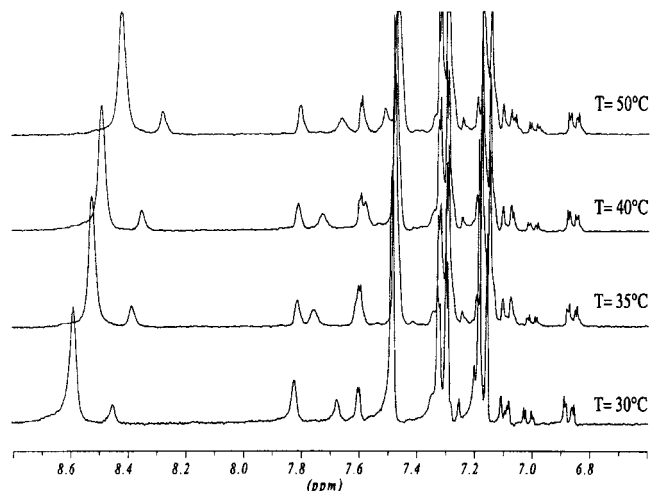


Figure 2 $^1\text{H-NMR}$ of the prepolymer obtained from 2,4-TDI and polypropylene glycol with $[\text{NCO}]/[\text{OH}] = 2$ recorded at variable temperatures in acetone- d_6 : shifts of urethane protons.

2,4-dimethylurethane model compound and on the basis of intensity ratios: the signal at 8.59 ppm was assigned to proton H_e belonging to the more abundant species (1); signals at 8.46 and 7.68 ppm (integration ratio 1:1) were assigned to, respectively, protons H_{e'} and H_{e''} belonging to species (3), considering the shielding effect due to the methyl group in ortho position^{4a}; the signal at 7.83 ppm, was attributed, by exclusion, to urethane proton H_{e'}.

It was possible to confirm this attribution by comparing the differences in T_1 relaxation times and considering the effect due to the major molecular mobility on the chain ends irrelevant. As expected, the following relation of relaxation times was observed (Table IV): $T_{1\text{ He}} \sim T_{1\text{ He}'} > T_{1\text{ He}''} \sim T_{1\text{ H}e''}$ due to the presence of a NCO group.

Aromatic protons

Molecular structures (1)–(4) (Table IV) are trisubstituted aromatic rings in positions 1, 2, and 4; the spin systems is of the type ABC with $J_{(\text{meta})} < J_{(\text{ortho})}$ and $J_{(\text{para})} = 0$ and each structure appears like two doublets and a double doublet.

Observing the aromatic region of the spectra (Fig. 1) it is possible to see three intense signals centered at 7.48 ppm (d), 7.31 ppm (dd), and 7.17 ppm (d) attributed to the more abundant terminal species (1): respectively to H_a, H_b, and H_c (Table IV). Other less intense signals partially superposed are present to which direct attribution could not made immediately.

Attribution were effected by taking into account the chemical shifts determined for toluene 2,4-diisocyanate and toluene 2,4-dimethylurethane model compounds, and using differences in spin–lattice relaxation times T_1 .

Observing at different delay times τ in “inversion recovery” ¹H-NMR experiment (Fig. 3) it was possible to identify the signals related to species (2)–(4) and to determine their chemical shifts. The spectra recorded with time τ equal to 1.7 s clearly showed the spin system related to species (3), which was the only one with positive signals having the shortest T_1 times due to the absence of isocyanate groups. T_1 values were lower than those measured for toluene 2,4-dimethylurethane probably owing to a lesser mobility. Experiment recorded with time τ equal to 2.0 s showed, still with negative signals, the spin systems corresponding to structures (2) and (4), eliminating the superposition with the intense signals at 7.31 and 7.17 ppm signals became positive. The chemical shifts at 7.01 ppm (dd), 7.09 ppm (d), and 7.27 ppm (d) were attributed to the 2,4-TDI residue, by comparison with the values found for pure 2,4-TDI (Table I) and in agreement with the very long relaxation times; consequently, the signals at 7.60 ppm (d), 7.19 ppm (d), and 6.87 ppm (dd) were attributed to species (2). Spin–lattice relaxation times

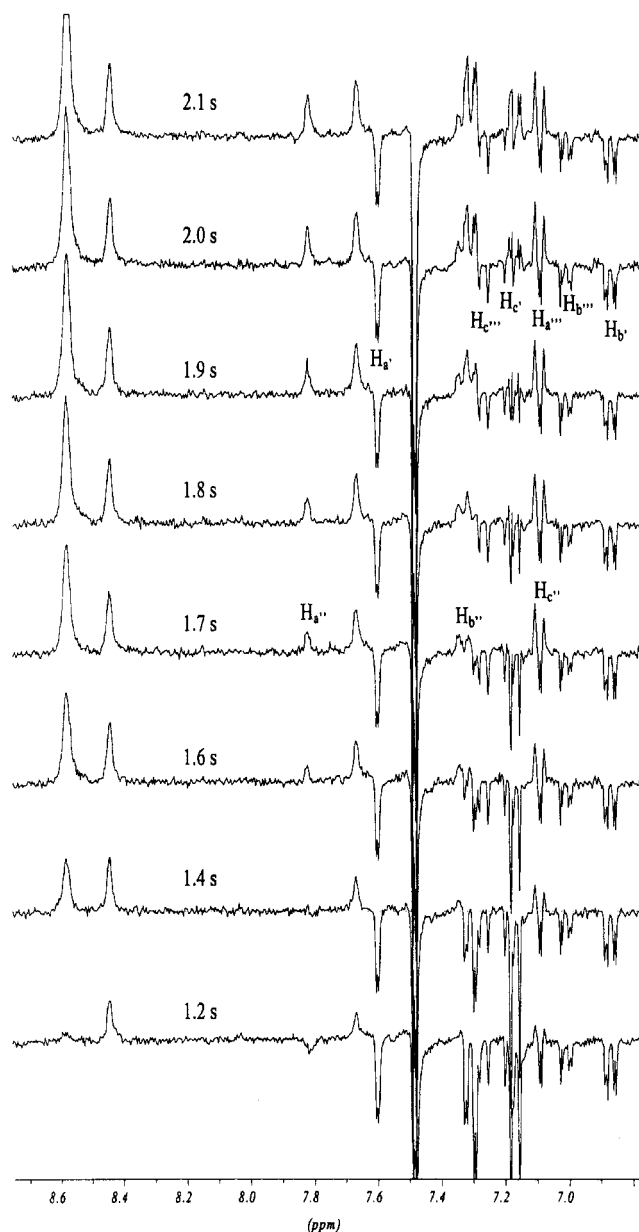
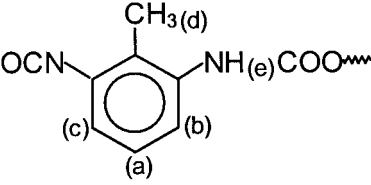
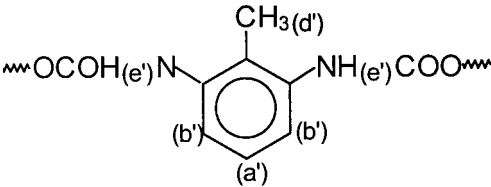
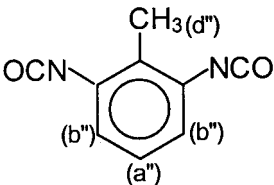
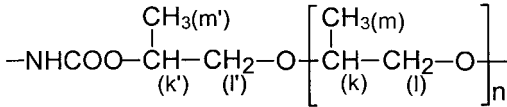


Figure 3 ¹H-NMR inversion-recovery experiment for the prepolymer obtained from 2,4-TDI and polypropylene glycol at $T = 30^\circ\text{C}$ in acetone- d_6 . Delay times τ related to each spectra are reported.

measured for species (2) were intermediate between those of species (3) (shortest) and (4) (longest), in agreement with the presence of an isocyanate group. The complete attribution to each species is reported in Table IV.

The presence of the same adjacent groups does not explain the difference between relaxation times of H_a and H_{a'} in chain end structures (1) and (2). This is probably due to different steric interactions between the methyl groups and the chains in the two species leading to dissimilar accessible conformations, and so to different dipolar interactions in the two species.

TABLE V
Structures Formed from Reaction of Excess Toluene 2,6-Diisocyanate with Polypropylene Glycol: $^1\text{H-NMR}$ Chemical Shifts and T_1 Times, Measured at $T = 30^\circ\text{C}$ in Acetone- d_6

		Chemical Shift (ppm)	T_1 Time (s)
 <p>(1)</p>	H_d	2.28	2.7
	H_c	7.04	9.7
	H_a	7.19	3.7
	H_b	7.50	4.5
	H_e	7.95	2.7
 <p>(2)</p>	$\text{H}_{d'}$	2.23	1.0
	$\text{H}_{a'}$	7.15	2.0
	$\text{H}_{b'}$	7.38	2.2
	$\text{H}_{e'}$	7.81	1.3
 <p>(3)</p>	$\text{H}_{d''}$	2.32	8.7
	$\text{H}_{b''}$	7.13	17.3
	$\text{H}_{a''}$	7.23	—
 <p>(5)</p>	H_m	1.12	1.2
	$\text{H}_{m'}$	1.26	1.0
	$\text{H}_{l,k,l'}$	3.2–3.9	1.2
	$\text{H}_{k'}$	4.98	2.3

Prepolymer from toluene 2,6-diisocyanate and polypropylene glycol

A polyurethane prepolymer synthesis from toluene 2,6-diisocyanate and polypropylene glycol, with a molar ratio equal to 2 between isocyanate groups and hydroxy group and in absence of side reactions, involves the formation of three aromatic systems (Table V): unreacted 2,6-TDI, a chain end structure (1), and a bireacted, internal to the chain, structure (2).

With reference to the polyether chain, the considerations are the same as those made previously: it is necessary to examine separately the oxy-propylene units directly bonded to urethane groups (structure (5)).

Figure 4 shows the $^1\text{H-NMR}$ prepolymer spectrum recorded at 30°C , in acetone- d_6 with an RD equal to 60 s.

The polyether chain

Looking at the spectra reported in Figure 4, there can be observed the intense signal related to the methyl protons internal to the polyether chains at 1.12 ppm (d); at 1.26 ppm (d) the methyl protons belonging to the units directly bonded to the urethane groups; internal methylene and methine protons in the 3.2–3.9 ppm range; methine protons directly bonded to the urethane groups present at 4.98 ppm (m) (Table V).

Short relaxation times measured are due to efficient dipolar interactions.

Methyl groups on aromatic rings

On spectra in Figure 4 there is reported the expansion in the region between 1.9 and 2.6 ppm: three singlets

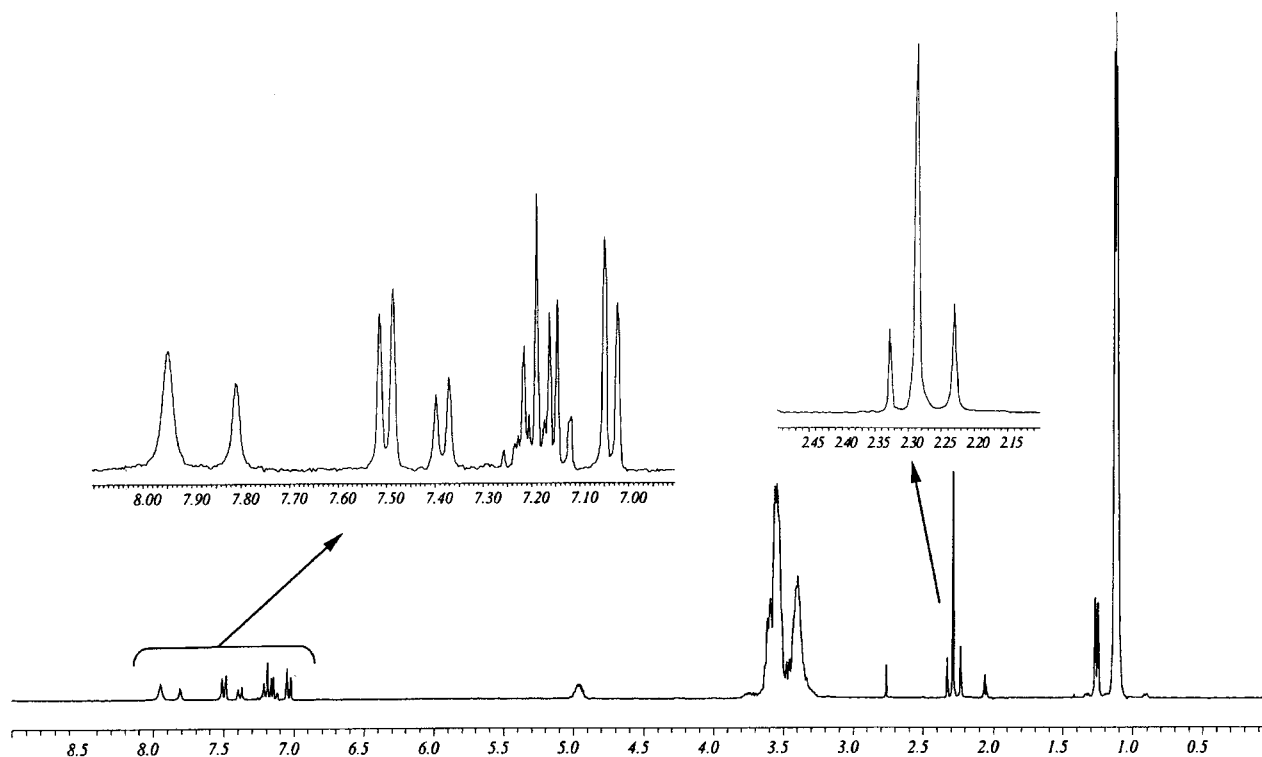


Figure 4 ¹H-NMR of the prepolymer obtained from 2,6-TDI and polypropylene glycol with [NCO]/[OH] = 2 at $T = 30^{\circ}\text{C}$ in acetone- d_6 , recorded with delay time $RD = 60$ s.

are observed in accordance with the three aromatic structures expected in absence of side reactions (Table V).

Attributions were possible by comparison with the chemical shift values obtained from spectra of toluene 2,6-diisocyanate (Table I) and toluene 2,6-dimethylurethane model compounds (Table II), and on the basis of the integration ratios.

The intense signal at 2.28 ppm was attributed to the most abundant chain ends species (1); signals at 2.32 and 2.23 ppm were attributed, respectively, to the toluene 2,6-diisocyanate residue in the reaction mixture ($\Delta\delta = 0$ ppm, relating to the spectra of the pure compound) and to the biurethane species (2) ($\Delta\delta = 0.03$ ppm, relating to the spectra of toluene 2,6-dimethylurethane model compound).

Spin-lattice relaxation times measured (Table V) showed how the methyl protons producing signal at 2.32 ppm and assigned to 2,6-TDI residue, had, as expected, the longest spin-lattice relaxation time (8.7 s, which is close to relaxation times T_1 measured for pure 2,6-TDI: 9.5 s); the signal at 2.23 ppm showed the fastest relaxation time in accordance with the biurethane structure (2); the one at 2.28 ppm, assigned to chain end structure (1), had an intermediate T_1 , in accordance with the presence of an isocyanate group. The relaxation time calculated for the biurethane structure (2) (1.0 s) was lower than the corresponding T_1 of the toluene 2,6-dimethylurethane (3.2 s) model molecule probably due to a minor molecular mobility.

Urethane protons, temperature, and concentration effects

Prepolymer solutions with concentrations of 0.5 and 17% w/v were recorded in the same conditions to exclude the presence of resonances due to inter- and intramolecular hydrogen bond between the urethane groups.^{5,6} Variations in the number of the signals, their position, and integration ratios were not observed: hydrogen bonds, with concentration lower than 17% w/v, are mainly between the urethane protons and the polar solvent acetone- d_6 . The presence of the chain end species (1) and of the species (2) having C_{2v} symmetry (Table V) presuppose the existence of three urethane protons, in which two are homotopic and isochronous.

The identification of the corresponding two signals was very simple due to their mobility: spectra recorded with variable temperature (Fig. 5) clearly showed only two signals moving to high field with temperature increase.

The relative attributions were effected on the basis of integration ratios, with the most intense signal at 7.95 ppm assigned to the more abundant species (1) and the signal at 7.81 ppm assigned to the less abundant species (2) (but corresponding to two protons); the latter attribution was also confirmed by comparison with the value obtained for the NH belonging to the toluene 2,6-dimethylurethane model compound ($\Delta\delta = 0.05$ ppm).

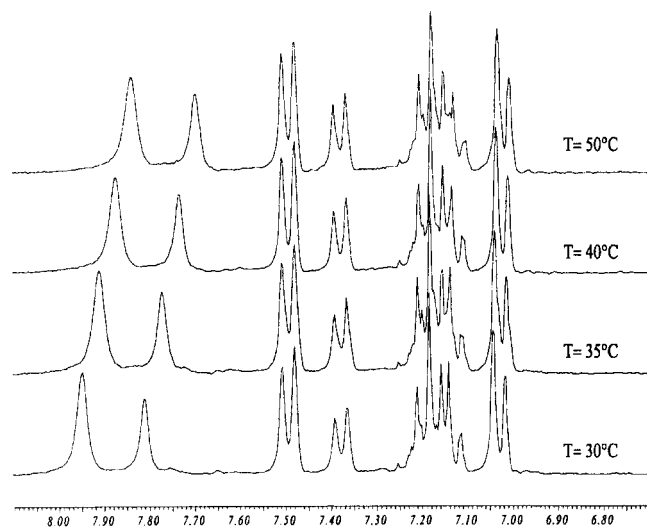


Figure 5 $^1\text{H-NMR}$ of the prepolymer obtained from 2,6-TDI and polypropylene glycol with $[\text{NCO}]/[\text{OH}] = 2$, recorded at variable temperatures in acetone- d_6 : shifts of urethane protons.

Reported spin-lattice relaxation times (Table V) agree with the prediction that the biurethane structure (2) must have the shortest T_1 due to the presence of very efficient dipolar interactions.

Aromatic protons

Signals that must be assigned to the predicted (Table V) aromatic structures (1) (spin-system ABC; one triplet and two doublets), (2) and (3) (spin system AB_2 ; one triplet and one doublets) were observed in the region between 7.00 and 7.55 ppm (Fig. 4). The identification was determined on the basis of a comparison with the chemical shifts obtained for the toluene 2,6-diisocyanate and toluene 2,6-dimethylurethane model compounds (Tables I and II), of the integration ratios [taking in account that the most abundant species must be the chain end (1)], and observing the differences in T_1 times due to the presence of a different number of NCO groups.

In this case, due to the symmetry of systems (2) and (3), it was easy to identify the structure (1) producing three intense signals at 7.50 ppm (d), 7.19 ppm (t), and 7.04 ppm (d) and the two protons H_{b} of the biurethane structure (2) generating the signal at 7.38 ppm (d).

Nevertheless, in the region between 7.10 and 7.28 ppm there is an overlapping between 2,6-TDI protons (3) and proton H_{a} of the biurethane structure (2)

The choice of proper delay time τ in the set of spectra obtained in the "inversion recovery" experiment (Fig. 6) made it possible to resolve this region, and to observe and measure the chemical shifts relating to species (3) and to proton H_{a} belonging to species (2). Spectra recorded with τ equal to 2.9 s showed, still with negative signals due to the longest

relaxation times, the spin system relative to the 2,6-TDI (3) residue in the reaction mixture; it was also possible to observe, still negative, the signal at 7.04 ppm due to proton H_{c} belonging to the terminal species (1) adjacent to a NCO group, and therefore having a longer relaxation time in relation to the other protons of the same species. The spectrum recorded with τ of 11.5 s clearly showed the spin systems (H_{a} , triplet; H_{b} , doublet) corresponding to structure (2), because, at this time, signals relative to toluene 2,6-diisocyanate were practically negligible.

CONCLUSIONS

Polyurethane prepolymers were prepared by reacting toluene 2,4-diisocyanate and toluene 2,6-diisocyanate with polypropylene glycol, using a molar ratio between isocyanate and hydroxyl groups equal to 2.

The products were investigated by $^1\text{H-NMR}$ spectroscopy in acetone- d_6 solution, at different tempera-

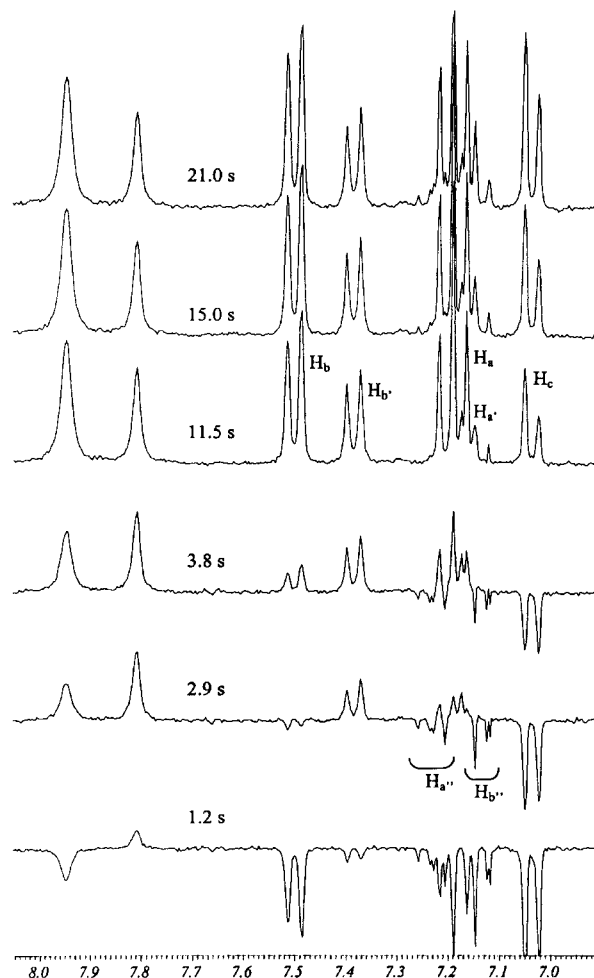


Figure 6 $^1\text{H-NMR}$ inversion-recovery experiment for the prepolymer obtained from 2,6-TDI and polypropylene glycol at $T = 30^\circ\text{C}$ in acetone- d_6 . Delay times τ related to each spectra are reported.

tures and concentrations. Spin-lattice T_1 relaxation times were measured by "inversion recovery" experiments.

"Inversion recovery" experiments and differences in T_1 times allowed us to complete attribution of the signals observed and to resolve some wide overlapping.

Spectroscopic results could be useful in the study of polyurethane TDI based prepolymers having isocyanate terminal groups in order to control the occurrence of secondary reactions.

The individuation of the signals produced by terminal groups as well as the knowledge of T_1 times allow conditions to be chosen for a rapid determination of the numerical average molecular weight by ¹H-NMR.

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