Extent of side reactions and gelation of polyether polyurethanes

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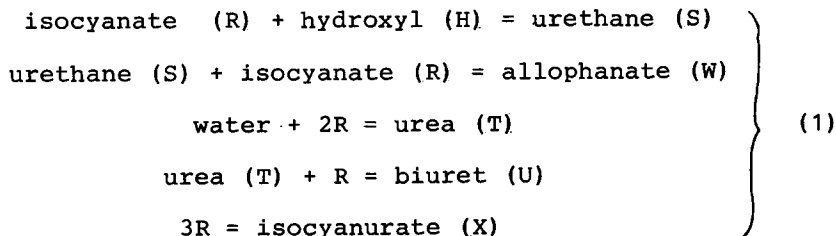
Summary

Gelation and gel build-up due to a side reaction in poly-(oxypropylene) diol – 4,4'-diisocyanatodiphenylmethane systems, catalyzed by dibutyltin dilaurate and containing excess NCO groups was studied at 60 to 140°C. Formation of allophanate groups from urethane and urea and biuret from traces of water were the main side reactions. The extent of these reactions was monitored by the determination of isocyanate reacted in excess to that consumed for the formation of urethane and urea groups. Two gel point were observed: one corresponding to the sol→gel transition at a low excess of NCO groups and the other one corresponding to the gel→sol transition at a high excess of NCO groups. The width of the gel and the maximum amount of gel decrease with increasing temperature.

Introduction

The high reactivity of isocyanates gives rise to a number of chemical reactions accompanying the formation of urethane groups from OH and NCO groups. Reactions with and induced by water, always present in trace amounts in technical products, must also be taken into account. Branch point are formed in a number of these side reactions. They are sometimes undesirable because they may cause gelation of linear polyurethanes, but can be also used intentionally for obtaining technically valuable products (1).

The main side reactions yielding stable products can be summarized as follows:

$$
\begin{aligned}
\text{isocyanate (R) + hydroxyl (H) } &= \text{ urethane (S)}\\
\text{urethane (S) + isocyanate (R) } &= \text{ allophanate (W)}\\
\text{water + 2R } &= \text{ urea (T)}\\
\text{urea (T) + R } &= \text{ biuret (U)}\\
\text{3R } &= \text{ isocyanurate (X)}
\end{aligned}
\right\} \quad (1)
$$

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Formation of urethane, allophanate and biuret are reversible re-actions, but urethanes prepared from aliphatic alcohols are re-latively stable even at elevated temperatures. The urethane and urea groups can be considered bifunctional (they cause chain extension), while allophanate, biuret and isocyanurate are tri-functional and cause branching, and possibly gelation.

The side reactions were subject of a number of studies of model and polyfunctional systems. They revealed the importance of traces of water in the system, because biuret is formed faster than allophanate and is more stable (2). These studies also provide important information on the relative rates of all reactions occurring in the system in dependence on temperature, catalyst, etc., which can be employed in studies of polyfunc-tional systems, where analytical characterization is much more difficult.

Gelation in polyurethane systems prepared from diol and diisocyanate was studied by Furukawa and Yokoyama (3,4) who assumed that allophanate formation is the only source of branch-ing. The amount of isocyanate reacted in excess to that re-quired for urethane formation was compared with the crosslink-ing density of the gels, assuming (incorrectly) that every branch point contributed to the number of elastically active network chains.

To correlate gelation and physical properties of gels with the extent of side reactions, a theoretical approach based on the *theory of branching processes* has been developed (5), based on network build-up from structural fragment. A simpler version was presented in this journal (6). A comparison of experimen-tal and theoretical gel fractions has revealed that the agree-ment is good at least at lower reaction temperatures. At higher temperatures (120-140°C), the experimental gel fractions were somewhat lower than the theoretical ones (5).

In this contribution, experimental results on gelation and development of the gel fraction in the course of a reaction of poly(oxypropylene) diol with 4,4'-diisocyanatodiphenylmethane (MDI) are presented, and reasons for the discrepancy between experimental and theoretical sol fractions are discussed.

Experimental

Materials. The polyol used was Union Carbide *Niax Polyol*[®] PPG-1200, number-average molecular weight M_n = 1230 (determined by VPO). It was dried by azeotropic distillation with benzene. Reaction with an excess of phenyl isocyanate was used for de-termination of OH groups. The unreacted phenyl isocyanate was determined by potentiometric titration with 0.3 M HCl using a combined glass electrode. Polyol contained after drying 2.68 wt.-% hydroxyl groups. The average functionality calculated from the hydroxyl content and M_n was 1.95. The water content determined by coulometry was 0.0027 wt.-%.

4,4'-diisocyanatodiphenylmethane (MDI) (Bayer) was dis-tilled at 180°C (270 Pa) and recrystallized from dry heptane. MDI was of 99.5-99.7% purity determined by a reaction with

dibutylamine and by potentiometric titration.

Dibutyltin dilaurate was a product of M&T International (*Termolite T 12*) and was used as received.

Reaction conditions. The components were mixed and reacted in sealed glass ampoules in nitrogen atmosphere. Dibutyltin dilaurate was added in a 0.1 M solution in dioxane; its concentration in the samples amounted to 0.037-0.039 wt.-%. The average mass of samples was about 0.5 g. The reaction was stopped by cooling to -78°C.

The dependences of the composition and sol fraction on time and on the initial composition were determined at reaction temperatures 60, 90, 120 and 140°C.

Analysis. *Determination of unreacted isocyanate groups.* The concentration of unreacted isocyanate groups in soluble samples and in the gel was determined with dibutylamine (DBA). The unreacted DBA was determined by potentiometric titration with 0.3 M HCl in isopropanol. About 0.5 g of the sample was dissolved or swollen in dioxane containing DBA in an amount chosen so as to keep the consumption of 0.3 M HCl below 3 ml, because at a higher excess of DBA a partial decomposition of allophanate and biuret groups may occur. Immediately before titration, conductivity was raised by addition of 7.5 ml ethanol. Titration of swollen samples lasted several hours until a constant value was reached.

Amine degradation of allophanate and biuret. This method was used for the determination of allophanate groups (3), but we have found that also biuret groups are split. About 0.5 g of the sample was kept in dimethylsulfoxide solution of butylamine (BA) at 40°C for 4 hours and then for 15 hours at room temperature. All samples eventually became soluble (absence of isocyanurates), and the excess of BA was titrated as in the case of BA. The consumption of BA corresponded to free isocyanate groups, allophanate and biuret. The concentration of allophanate and biuret was obtained by subtracting the concentration of free isocyanate groups determined as described above.

Determination of gel fraction. The weight fraction of the gel was determined after the deactivation of NCO groups with DBA by repeated extraction with dioxane. The extracted gel was dried to constant weight at 50°C under reduced pressure. The weight of the gel obtained by this procedure was higher by the amount of bound DBA. The recalculation of this value to the actual gel fraction in the sample was explained elsewhere (5).


Results and Discussion

Already the study of model reactions (phenyl isocyanate, butanol and water in dioxane solution at a concentration corresponding to the bulk reactions with polyols) has shown that urethane formation is the fastest reaction and that the conversion of OH groups in stoichiometric systems or with isocyanate in excess is practically complete. Reaction with water under formation of urea was the second fastes one while biuret and allophanate formation was much slower. This difference

made it possible to choose reaction temperature and time after which the consumed NCO groups corresponded only to urethane and urea groups.
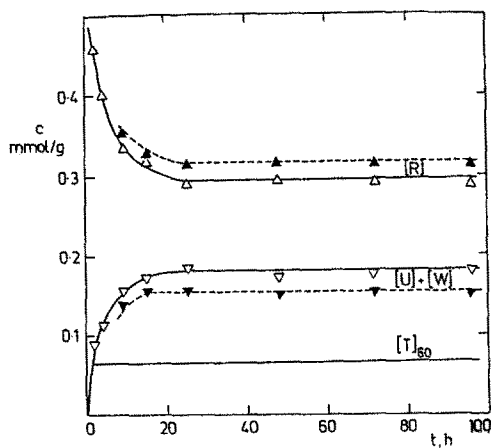
Figures 1a-c show the time dependence of NCO and urea and the sum of allophanate and biuret groups in the PPG-MDI system
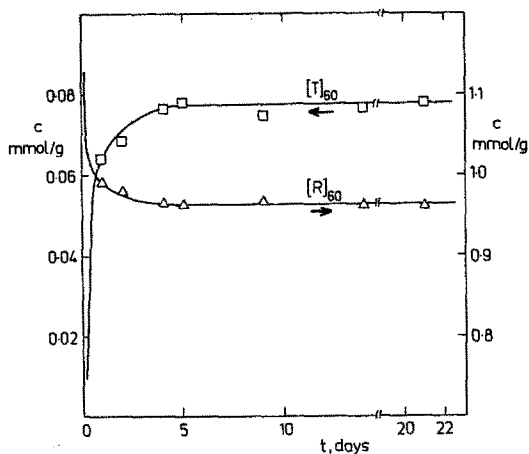
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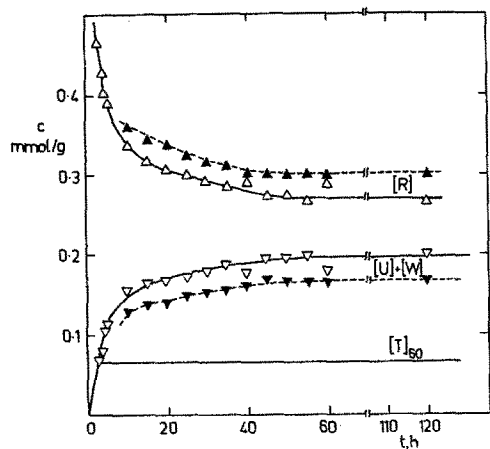
b

c

Figure. 1a-c. Time dependence of the concentration of isocyanate, [R] , urea, $[T]_{60}$, and the sum of biuret and allophanate, [U] + [W] , groups; 1a: $r_I = [R]_0/[H]_0 = 2.0$, 60°C; 1b $r_I = 1.5$, 120°C, 1c $r_I = 1.5$, 140°C; ---- corrected dependences for deactivation of NCO groups, see text.

at 60-140°C. At 60°C (Fig. 1a), the content of NCO groups determined with dibutylamine is equal to that determined by butylamine degradation in DMSO, which means that no biuret and allophanate groups are present at reaction times up to 20 days. Constant values of NCO groups were reached after 5 days. The reaction of OH groups and water was practically complete after 3 h. Thus, 60°C and 5 days were selected as conditions for the determination of the concentration of NCO groups, $[R]_{60}$, remaining after the formation of urethane and urea groups. From the mass balance we have (cf.Eq. (1))

$$\left.\begin{aligned}
[U] + [W] &= [R]_{60} - [R] \\
2[T]_{60} &= [R]_0 - [R]_{60} - [H]_0 \\
[T] &= [T]_{60} - [U] \\
[S] &= [H]_0 - [W]
\end{aligned}\right\} \quad (2)$$

For notation cf. Eq. (1); the subscript 0 refers to the initial concentrations. Since one can determine only $[U] + [W]$, $[T]$ and $[S]$ cannot be determined unless some assumptions are made.

Figures 1b and 1c show the time dependence of $[R]$, $[T]$ and $[U] + [W]$ for 120 and 140°C. The reaction becomes faster and steady values are attained sooner. In the figures, also"corrected" dependences are displayed. The correction concerns a possible deactivation of NCO groups to be discussed below.

In Figs 2a and 2b, the time dependence of the gel fraction for reactions at 120 and 140°C are displayed. The dependences are similar to those of NCO groups (Fig. 1). Steady values of w_g are obtained approximately after the same time as the $[R]$ values, which means that reactions of isocyanate groups and not successive transformations of the formed groups without participation of isocyanate are responsible for network build-up.

Figures 3a - 3b show an example of the dependence of the concentration of groups on the initial molar ratio of NCO to OH groups. At 90°C, $[U] + [W]$ is considerably higher than at 140°C. The value of $[T]_{60}$ corresponding to the initial amount of water is almost constant but deceases at a low excess of isocyanate.

The gel fractions are displayed in Fig. 4. It is clearly seen that two gel points exist, depending on the excess of isocyanate groups. The first gelation (sol→gel transition) occurs at a low excess of NCO groups. Relatively long chains formed near the stoichiometric ratio are crosslinked by a few branch points. The other gelation (gel→sol transition) occurs at a high excess of isocyanate. The structure is highly branched due to many allophanate and biuret points but many chains are terminated by unreacted NCO groups by which gelation is prevented. The diminishing region of the gel with increasing temperatue corresponds to decreasing stability of allophanate and biuret.

For the comparison of the measured gel fraction with the calculated one both extremes in composition were examined:
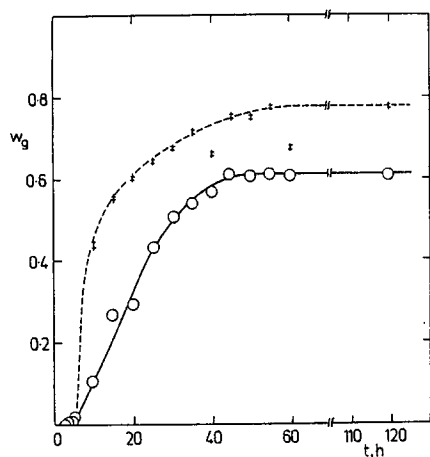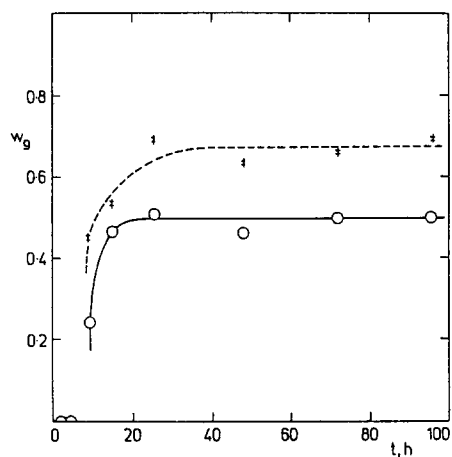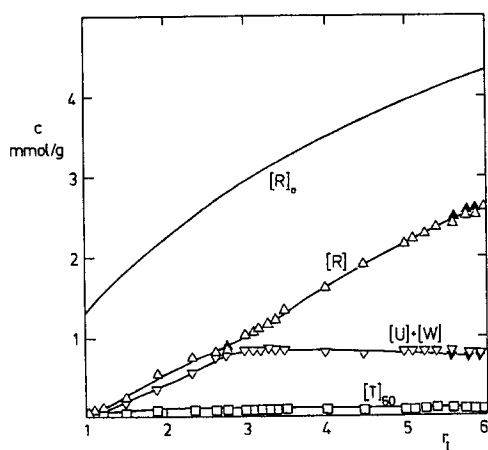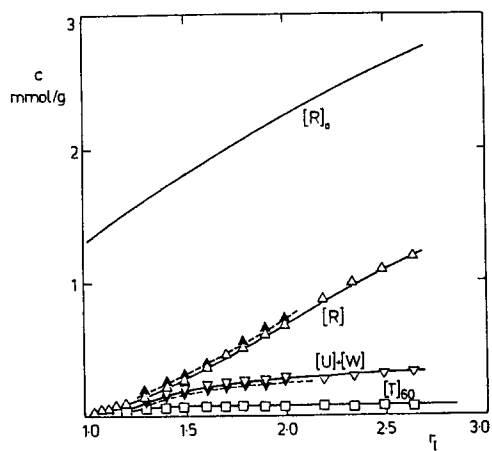
Figure 2a,b. Time dependence of the gel fraction, w_g. Fig. 2a 120°C, Fig. 2b 140°C; ---- interpolated dependence of w_g calculated from analytical data using the branching theory (5).

Figure 3a,b. Dependence of the steady state concentrations of isocyanate, [R], urea, $[T]_{60}$, and the sum of biuret and allophanate groups, [U] + [W], on the initial molar ratio of NCO to OH groups, r_I. Fig. 3a: 90°C, Fig. 3b: 140°C.

either 100% conversion of urea to biuret, or 100% conversion to allophanate of the NCO groups reacted in excess. The analysis has shown that in most cases this difference is not too large (5). The experimental gel fractions were practically the same as the calculated ones at 90°C but lower at 120°C and 140°C. With increasing reaction temperature, the difference increased (Fig. 5).
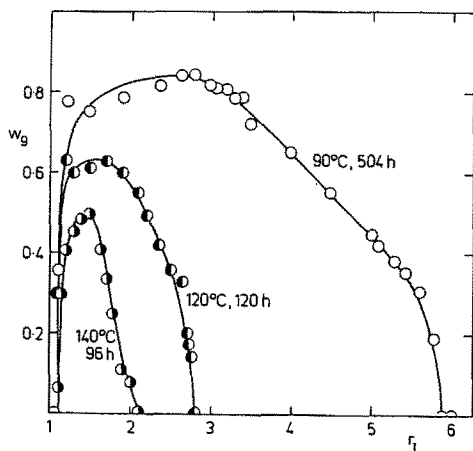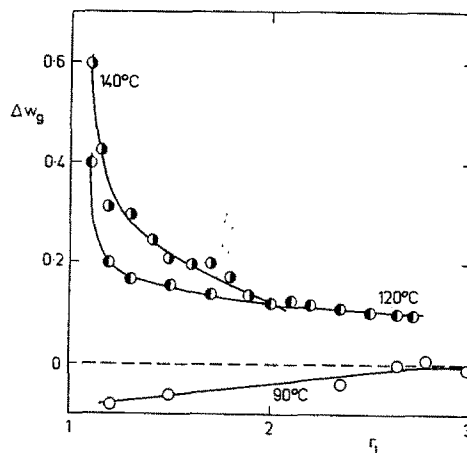

Figure 4

Figure 5

Figure 4. Gel fractions, w_g, in poly(oxypropylene) diol-4,4'--diisocyanatodiphenylmethane in dependence on the molar ratio of NCO to OH groups, r_I, at temperatures indicated.

Figure 5. The difference between the calculated and experimental gel fraction, Δw_g, in dependence on r_I.

The reasons for this difference have not been found yet. A reinvestigation of the model reactions in this temperature region has revealed that under these conditions some other side reactions may occur in a low extent. If water were present, urea could be split into amine and carbon dioxide, but water cannot be present due to a high concentration of NCO groups. Also, at high temperature two urethane groups can yield a urea and an ether group. The latter reaction cannot affect the gel fraction because the number of bonds is not changed and isocyanate is not involved. The possible splitting of urethane into hydroxyl and isocyanate followed by splitting off water and formation of a double bond was not observed in model experiments. If it were operative, it would have to proceed continuously

with time and the concentration of NCO group would have to de-
crease after reaching a maximum value. This was not observed,
however.

The branching theory of network formation due to side re-
actions explained in Ref. (5) was used to estimate the extent
of the unknown side reaction necessary to produce the observed
differences in the calculated and experimental gel fractions.
It was assumed that in this side reaction, the NCO group reacts
but does not produce any intermolecular bond (deactivation re-
action). The calculated values of [R] and the corresponding
values of [U] + [W] are shown in the figures by dashed curves.
It can be seen that the difference develops rather soon and
not in the later stages of the reaction. Furthermore, the ex-
tent of this side reaction, relative to the concentration of
NCO groups, is rather small. At 140°, where the deviations are
the highest, deactivation of less than 2% of the original NCO
groups $[R]_0$ is sufficient to produce the observed decrease in
the gel fraction. In light of the finding that w_g is very sen-
sitive to the number of bonds (especially if it is not too
close to unity), it is difficult to trace the origin of deac-
tivation. Such small amounts may not be detectable in model ex-
periments by HPLC. Also, one should take into account the pos-
sible errors in the determination of NCO groups and calcula-
tion of the concentration of branch points from the difference
between two determinations of the (relatively large) concen-
trations of NCO groups.

References

1. Saunders, J.H., Frisch, K.C., Polyurethane Chemistry and
   Technology, Pt 1, Interscience, New York 1963
2. Špírková, M., Kubín, K., Dušek, K., J. Macromol. Sci.-Chem.,
   A24, 1151 (1987)
3. Yokoyama, T., Furukawa, M., International Progress in Poly-
   urethanes, 125, Technomic Publ. Co., Westport 1980
4. Furukawa, M., Yokoyama, T., Makromol. Chem., 182, 2201
   (1981)
5. Dušek, K., Špírková, M., Havlíček, I., Macromolecules,
   submitted
6. Dušek, K., Polym. Bull., 17, 481 (1987)