Study of the Reaction between Ethylene Glycol or 1,2-Propylene Glycol with Diphenylmethane. 4,4'-diisocyanate

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ABSTRACT

A ^{13}C-NMR study of the reaction between ethylene glycol or 1,2-propylene glycol with diphenylmethane-4,4'-diisocyanate is reported. Assignation of $-CH_2-$, $-NHCOO-$, and $-CH_3$ groups was made and their concentration dependence on reaction time established. On the basis of these data, the rate constants for different reactions were calculated. It was found that the primary groups of 1,2-propylene glycol are more reactive than the secondary $-OH$ group, and that ethylene glycol is more reactive than 1,2-propylene glycol. Side reactions at low temperature and without catalyst do not take place.

INTRODUCTION

The reaction between isocyanates and polyhydric alcohols resulting in the formation of polyurethanes can be manifold. The first step of the reaction is the formation of oligomers which later react through different mechanisms to produce linear or cross-linked macromolecules. The reaction mechanism and the domination of individual reactions depend on such factors as temperature, ratio of monomers, and catalysts. Beside the addition of hydroxyl groups to isocyanate groups and the formation of –NHCOO– groups, the formation of allophanate and biuret groups, the reaction between isocyante and water, and other side reactions can take place.

Due to the similarity of different reaction products, it is difficult to follow the individual reactions. In the present work ^{13}C-NMR was used for the determination of oligomers at different reaction time intervals. The time dependence of concentrations for single products were determined from these data and some rate constants were calculated.

EXPERIMENTAL

Materials. Diphenylmethane-4,4'-diisocyanate was produced by Bayer. All the other materials were produced by Merck and Schuchardt.

Ethylene glycol (EG) or 1,2-propylene glycol (PG) was mixed with diphenylmethane-4,4'-diisocyanate (MDI) without catalyst at 293 K in molar ratios of 1:1, 1:2, and 2:1 in acetone-d_6. The molar concentration ratio for EG or PG was 1.87 mol/L. The ^{13}C-NMR spectra were recorded at 15 to 60 min intervals until the solutions were transparent (about 7 h). In a similar way, mixtures without solvent were prepared. In this case samples were dissolved in acetone-d_6 later for taking spectra.

Model substances for the identification of individual signals in the spectra of reaction mixtures were prepared from MDI with ethanol and phenyl isocyanate with ethanol, EG, PG, and diethylene glycol. The ^{13}C-NMR spectra were recorded on a JEOL FT 90QX spectrometer. Spectra were cumulated 600 times (10 min), pulse width was 14 μs, and spectral width was 5000 Hz. For all spectra, chemical shifts were quoted with respect to TMS as standard. All signals were proton decoupled.

RESULTS AND DISCUSSION

The reaction between isocyanates and hydroxyl groups at lower temperatures and without catalyst leads to the formation of urethane bonds between polyols and isocyanates. The formation of other possible bonds is less distinctive [1]. Figure 1 shows the ^{13}C-NMR spec-
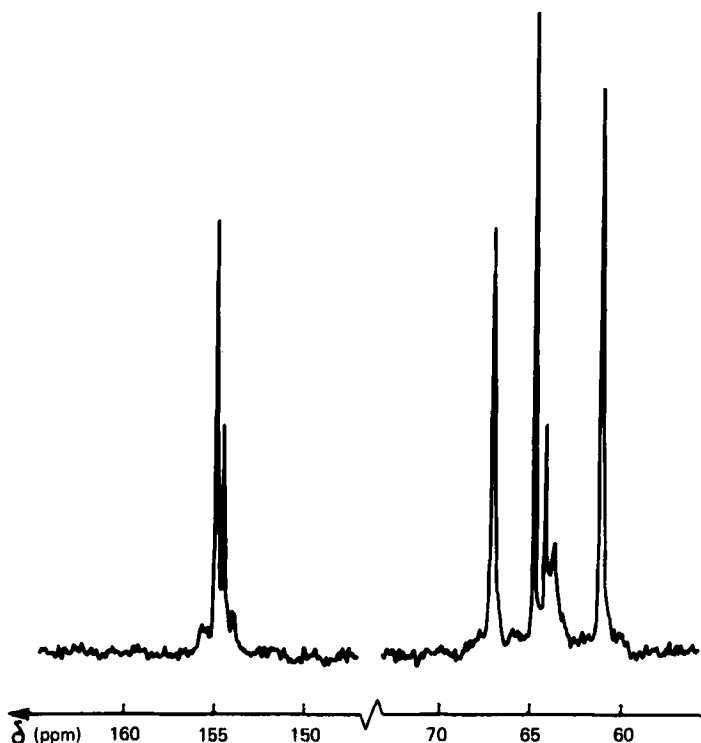
FIG. 1. ^{13}C-NMR spectra of reaction products between ethylene glycol and diphenylmethane-4,4'-diisocyanate.

trum of the reaction products between EG and MDI in a molar ratio of 1:1. Several regions of signals appear. The region of $-CH_2 O-$ groups is between 60 and 73 ppm, the region of $-NHCOO-$ groups is between 153 and 156 ppm, and the shift of the C_4 atoms of the ben-zene ring is 119.4 ppm. The signal for $-NCO$ groups, which should be at 125.4 ppm, disappears. In the region between 118 to 135 ppm, which belongs to the benzene ring, four signals of the para-substituted benzene ring appear. All chemical shifts are given in Table 1.

To determine the kinetics and the mechanism of the reaction be-tween EG and MDI, the well-separated signals of $-OCH_2-$ and $-NHCOO-$ have been used. The chemical shifts of these groups were determined on the basis of a large number of reference substances [2-4] on model compounds which we synthetized from monofunctional alcohols with bifunctional isocyanate and bifunctional alcohols with monofunctional isocyanate and on the basis of concentration changes of individual sub-stances during the reaction by the elimination method. The identified signals are given in Table 1. The integrals of signals of $-OCH_2 CH_2 OH$

TABLE 1. ¹³C Chemical Shift Data for the Reaction Product between EG and MDI

Compounds	Structure	Chemical shift (ppm)	
		Predicted	Observed
4,4'-MDI + EG			
	C_1	136.5	136.5
	C_2	117.9	119.2
	C_3	128.9	129.7
	C_4	141.1	137.9
	C_5	141.2	139.4
	C_6	128.9	129.7
	C_7	124.5	125.4
	C_8	130.8	130.5
	C_9	43.3	40.9
	C_{10}	157.8	154.7
	C_{11}	61.6	61.1
	C_{12}	–	67.1
	C_{13}	–	125.4
	C_{14}	–	64.7
	C_{15}	157.8	154.3
	C_{16}	–	63.6
	C_{17}	–	153.7

groups (61.7 ppm and 67.1 ppm) differ by 8% due to different relaxa-
tion times. Signals at 64.7 and 63.7 ppm belong to EG bonded on both
sides of the groups –NHCOOCH$_2$CH$_2$OOCNH–. The signal of –NHCOO–
groups is split into four signals, each belonging to the structures (PI)
and (PIP) at 154.7 ppm, (IPI) at 154.3 ppm, and to higher molecular
weight compounds [1]. The structures for (PI) and (PIP) cannot be
separated by measuring the ^{13}C-NMR spectra. Apparently the end-
to-end distance is too large for the C atoms of the EG bonded to the
MDI, and therefore shields the C atoms on the other side of the MDI
molecules.

For the reaction between EG and MDI, the following scheme is
possible:

$$P + I \xrightarrow{k_1} PI \xrightarrow{k_3} IPI$$

(1)
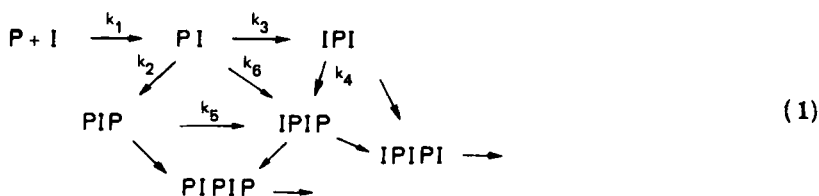
where I is the concentration of the isocyanate, P the concentration of
the polyol, and IP, IPI, PIP, and IPIP the concentrations of the corre-
sponding oligomers.

The experimentally determined concentration as a function of time
from the integral of the –CH$_2$O– groups (region between 61.7 and 67.1
ppm) is presented in Fig. 2. For molar ratios of 1:2 and 2:1 of EG to
MDI, the course of reaction is similar to a molar ratio of 1:1, except
for the concentrations of the individual compounds. For a mixture of
EG to MDI in a molar ratio of 2:1 the signal at 63.6 ppm belonging to
higher oligomers disappears. For all molar ratios the concentration
of compounds with free –OCH$_2$CH$_2$CH$_2$OH groups initially increases
very fast and reaches a maximum in about 2 h.

The ^{13}C-NMR spectra of reaction products between PG and MDI
have three significant regions useful for identification. Signals of
–CHO– and –CH$_2$O– groups have been found in the region between 65
and 73 ppm, of –CH$_3$ groups between 16.8 and 19.8 ppm, and of
–NHCOO– groups (Table 2) between 153.5 and 154.5 ppm (Fig. 3).
In Fig. 3 a signal is also seen of –CH$_3$ groups of the unbonded PG,
three signals of –CH$_3$ groups of PG bounded at different positions to
MDI, four signals of –NHCOO– groups, and eight signals of –CH$_2$O–
and –CHO– groups. Due to the low reaction temperature in the case
when EG as well as when PG has been used in the mixture with MDI,
the side reactions do not appear.

On the base of the identified signals, the following reaction scheme
between PG (P) and MDI (I) can be predicted:

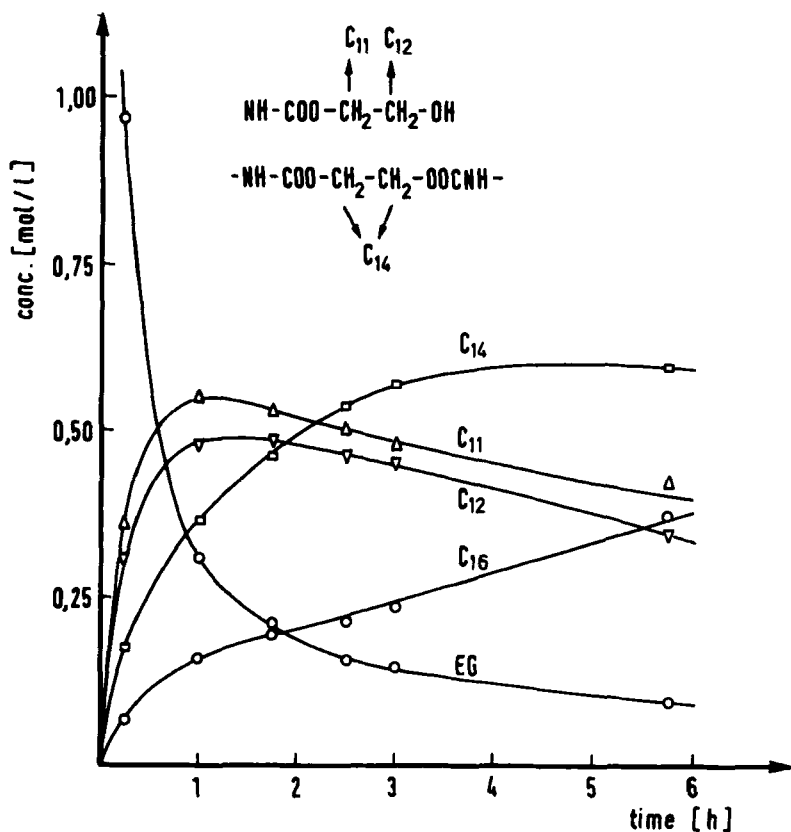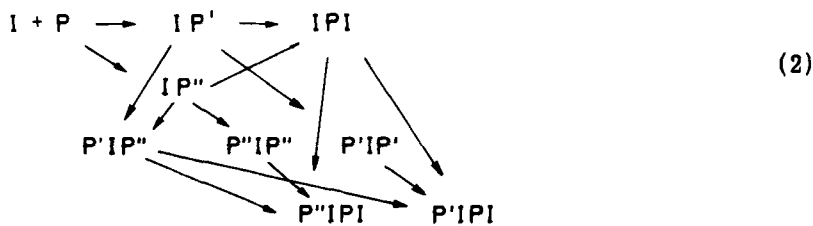FIG. 2. Concentrations of the components appearing in the reaction between ethylene glycol and diphenylmethane-4,4'-diisocyanate. Molar ratio 1:1.

$$I + P \longrightarrow IP' \longrightarrow IPI$$

(2)

where P' is PG bonded to primary and P" is PG bonded to secondary —OH groups. For the determination of the concentration of individual compounds, the signals of —CH₃ groups are the most useful. The ex-

TABLE 2. ^{13}C Chemical Shift Data for the Reaction Product between 1,2-PG and 4,4'-MDI

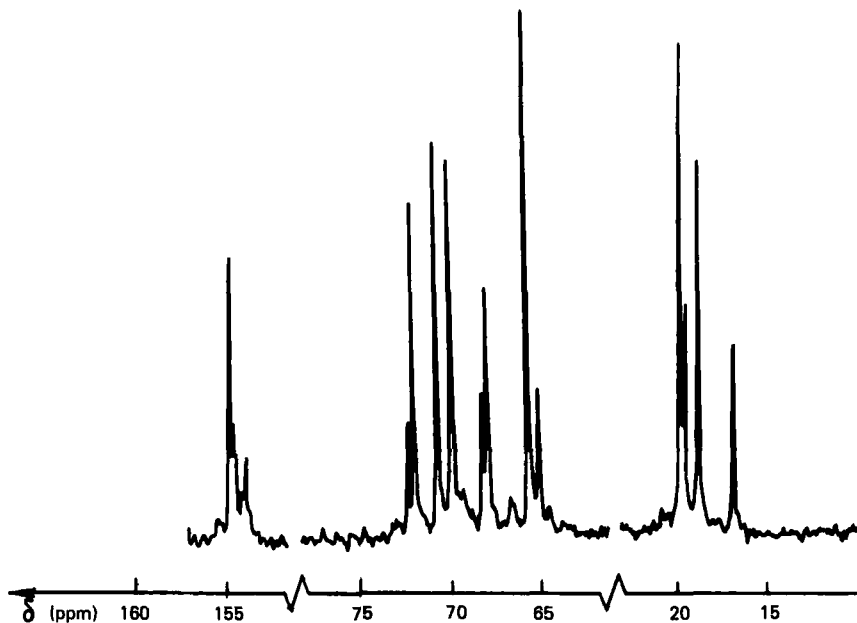| Compounds	Structure	Chemical shift (ppm)	
		Predicted	Observed
1,2-PG + 4,4'-MDI			
	C_1	–	66.0
	C_2	–	70.3
	C_3	19.6	19.8
	C_4	–	154.4
	C_5	–	72.3
	C_6	–	18.8
	C_7	–	71.1
	C_8	–	154.0
	C_9	65.9	65.4
	C_{10}	68.1	72.8
	C_{11}	17.8	16.8
	C_{12}	–	153.7

FIG. 3. ^{13}C-NMR spectra of reaction products between propylene glycol and diphenylmethane-4,4'-diisocyanate.

perimentally determined concentrations of these groups are given in Fig. 4. The concentration of PG decreases with reaction time while the concentration of compounds formed during the reaction increases and reaches a maximum in about 3 h.

Kinetics of the Reaction between EG or PG with MDI

When using the concentration of individual compounds (Figs. 2 and 4) to determine the reaction kinetics, it must be remembered that due to differences in relaxation times, the ^{13}C-NMR method does not give quantitative results. For this reason we compared the concentrations of individual groups only, which represented the total molecules. The signals from the spectra were calibrated by titration of the complete –OH and –NCO groups [5]. The rate constants for the reaction between EG and MDI were calculated on the basis of $-CH_2 O-$ groups (Fig. 2) while those for the reaction between PG and MDI were calculated on the basis of $-CH_3$ groups (Fig. 4).

From Eqs. (1) it can be seen that three kinds of reactions for the oligomer PI are possible. The integral of signals C_{11} and C_{12} (Table 1), which are represented as $-OCH_2 CH_2 OH$ groups, and the integral
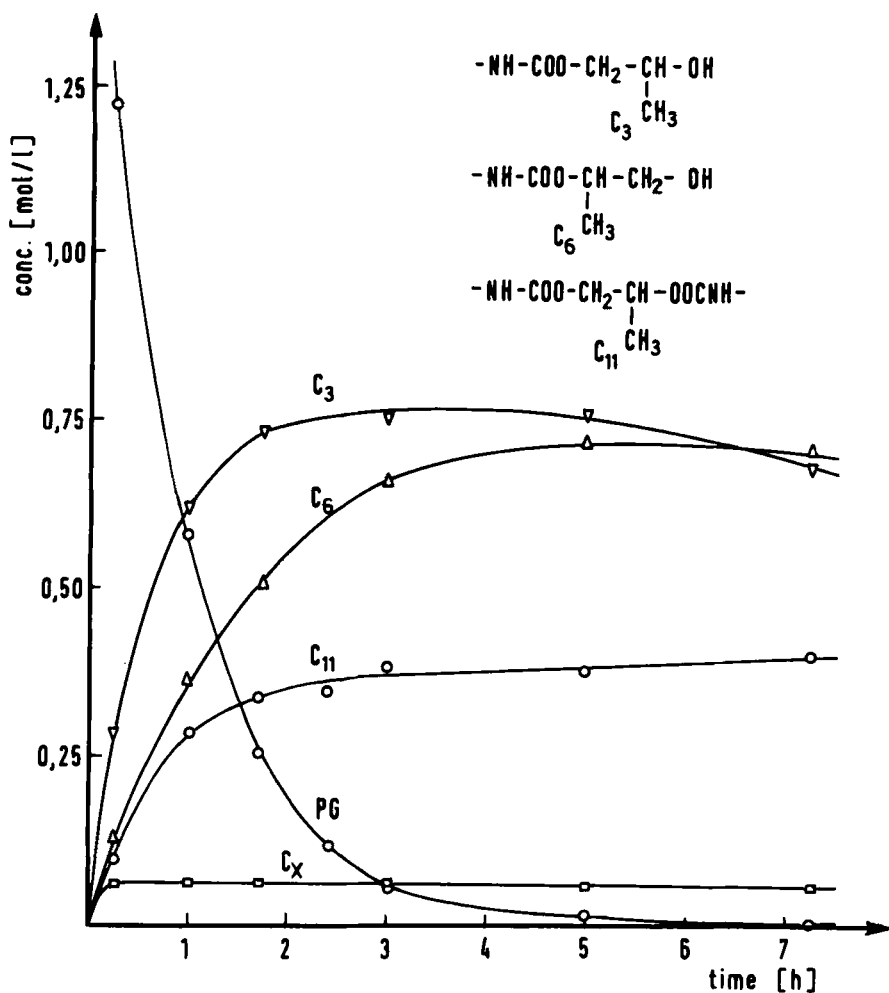
FIG. 4. Concentrations of the components appearing in the reaction between propylene glycol and diphenylmethane-4,4'-diisocyanate. Molar ratio 1:1.

of C_{14}, which is represented as the $-OCH_2 CH_2 O-$ group, can be written as

$$C_{11} + C_{12} = PI + 2 PIP + IPIP + \ldots \tag{3}$$

$$C_{14} = IPI + IPIP + \ldots \tag{4}$$

The kinetic equations for the first step of the reaction are

$$\frac{dP}{dt} = -k_1 P^2 \tag{5}$$

$$\frac{dPI}{dt} = k_1 \cdot P^2 - k_2 \cdot PI \cdot P - k_3 \cdot PI \cdot P - k_6 \cdot PI^2 \tag{6}$$

$$\frac{dPIP}{dt} = k_2 \cdot PI \cdot P - k_5 PIP \cdot P \tag{7}$$

$$\frac{d\, IPI}{dt} = k_3 PI \cdot P - k_4 IPI \cdot P \tag{8}$$

The computed spectrum in Fig. 2 can be expressed as a time function:

$$P = \frac{0,2256}{t} - 0,006\,t + 0,0883 \tag{9}$$

$$C_{11} + C_{12} = 1,1948 - 0,0714\,t - \frac{0,1090}{t} \tag{10}$$

$$C_{14} = 0,62 - 0,0032\,t - 0,6012\,e^{-t} \tag{11}$$

By integrating Eq. (5) we get the rate constant k_1, which is time independent during the interval from the beginning of the reaction to 2 h of reaction time. The rate constant for reactions starting after 2 h are time dependent. The values of the rate constants are given in Table 3.
Since

$$P_0 = P + IP + IPI + 2\,PIP + 2\,PIPI + \ldots = I_0 \tag{12}$$

$$I_0 = I + PI + 2\,IPI + PIP + 2\,PIPI + \ldots \tag{13}$$

we concluded that

$$IPI = PIP \tag{14}$$

The same conclusion can be made from the reaction scheme. This means that k_2 is identical to k_3 and k_4 is identical to k_5.
Combining Eqs. (3) and (4) and supposing that in the first step of the reaction

$$IPI > IPIP \tag{15}$$

TABLE 3. Calculated Values for Rate Constants for the Reaction of Ethylene Glycol and Diphenylmethane-4,4'-diisocyanate in a Molar Ratio of 1:1 (L/mol·s)

k_1	6.9×10^{-4}
k_2	7.1×10^{-4}
k_3	7.1×10^{-4}
k_4	6.2×10^{-4}
k_5	6.2×10^{-4}

we get

$$PI = C_{11} + C_{12} - 2C_{14} \tag{16}$$

and

$$\frac{dPI}{dt} = \frac{d(C_{11} + C_{12})}{dt} - \frac{2dC_{14}}{dt} \tag{17}$$

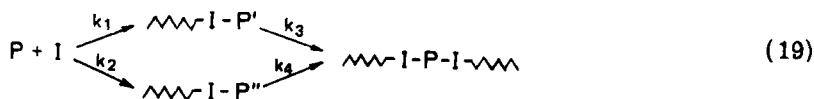Using Eqs. (10), (11), (14), (16), and (17) in Eq. (6), we get

$$\frac{d(C_{11} + C_{12})}{dt} - \frac{2dC_{14}}{dt} = k_1 P^2 - 2k_2(C_{11} + C_{12} - 2C_{14}) \cdot P \tag{18}$$

By time differentiation of the experimental values for $(C_{11} + C_{12})$ and C_{14} from Eqs. (10) and (11) and by using the values for $(C_{11} + C_{12})$, C_{14}, k_1, and P computed from Eq. (9) in Eq. (18), the value for k_2, which is the same as k_3, can be obtained. In a similar way the values for k_4 and k_5 from Eqs. (7) and (8) were calculated.

Since many generalizations had to be made, further rate constants have not been calculated. Anyhow, by comparing the rate constants in Table 3 it can be concluded that the rate of formation of dimers can be compared with the rate of formation of trimers and tetramers. It seems that the bonding of EG on both sides of MDI proceeds simultaneously due to the symmetrical structure of both reacting molecules.

The reaction between PG and MDI [2] is even more complex than the reaction of EG and MDI. The signals of the $-CH_3$, $-CH_2O-$, $-CHO-$ and $-NHCOO-$ groups (Fig. 3) make possible the determination of the bonding of MDI to the primary or secondary $-OH$ groups of PG and the bonding of MDI to the other site of PG.

For the calculation of the rate constants for the bondings mentioned, the following reaction scheme was used ($I_0 = P_0$):

$$P + I \xrightarrow[k_2]{k_1} \begin{array}{c} \text{\char`~~I-P'} \\ \text{\char`~~I-P''} \end{array} \xrightarrow[k_4]{k_3} \text{\char`~~I-P-I\char`~~} \tag{19}$$

where I can be nonbonded on one or both sides.

For Scheme (19) the following kinetics equations can be supposed:

$$\frac{dP}{dt} = -k_1 P^2 - k_2 P^2 \tag{20}$$

$$\frac{dP'}{dt} = k_1 P^2 - k_3 P' \cdot P \tag{21}$$

$$\frac{dP''}{dt} = k_2 P^2 - k_4 P'' \cdot P \tag{22}$$

At the beginning of the reaction (up to 30 min) the probability of formation of PI compounds is higher than the probability of formation of higher oligomers. For this reason it is likely that the rate of bonding of –NCO groups to the primary or secondary places of PG is proportional to the concentrations of P' and P''. From the ratio of the derivatives of the curves in Fig. 4 and using Eqs. (21) and (22), we get

$$\frac{\frac{dP'}{dt}}{\frac{dP''}{dt}} = \frac{k_1}{k_2} = 1.5 \tag{23}$$

Using the ratio $k_1/k_2 = 1.5$, Eq. (20), and the derivative of the curve in Fig. 4, values for k_1 and k_2 were obtained. The rate constants for k_3 and k_4 were calculated from Eqs. (21) and (22). The values are given in Table 4.

From these data it can be concluded that the rate of reaction between primary –OH groups and MDI is higher than in the case of secondary –OH groups. This is valid whether PG is unbonded (k_1) or bonded (k_4). The differences in reactivity of PG can be explained by steric hindrances of –OH and –NCO groups.

CONCLUSIONS

^{13}C-NMR makes possible the determination of oligomers which are formed by bonding isocyanate groups to one or both sides of glycols. The spectra give enough information to calculate the rate constants of

TABLE 4. Rate Constants for the Reactions of 1,2-Propylene Glycol and Diphenylmethane-4,4'-diisocyanate in a Molar Ratio of 1:1 (L/mol·s)

k_1	1.7×10^{-4}
k_2	1.2×10^{-4}
k_3	0.7×10^{-4}
k_4	1.2×10^{-4}

individual reactions. It is found that the values of rate constants for different reactions are comparable, which means that all oligomers have the same possibility of being formed.

It is also found that 1,2-propylene glycol reacts with diphenylmethane-4,4'-diisocyanate, dominantly with the primary –OH groups, and that in comparison to ethylene glycol, 1,2-propylene glycol is less reactive due to steric hindrances of monomers and oligomers.

Side reactions do not take place at the chosen reaction conditions.

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