Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Identification of Oligomers in the Reaction of Polyols with Isocyanates by ^{13}C-NMR and GPC

A. Šebenik[a]; U. Osredkar[a]; I. Vizovišek[a]
[a] Boris Kidrič Institute of Chemistry, Ljubljana, Yugoslavia

To cite this Article Šebenik, A. , Osredkar, U. and Vizovišek, I.(1986) 'Identification of Oligomers in the Reaction of Polyols with Isocyanates by ^{13}C-NMR and GPC', Journal of Macromolecular Science, Part A, 23: 3, 369 — 379
To link to this Article: DOI: 10.1080/00222338608063400
URL: http://dx.doi.org/10.1080/00222338608063400

J. MACROMOL. SCI.–CHEM., A23(3), pp. 369-379 (1986)

Identification of Oligomers in the Reaction of Polyols with Isocyanates by ^{13}C-NMR and GPC

A. ŠEBENIK, U. OSREDKAR, and I. VIZOVIŠEK

Boris Kidrič Institute of Chemistry
Ljubljana, Yugoslavia

ABSTRACT

Kinetics and mechanism of formation of urethane, biuret, allophanate, and isocyanurate in the synthesis of polyurethanes were studied by means of ^{13}C-NMR and GPC. In the spectra, the regions of urethane, allophanate, biuret, and isocyanurate were used to study the mechanism of reaction between isocyanates and glycols under different reaction conditions. Urethane groups give signals between 153 and 156 ppm; isocyanurate groups between 149 and 151 ppm. For the determination of secondary rate constants, the well-separated signals of urethane and allophanate in the ^{13}C-NMR spectra were used.

INTRODUCTION

The primary reactions between compounds containing active hydrogen groups and isocyanates lead to the formation of oligomers with urethane linkages. The oligomers then react by different reaction mechanisms to form linear or crosslinked macromolecules. In the presence of water, the isocyanates react via a substituted carbamic acid and amine into a substituted urea and later into biuret. Isocyanates may also react with active hydrogen atoms in urethanes to form allophanates. On heating the isocyanates, the corresponding isocyan-

0022-233X/86/2303-0369$3.50/0

urates can be formed. The prevalence of any of these reactions depends on temperature, molar ratio between isocyanates and polyols or water, catalyst, and other reaction conditions. The formation of allophanate crosslinking is favored in low-catalyzed systems in the absence of water and a temperature range from 120 to 140°C. Beside the formation of urethanes, biurets, allophanates, and isocyanurates, still other reactions are possible [1, 2].

The present work describes some results of a study of primary and secondary reactions between isocyanates, polyols, and water by ^{13}C-NMR spectroscopy in combination with GPC. The aim of the investigation was to determine the concentration of individual urethane, allophanate, and isocyanurate oligomers and some kinetic parameters.

EXPERIMENTAL

All reagents were of analytical grade. Isocyanates, polyols, and solvents were purified and dried before use.

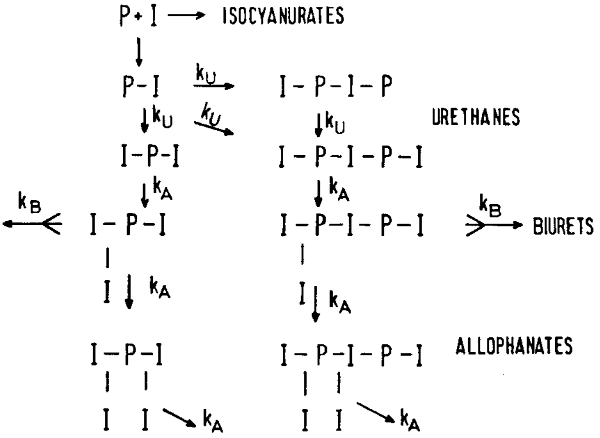
Ethylene glycol (EG), 1,2-propylene glycol (PG), 1,4-butandiol (BD), diethylene glycol (DEG), or water were mixed with phenyl isocyanate (PhI), 4,4'-methylenebis(phenyl isocyanate) (MDI), or toluendiisocyanate (TDI; 2,4:2,6 = 80:20) in molar ratios of –NCO to –OH groups 1:1, 2:1, and 4:1, at 20°C. The compositions of reaction products were determined by ^{13}C-NMR and GPC analysis. After 2 h, when most of the urethanes were formed, the mixtures were heated up to 6 h at 130°C. At intervals of 15 to 60 min, samples were taken, cooled, and dissolved in DMF-d_6. For GPC analysis in μ-Styragel columns (100 and 500 Å), THF and chloroform were used as solvents (50 mL/h). Polystyrene standards and model substances prepared from MDI and TDI with ethanol, propanol, or butanol, and from PhI with ethanol, EG, PG, BD, or DEG, which have similar structure and absorption in the UV as the oligomers, were used for qualitative and quantitative calibration of GPC chromatograms. A UV spectrometer (λ = 254 nm) was used as the detector. ^{13}C-NMR spectra were recorded on a Jeol FT 90Q spectrometer. Spectra were accumulated for 2 h (6000 repetitions), pulse width was 14 μs, and spectral width was 5000 Hz. For all spectra, chemical shifts were calculated with TMS as reference. All signals were proton decoupled. The integrals of individual signals used for quantitative measurements were calibrated by T_1 effects, which were determined by measurement of the relaxation times of individual carbons of model substances.

Model substances for identification of individual signals of urethane, allophanate, and isocyanate groups in NMR spectra and chromatograms of reactive mixtures, were prepared by using MDI and TDI with ethanol, propanol, or butanol, and from PhI with ethanol, EG, PG, BD, or DEG at 20 and 130°C in molar ratios of 1:1, 2:1, and 4:1 of –NCO to –OH groups. Model substances for identification of individual signals of biuret groups were prepared by using PhI, MDI, and TDI with water in molar ratios of 4:1, 2:1, and 1:1 between –NCO and water.

RESULTS AND DISCUSSION

In the first step of the reaction between isocyanates and polyols, urethane oligomers are formed. The urethane oligomers react with isocyanates at 120 to 140°C to form allophanate oligomers, while substituted carbamic acids are formed in the reaction between isocyanates and water. Carbamic acids are unstable and decompose into amines and CO_2. The amines react with isocyanates to form biurets.

Beside the allophanates and biurets, isocyanurates oligomers may be formed. The schemes of reactions are



(1)

where P is polyol, I is isocyanate, and PI, IPI, IPIP, and IPIPI are urethane, biuret, allophanate, and isocyanurate oligomers.

To determine the urethane oligomers, the region for $-CH_2O-$ groups between 60 and 73 ppm in the ^{13}C-NMR spectra and for –NHCOO– groups between 153 and 155 ppm were used. Concentrations of individual oligomers in different reaction mixtures were calculated from the integrals of the corresponding signals [3, 4] of similar types of carbons corrected by the factors accounting for differences in relaxation times.

In the present work, GPC and ^{13}C-NMR were used to determine the concentration of urethane oligomers, and ^{13}C-NMR to determine the concentration of allophanate, isocyanurate, and biuret oligomers. Figure 1 shows an example of concentrations of different reaction products

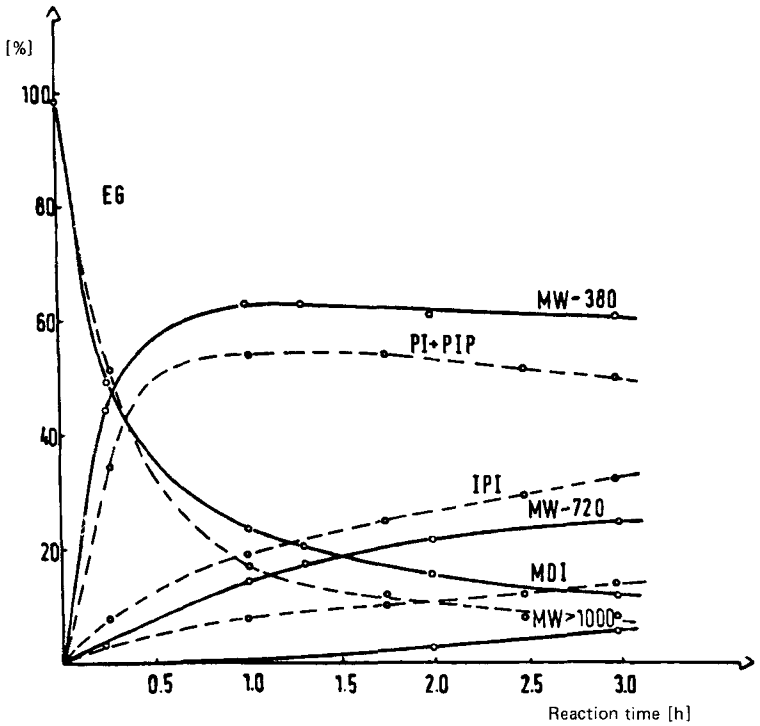


FIG. 1. Concentration of the components appearing in the reaction between EG and MDI, molar ratio 1:1, determined by ^{13}C-NMR (- -) and GPC (—).

as a function of time for the reaction between MDI and EG in the molar ratio 1:1 determined from ^{13}C-NMR spectra and GPC chromatograms. The agreement between the two methods is satisfactory, even though, due to different relaxation times of individual carbon atoms, ^{13}C-NMR is not a quantitative method.

For molar ratios 2:1 and 4:1 of MDI:EG and for other isocyanates and polyols, the courses of reactions are similar to the reaction of MDI:EG in molar ratio 1:1, except for the concentrations of individual compounds. In the spectra of the urethanes prepared at room temperature and in the absence of water, only urethane bonds were detected even when the molar ratio between isocyanate and polyol was 4:1. The concentrations of individual urethane oligomers determined by GPC are given in Table 1. Chloroform, which gives better separation than THF due to different interactions between oligomers and solvent, was used as solvent (Fig. 2). When the ratio between isocyanate and polyol was higher than 1, the oligomers IPI and PIPI prevailed. Allo-

TABLE 1. Concentration of Individual Oligomers in the Reaction Mixture between Isocyanates and Polyols (%), t_r = 90 min

	I	PI	PIP	IPI	Higher oligomers
TDI:EG 1:2	7.2	64.6	14.4	7.9	4.9
TDI:EG 2:1	36.0	31.2	7.2	20.8	7.2
TDI:EG 1:1	8.6	52.2	12.4	14.7	12.1
TDI:1,2-PG 1:1	23.6	56.6^{a}	-	15.5	4.3
TDI:1,3-PG 1:1	23.8	41.4^{a}	-	21.3	13.5
TDI:1,4-BD 1:1	15.5	33.2	20.1	21.2	10.0
MDI:EG 1:1	22.3	60.7^{a}	-	15.0	2.0
MDI:1,2-PG 1:1	89.2^{a}	-	-	10.8	2.0
MDI:1,4-BD 1:1	49.6^{a}	-	23.4	19.6	7.5

[a] The sum of unseparated oligomers (PI, PIP).

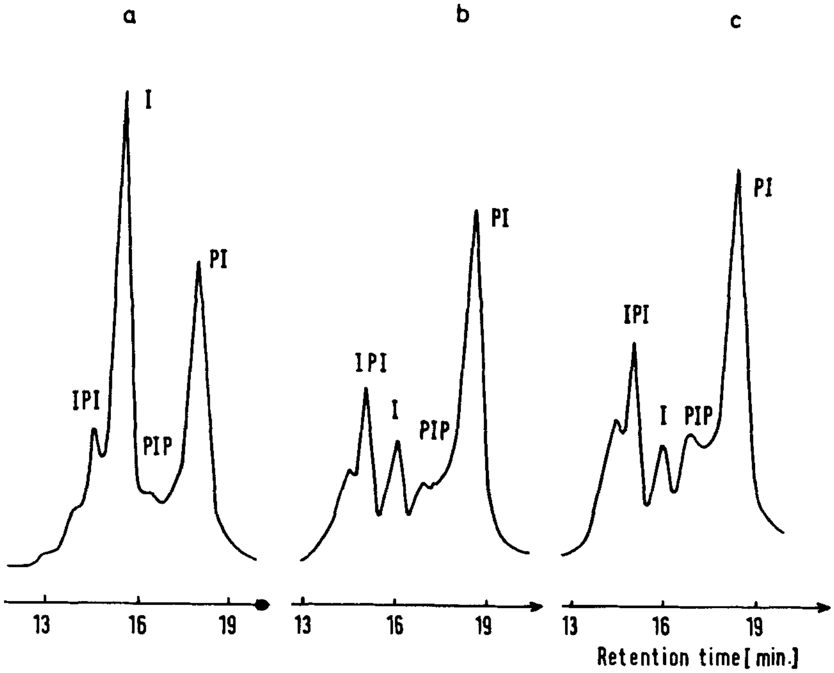


FIG. 2. GPC chromatogram of the reaction products between TDI and EG, molar ratio 1:1, solvent $CHCl_3$, reaction time: (a) 90 min, (b) 145 min, (c) 260 min.

phanates were prepared from urethane oligomers and isocyanates with a starting molar ratio of isocyanate to polyol of 2:1 and 4:1.

For the determination of the allophanate group $R{-}NH{-}CO{-}\overset{\overset{R}{|}}{N}{-}COO{-}R$ and the biuret group $R{-}NH{-}CO{-}\overset{\overset{R}{|}}{N}{-}CO{-}NH{-}R$ in the ^{13}C-NMR spectra, the signals of $-CO-$ at 152 to 165 ppm, the signals of $-\overset{|}{C}HO-$ and $-CH_2O-$ at 60 to 73 ppm, and the signals of $-CH_3$ at 15 to 20 ppm were used (Fig. 3). The isocyanurates have signals of $-\overset{|}{N}{-}CO{-}\overset{|}{N}-$ between 149 and 151 ppm. Chemical shifts, given in Table 2, for all of these

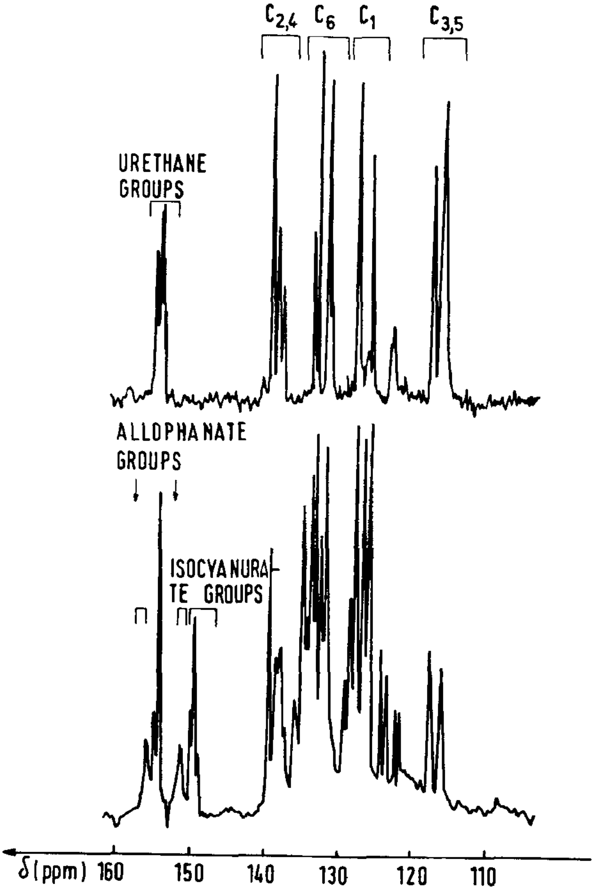
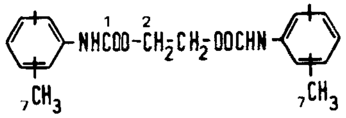
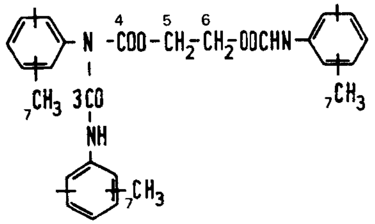
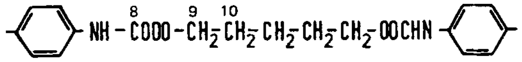


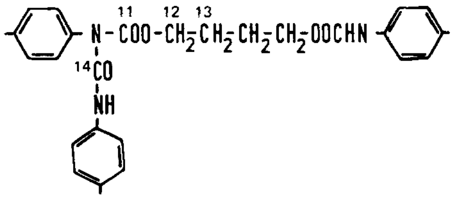
FIG. 3. ^{13}C-NMR spectra of reaction products between TDI and 1,2 PG in molar ratio 2:1, reaction time 15 min at 130°C.

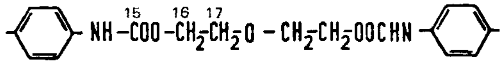
TABLE 2. Chemical Shifts of Allophanate Groups in Polyurethane Oligomers

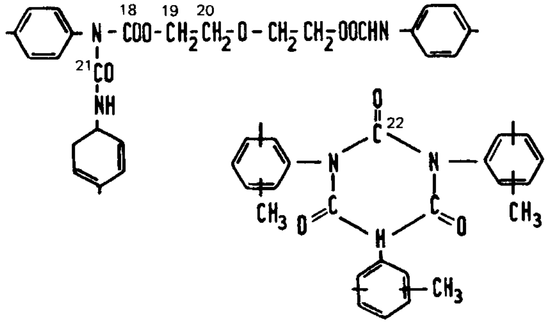












Observed chemical shifts (ppm)	
1	from 154,6 to 155,2
2	63,8
3	155,7
4	151,3 and 150,8
5	66,2
6	62,7
7	from 16,1 to 16,6
8,15	153,6
9	63,2
10,13	24,8
11	152,1
12,16	66,2
14,21	154,5
17	69,7
18	152,1
19	67,4
20	69,1
22	from 149 to 150

groups, were determined on the basis of references [5, 6] and model substances, which were synthesized under the same conditions as the investigated reactions either from monofunctional isocyanates and bifunctional alcohols or from bifunctional isocyanates and monofunctional alcohols. The bonding of isocyanates to urethanes to form allophanates shifts the urethane –CO– groups 2 ppm upfield. Correspondingly, the signals of aromatic rings and bonded polyols are also changed.

To determine the influence of reaction time on the concentration of individual groups in the reaction products between isocyanates and polyols, the well-separated signals of urethane, allophante, isocyanurate, $-CH_2O$, and $-CH_3$ groups were used. The starting point for the preparation of allophanates were the urethane oligomers PI, IPI, and IPIP (Table 1), whose spectra and chromatograms after 2 h of reaction time show only urethane bonds, with hardly any free $-CH_2OH$ groups present. At the beginning of heating, these groups form urethane oligomers, which further transform to allophanate oligomers.

The concentrations of total groups were determined by ^{13}C-NMR. The concentration of urethane groups decreased with reaction time, while the concentration of allophanate and isocyanurate groups increased (Fig. 4). Part of the isocyanate reacted to isocyanurate.

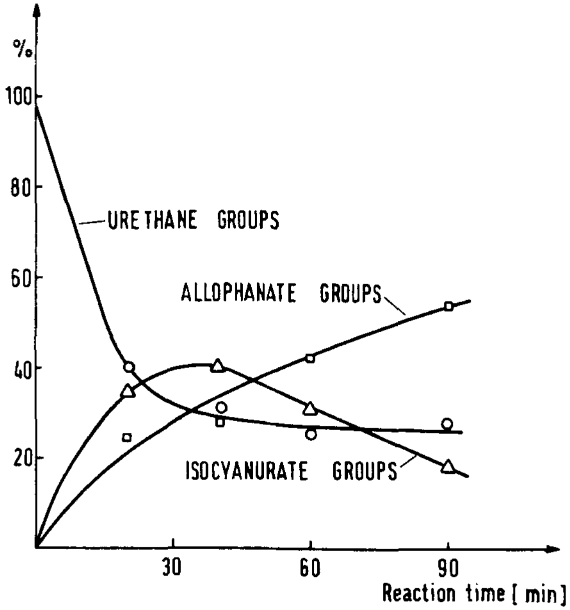


FIG. 4. Concentration of urethane, allophanate, and isocyanurate groups appearing in the reaction between TDI and EG at 130°C as a function of reaction time.

This reaction is more marked for TDI than for MDI. Even the heating of urethane oligomers with free –NCO groups (molar ratio 2:1) results in no formation of isocyanurate, which means that isocyanurates were mostly formed from isocyanates. The rate constants of the formation of allophates were calculated on the basis of –NHCOO– or $-CH_2O-$ groups bonded as urethane, which represented the total molecules. The integral of urethane signals can be written as:

$$U = PI + 2PIP + 2IPI + 3IPIP + \cdots. \tag{2}$$

$$P_o < I_o. \tag{3}$$

$$U = \sum I_u = I_o - I = 2IPI + 4IPIPI + \cdots. \tag{4}$$

The kinetic equation for the decreasing concentration of urethane oligomers is:

$$dU/dt = -k_u \cdot U \cdot I - k_a \cdot U \cdot I - k_b \cdot U \cdot [H_2O] - k_i \cdot U \cdot I, \tag{5}$$

where U is the urethane concentration, k_u is the rate constant of formation of higher urethane oligomers, k_b is the rate constant of formation of biuret oligomers, k_a is the rate constant of formation of allophanate oligomers, and k_i is the rate constants of formation of isocyanurate oligomers. At room temperature and after 2 h of reaction, only urethane groups were observed in the spectra. That means that $k_b > k_u > k_a$. The allophanates were formed after the reactions of urethanes were completed and at temperatures over 100°C. As mentioned, the isocyanurates were formed mostly from isocyanates, not from urethane oligomers. Due to big differences in the reactivities of biurets, urethanes, allophanates, and isocyanurates, in the first approximation the kinetic equation (6) can be separated into four independent parts:

$$dU/dt = -k_u \cdot I \cdot U. \tag{6}$$

$$dU/dt = -k_b \cdot I \cdot [H_2O]. \tag{7}$$

$$dU/dt = -k_a \cdot I \cdot U. \tag{8}$$

$$dU/dt = -k_i \cdot U \cdot I. \tag{9}$$

At 130°C only about 25% of the urethane bonds reacted in 2 h. By time differentiation of the experimental values for concentrations of

TABLE 3. Rate Constants for the Formation of Allophanate from Different Isocyanates and Polyols in Molar Ratio 1:4 at 130°C

	$K \times 10^5$, L/(mol·s)
PhI and EG	6.9
PhI and PG	5.1
MDI and EG	4.1
MDI and PG	4.1
PhI and diethylene glycol	4.2
PhI and 1,4-butanediol	4.1
MDI and diethylene glycol	3.5
MDI and 1,4-butanediol	3.6
TDI and EG	5.0

urethane bonds, the values of k_a for different isocyanates and polyols were calculated. The rate constants for the formation of allophanate groups given in Table 3 approximate the secondary rate constants in the complex reactions between isocyanates and polyols.

CONCLUSION

From the well-separated signals of urethane, biuret, allophanate, and isocyanaurate groups in the ^{13}C-NMR spectra and the separated signals of urethane oligomers in GPC chromatograms, important information on the structure and on kinetics in the formation of polyurethanes can be deduced. Besides the main reaction, a multitude of side reactions occur, and ^{13}C-NMR spectroscopy in combination with GPC seems to be a very appropriate technique to study these complex reaction systems.

REFERENCES

[1] G. Woods, Flexible Polyurethane Foams, Chemical and Technical Applications, Science Publishers, London, 1982, p. 3.

[2] D. H. Solomon, Step Growth Polymerization, Dekker, New York, 1972, p. 95.

[3] C. Delides, R. A. Pethrick, A. V. Cunliffe, and P. G. Klein, Polymer, 22, 1205 (1981).

[4] A. Sebenik, C. Kastelic, and U. Osredkar, J. Macromol. Sci.–Chem., A20(3), 341 (1983).
[5] E. Breitmaier, G. Hass, and W. Woelter, Atlas of Carbon-13 NMR Data, Vols. 1-3, Heyden, London, 1979.
[6] F. L. Johnson and W. C. Jankowski, Carbon-13 NMR Spectra, Wiley, New York, 1972.

Received November 13, 1984
Revision received February 11, 1985