

# Characterization of Oligomers from 1,4-Butanediol and Toluene Diisocyanate

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## SYNOPSIS

Polyurethane oligomers from 1,4-butanediol (BD) and toluene diisocyanate (TDI) with a various excess of BD were synthesized. Their molar masses were measured by gel permeation chromatography and the molar mass distribution correlated with the statistic theory.  $^1\text{H}$ -,  $^{13}\text{C}$ -,  $^1\text{H}$ - $^1\text{H}$ -COSY-, ATP-, and  $^{15}\text{N}$ -NMR spectra of reaction products were recorded, and from the ratio of proton integrals of characteristic terminal and inner urethane groups, the reactivity ratio of the *para* and *ortho* NCO groups in 2,4-TDI was calculated to be approximately 1.8 at a lower excess of BD.  $^{15}\text{N}$ -NMR spectroscopy was found not to be selective enough to detect small amounts of side reactions. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Polyurethanes based on toluene diisocyanate (TDI) are widely used and many works on their morphology and properties<sup>1-5</sup> and some on NMR investigations<sup>6-13</sup> can be found in the literature. However, only few data on reactions with TDI have been published,<sup>14</sup> probably due to the complexity of the system resulting from the presence of two isomers in commercial diisocyanate and to different reactivities of the *ortho* and *para* NCO groups in the 2,4-isomer, which is, additionally, temperature-dependent.<sup>15</sup>

In this work, the synthesis of oligomers from 1,4-butanediol (BD) and TDI with different excess of diol and the characterization of products by  $^1\text{H}$ -,  $^{13}\text{C}$ -, attached proton test (APT)-, homonuclear shift correlation ( $^1\text{H}$ - $^1\text{H}$ -COSY)-,  $^{15}\text{N}$ -NMR, and GPC techniques are presented.

## EXPERIMENTAL

### Materials

Toluene diisocyanate (TDI 80) (Bayer), a mixture of 80% of 2,4-isomer and 20% of 2,6-isomer and 1,4-butanediol (Aldrich) of analytical grade were used.

### Methods

The molar ratios between the diol and the diisocyanate were 2 : 1, 3 : 1, 4 : 1, 5 : 1, and 6 : 1. The samples were weighted and mixed in a dry box and the reaction run at 30°C (temperature of the bath) under a dry nitrogen atmosphere to complete conversion of NCO groups.

For GPC measurements (Perkin-Elmer apparatus), tetrahydrofuran (THF) (1 mL/min), two PLgel columns (pore size 1 and  $5 \times 10^{-8}$  m), and an RI detector were used.

The NMR spectra (Varian VXR 300 spectrometer) were recorded under the following conditions:

- $^1\text{H}$ : spectral width 400 Hz, pulse width 7  $\mu\text{s}$  ( $36^\circ$ );
- $^{13}\text{C}$ : spectral width 16,500 Hz, pulse width 10.7  $\mu\text{s}$  ( $60^\circ$ ), delay time 2 s;
- $^{15}\text{N}$ : spectral width 23,000 Hz, pulse width 30.0  $\mu\text{s}$  ( $64^\circ$ ), delay time 15 s;
- ATP: spectral width 16,500 Hz, first pulse width 10.3  $\mu\text{s}$  ( $60^\circ$ ), second pulse width 15.5  $\mu\text{s}$  ( $90^\circ$ ), first delay time 1.0 s, and second delay time 7.5  $\times 10^{-3}$  s or 1  $\times 10^{-3}$  s;
- $^1\text{H}$ - $^1\text{H}$ -COSY: spectral width 4,000 Hz, first pulse width 11.7  $\mu\text{s}$  ( $60^\circ$ ), second pulse width 17.5  $\mu\text{s}$  ( $90^\circ$ ), delay time 3 s.

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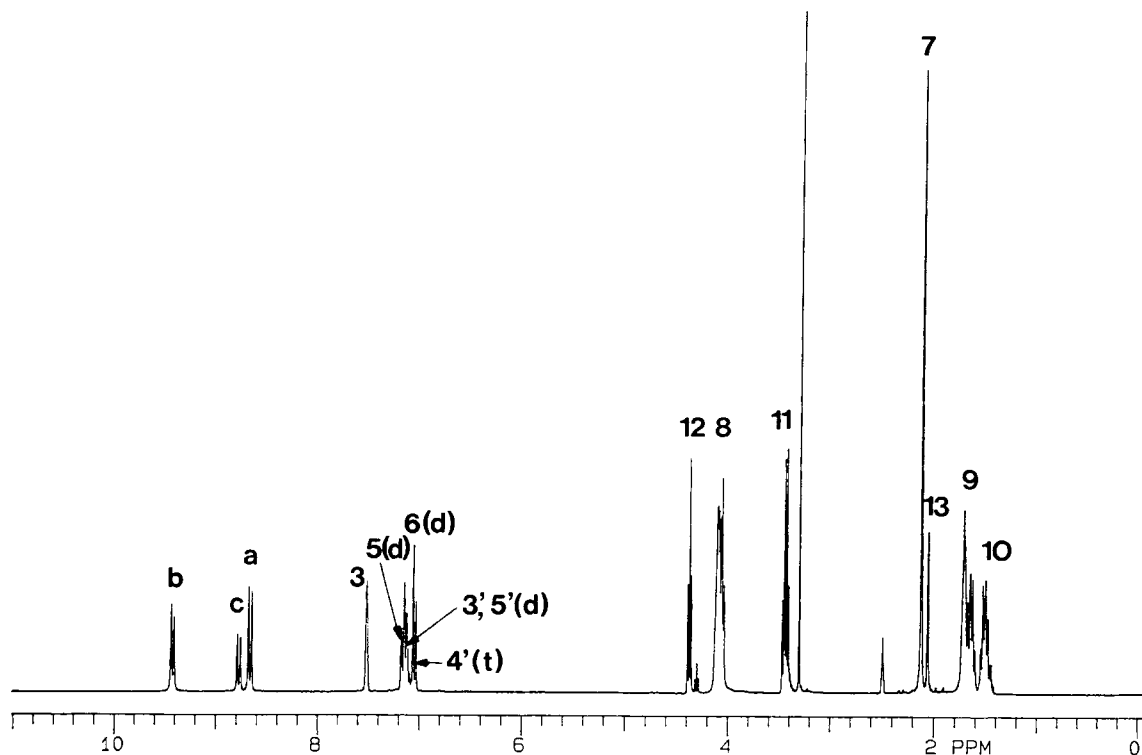


Figure 2  $^1\text{H-NMR}$  spectrum of the system BD : TDI 2 : 1.

In Table I, the calculated statistical [eqs. (2) and (3)] and experimental (GPC measurements) values for  $w_x$  are given. For calculation of the experimental  $w_x$  values, some variations in the way of calculation

and establishment of the calibration curves were made (cases 1-5).

The theoretical molar masses of oligomers were in all cases enlarged for one associated molecule of

Table IV Assignment of the Chemical Shifts in  $^1\text{H-NMR}$  Spectra

Structure	Chemical Shift (ppm)
	1.42-1.57
	1.59-1.75
	2.10
	2.12
	3.40-3.48
	4.01-4.15
	4.27-4.32
	4.32-4.40
	7.03-7.08
	7.03-7.06
	7.12-7.16
	7.10-7.14
	7.10-7.14
	7.50
(terminal) $-\text{NHCOO}-$ (a)	8.65
(inner) $-\text{NHCOO}-$ (a)	8.68
(terminal) $-\text{NHCOO}-$ (c)	8.76
(inner) $-\text{NHCOO}-$ (c)	8.79
(terminal) $-\text{NHCOO}-$ (b)	9.41
(inner) $-\text{NHCOO}-$ (b)	9.43

THF per each OH end group.<sup>18</sup> For drawing the calibration curve in case 1, the experimental points were fitted with a straight line. The point for unreacted BD was not taken into account. In case 2, the experimental points, including the point for unreacted BD, were fitted with a third-order polynomial. In both cases,  $w_x$  values were calculated by the PE Nelson GPC computer program,<sup>19</sup> but far too low  $w_x$  values for unreacted BD and the lowest oligomer ( $x = 3$ ) were obtained.

The disagreement with statistical values was ascribed to the big difference in refractive indices of the two monomers to the solvent, since for TDI, the  $n_D^{20}$  is 1.5693, for BD 1.4452, and for THF 1.4070. As a consequence, a nonproportionality in the detector's response for the two monomers occurs. To obtain a better agreement with theoretical values, modifications of the  $w_x$  calculation (cases 3–5) for the system BD : TDI 2 : 1 were made.

The difference in the detector's response in regard to the number of individual monomer units per molecule of oligomer were overcome as follows:

The chromatogram was split into slices and  $w_x$  calculated using eq. (4)<sup>19</sup>:

$$w_i = \frac{h_i}{\sum h_i} \times \frac{M_i \Delta V}{\Delta M_i} \quad (4)$$

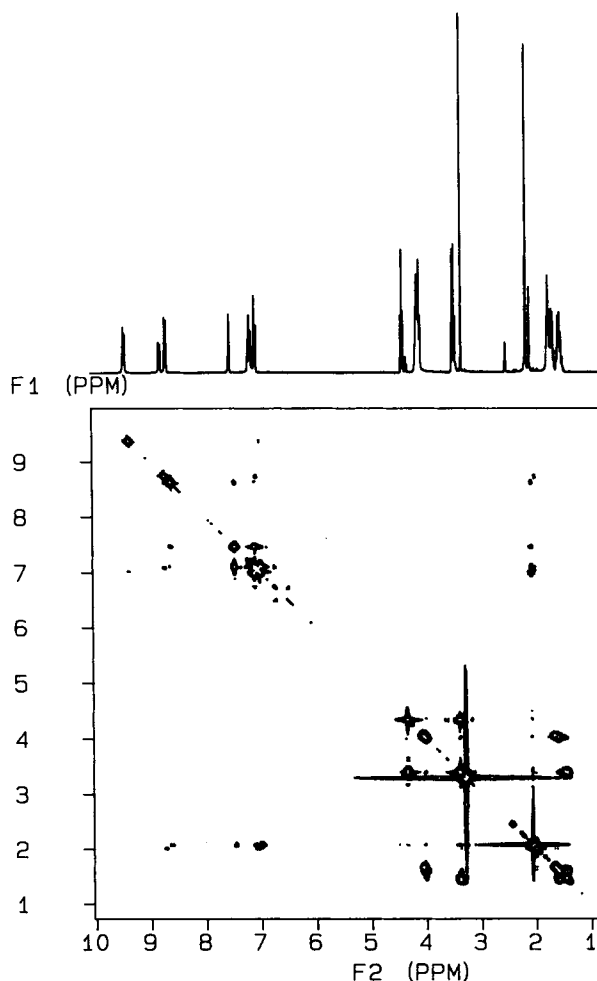
where  $w_i$  is the weight fraction of the single slice;  $h_i$ , the height of the data point;  $M_i$ , the molar mass of the data point;  $\Delta V$ , the change in time or volume per data point; and  $\Delta M_i$ , the change in molar mass per data point.  $h_i$  were corrected with a factor calculated on the basis of the principle of refractive indices additivity: The mass fraction of TDI in the oligomer molecule was multiplied by a correction factor of 4.25, which is the quotient of the refractive index differences between TDI and THF and between BD and THF, the latter taken as unity.

In case 3, the calibration curve from case 1, and in case 4, the calibration curve from case 2 were taken into account. Compared to the statistical values, in case 3, the  $w_x$  value for BD was still nine times, and in case 4, five times too low, but the values for oligomers decreased in the expected way, although there were some deviations from the statistical values. In case 5, the calibration curve from case 4 without the point of unreacted BD was applied.

From Table II it can be seen that for case 4 the best approximation to the statistical values was obtained. Therefore, the  $w_x$  values for other monomer ratios were calculated in the same way and are given in Table I. The approximation is even better, if only

the molar mass distribution of oligomers with  $x \geq 3$  is considered (Table III). For the molar ratios BD : TDI 2 : 1 and 3 : 1, i.e., for the systems with less excess of BD, the agreement is better than for higher molar ratios. In these cases, the calculation using correction factors does not give a satisfactory agreement.

There are more possible explanations for deviation from the statistical values at a high excess of BD: The Flory distribution has not been foreseen for a great excess of one of the components. On the other hand, the theory is valid only in the range of higher molar masses (equal reactivity of end groups); the agreement with the theory is much better in the system studied by Lorenz and Rose,<sup>16</sup> where a polytetramethylene oxide with  $M_n$  2000 was taken as the hydroxy component. In addition, the unreacted BD in samples with a great excess of BD could affect the GPC analysis as well.



**Figure 3**  $^1\text{H}$ - $^1\text{H}$ -COSY-NMR spectrum of the system BD : TDI 2 : 1.

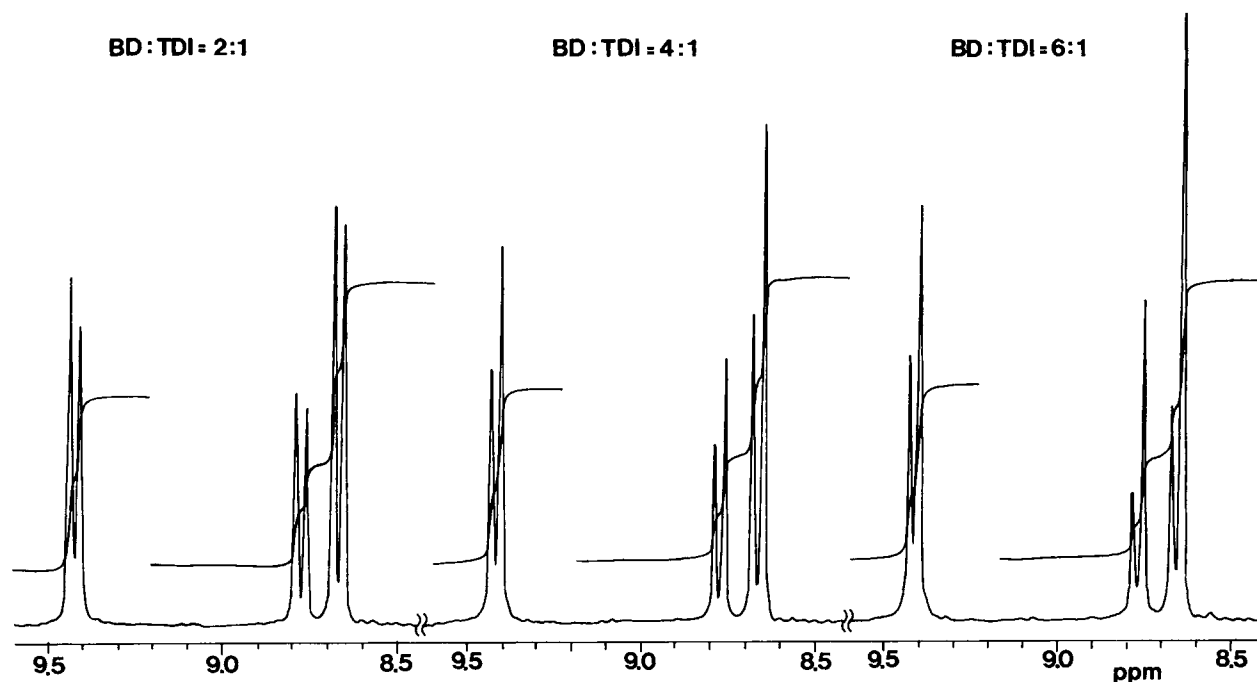


Figure 4  $^1\text{H}$ -NMR spectra of the urethane proton signals at different BD : TDI ratios.

## NMR

The basic assignment of reaction products was made by  $^1\text{H}$ -<sup>1,6,9,11</sup> and  $^{13}\text{C}$ -NMR<sup>2,7,8,10</sup> and the more detailed one by  $^1\text{H}$ - $^1\text{H}$ -COSY<sup>-9</sup> and ATP-NMR. Attention was paid to the chemical shifts of H atoms in equivalent groups in the inner or terminal positions of the oligourethane molecules as a function of the increased amount of BD in the reaction mixture.

In Figure 2, the  $^1\text{H}$ -NMR spectrum of the reaction products of BD : TDI 2 : 1 mixture is given as an example. The detailed assignment of the spectrum is given in Table IV. The signal of  $-\text{CH}_2\text{CH}_2\text{OCONH}-$  at 1.72 ppm increases with an increased excess of BD and is ascribed to the groups at the end of the oligomer molecule, whereas the signal at 1.78 ppm decreases and is ascribed to the inner groups. The two triplets at 4.3 and 4.4 ppm are characteristic for hydroxyl groups, the first

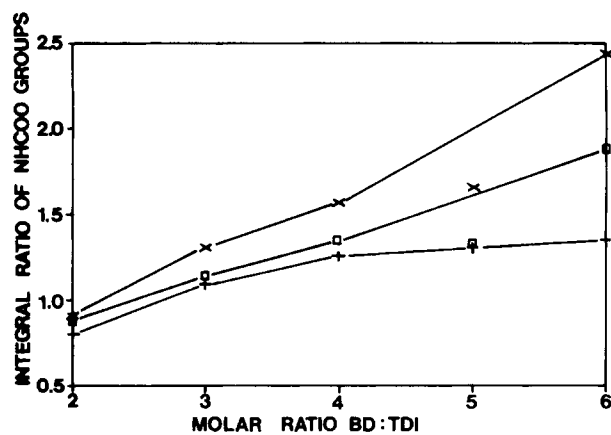


Figure 5 Ratio between proton integrals of terminal and inner ( $t/i$ ) urethane groups in positions a ( $\times$ ), b ( $+$ ), and c ( $\square$ ) vs. BD : TDI ratio.

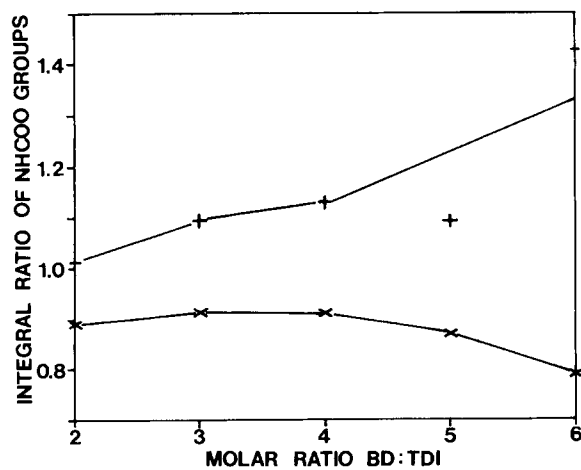


Figure 6 Ratio between proton integrals of  $p$ - and  $o$ -NCO groups in terminal ( $t_{b/a}$ ,  $\times$ ) and inner ( $i_{b/a}$ ,  $+$ ) position vs. BD : TDI ratio.

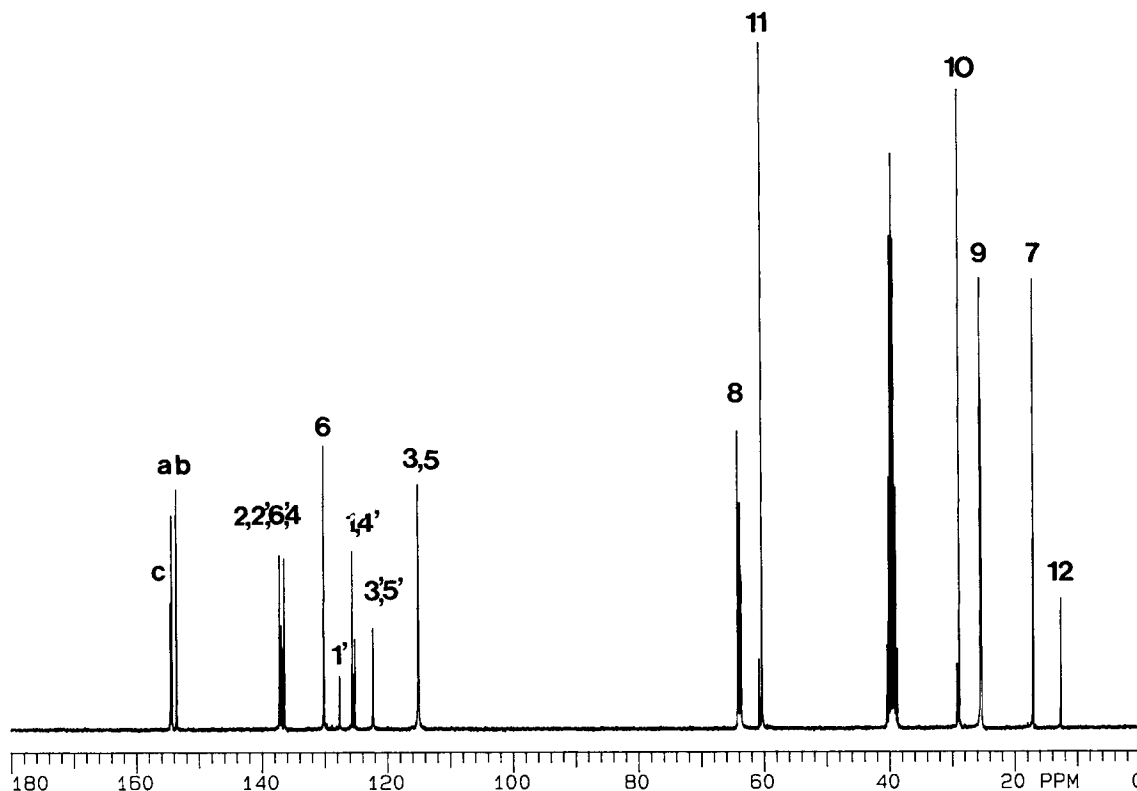


Figure 7  $^{13}\text{C}$ -NMR spectrum of the system BD : TDI 2 : 1.

belonging to the free and the second to the bounded BD, as seen from the couplings in  $^1\text{H}$ - $^1\text{H}$ -COSY spectrum (Fig. 3). From the ratio of integrals of the multiplet at 4.1 ppm ( $-\text{CH}_2\text{OCONH}-$ ) and the protons on the aromatic ring at 7.0–7.6 ppm, the extent of side reactions in all five compositions was estimated to be about 2%. The proton signals in the urethane bonds for the samples with different BD:TDI ratios are shown in Figure 4. The intensity of signals at 8.65, 8.76, and 9.41 ppm increases with an increased excess of BD, and, therefore, these signals are ascribed to the terminal urethane groups, whereas the signals at 8.68, 8.79, and 9.44 ppm are ascribed to the inner urethane groups.

From the spectra of the reaction products, the ratios between terminal (*t*) and inner (*i*) urethane groups in positions a, b, and c as well as the ratios  $t_{b/a}$  and  $i_{b/a}$  in the 2,4-isomer in dependence on the molar ratio between BD : TDI were calculated. From Figure 5, it can be seen that NCO groups in TDI isomers are different in reactivity, i.e., the *o*-NCO groups in 2,4-TDI are the least reactive, both *o*-NCO groups in 2,6-TDI are, on average, more reactive, whereas the *p*-NCO groups in 2,4-TDI are the most reactive. The quotient at the lower excess of BD is

1 : 1.2 : 1.4. The reactivity ratio of the *para* and *ortho* NCO groups in 2,4-TDI is—calculated from the ratio of urethane groups in terminal and inner positions (Fig. 6)—at a lower BD : TDI ratio, on average, approximately 1.8, and increases with the increasing excess of BD.

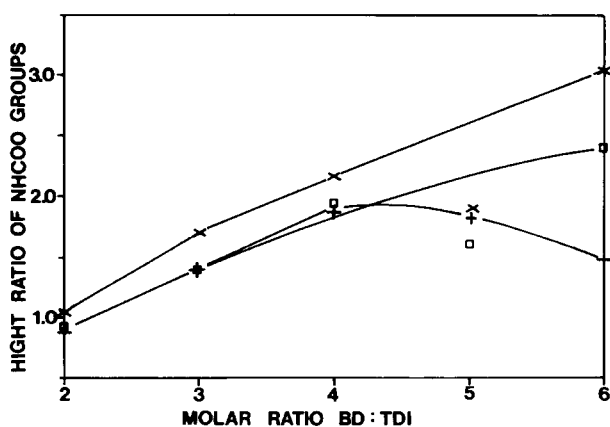
The  $^{13}\text{C}$ -NMR spectrum of the reaction product of BD : TDI 2 : 1 composition is presented in Figure 7 and a detailed assignation is given in Table V. Similarly, as in  $^1\text{H}$ -NMR spectra, an increase of terminal signals in the case of greater excess of BD can be observed. Again, the ratios of heights of the signals in the end and inner positions were estimated, showing a greater reactivity of NCO groups in the *para* position (Fig. 8). The calculated ratio values cannot be considered as quantitative due to too short a delay time during measurements (2 s) in comparison to the relaxation time of observed C atoms [1.987 s (*i*) and 2.559 s (*t*) for  $\text{C}_a$ ; 1.822 s (*i*) and 2.235 s (*t*) for  $\text{C}_b$ ; 2.037 s (*i*) and 2.639 s (*t*) for  $\text{C}_c$ ]. The signals of C atoms in the aromatic ring from 115.0 to 137.2 ppm were assigned by the ATP spectrum (Fig. 9).

In the  $^{15}\text{N}$ -NMR spectrum of the BD : TDI 2 : 1 system, two signals are present (Fig. 10), the signals

**Table V** Assignment of the Chemical Shifts in  $^{13}\text{C}$  NMR Spectra

Structure	Chemical Shift (ppm)	
	Observed	Predicted
$\text{C}_{12}$	12.5	19.8
$\text{C}_7$	16.9	19.8
$\text{C}_9$	25.2-25.4	25.6
$\text{C}_{10}$ (bounded BD)	28.8	29.4
$\text{C}_{10}$ (free BD)	28.9	29.4
$\text{C}_{11}$ (bounded BD)	60.3	63.0
$\text{C}_{11}$ (free BD)	60.4	63.0
$\text{C}_8$	63.6-64.1	65.4
$\text{C}_3$	114.9	108.8
$\text{C}_5$	114.9	112.5
$\text{C}_{5'}$	122.2	112.5
$\text{C}_{3'}$	122.2	112.5
$\text{C}_{4'}$	125.5	125.3
$\text{C}_1$	125.6	121.8
$\text{C}_{1'}$	127.5	117.5
$\text{C}_6$	130.0	129.0
$\text{C}_4$	136.4	136.2
$\text{C}_{2'}$	136.8	139.9
$\text{C}_{6'}$	136.8	139.9
$\text{C}_2$	137.1	139.9
(inner) $\text{C}_b$	153.4	157.8
(terminal) $\text{C}_b$	153.5	157.8
(inner) $\text{C}_a$	154.2	157.8
(terminal) $\text{C}_a$	154.3	157.8
(inner) $\text{C}_c$	154.4	157.8
(terminal) $\text{C}_c$	154.5	157.8

of the *ortho* (281.6 ppm) and *para* (277.0 ppm) urethane groups being in the ratio 3.4 : 1. The signals of the inner and terminal urethane groups are not resolved. Because of the small signal-to-noise ratio,



**Figure 8** Ratio between carbon resonances heights of terminal and inner (*t/i*) urethane groups in positions a ( $\times$ ), b (+), and c ( $\square$ ).

the signal of the few urea groups resulting from side reactions cannot be detected under specified conditions. These groups could be measured only if more than 5 wt % of water was added to the reaction mixture. Therefore, the method could not be used for the detection of small amounts of side reactions.

## CONCLUSIONS

The oligomer composition formed in the urethane reaction between BD and TDI with a various excess of diol was determined by GPC using an RI detector. Because of a great difference in refractive indices between both monomers and solvent, the quantitative determination of the MWD values ( $w_x$ ) was not in agreement with the statistical values. Better agreement was achieved by the modification of the calculation method, taking into account the difference in the detector's response, although the calculated  $w_x$  for unreacted BD still remained lower than the statistic ones.



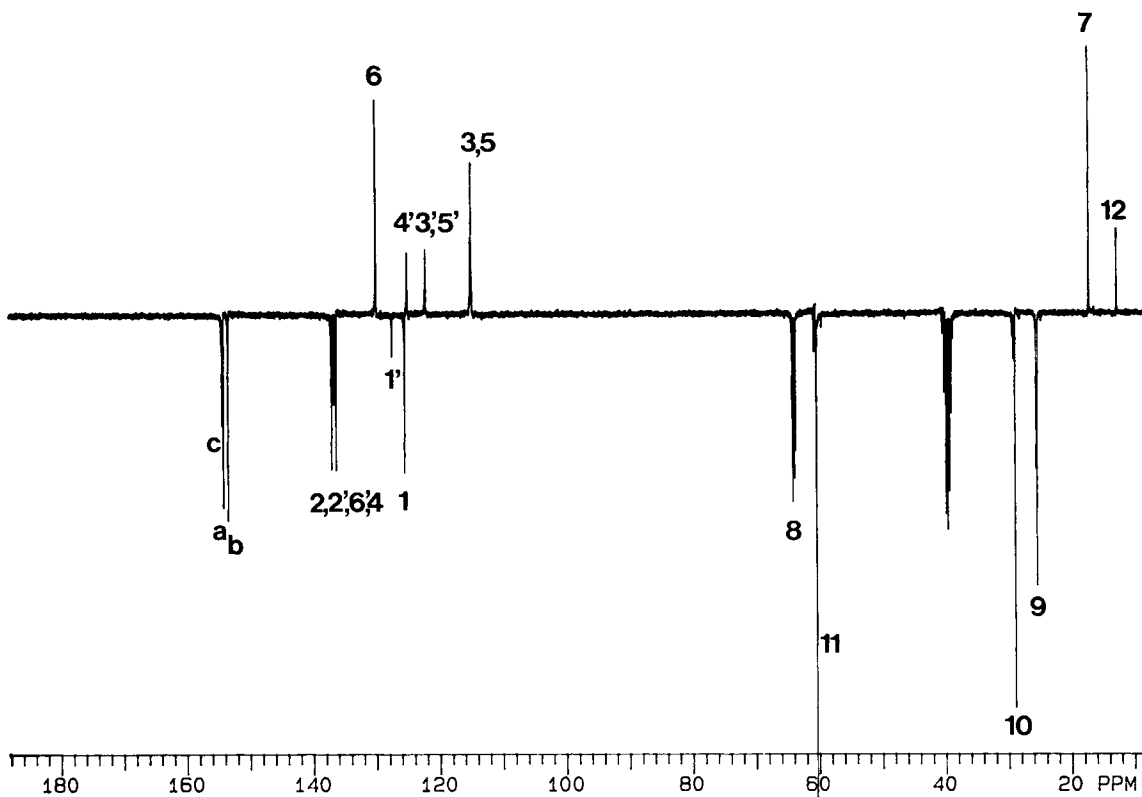


Figure 9 APT-NMR spectrum of the system BD : TDI 2 : 1.

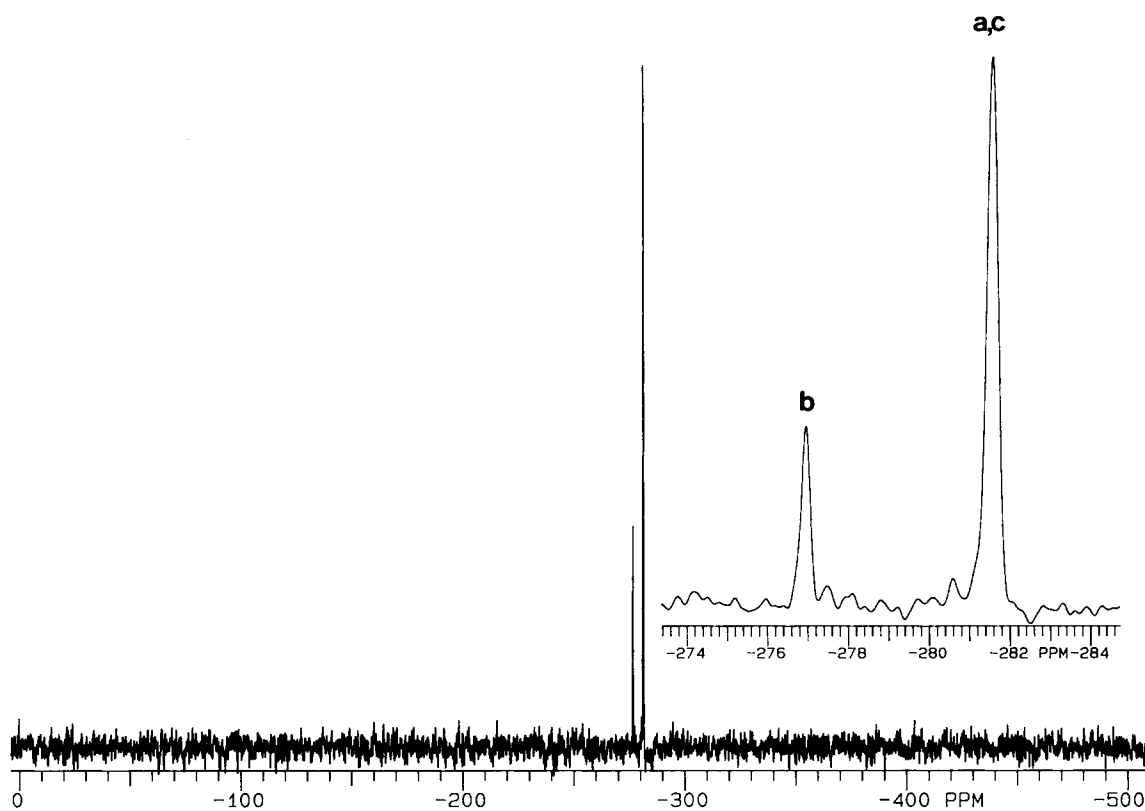


Figure 10 <sup>15</sup>N-NMR spectrum of the system BD : TDI 2 : 1.

By  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy, the signals of characteristic groups in inner and terminal positions of the oligomers could be resolved. From the spectra of reaction products, it was calculated that in 2,4-TDI at the selected reaction conditions *p*-NCO groups are approximately 1.8 times more reactive than are *o*-NCO groups. The  $^{15}\text{N}$  spectroscopy was not sensitive enough to detect small amounts of side reactions.

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