Polymer Bulletin 17, 481–488 (1987)

Polymer Bulletin

Theory of network formation by additional crosslinking of polyurethanes due to biuret and allophanate formation

Karel Dušek

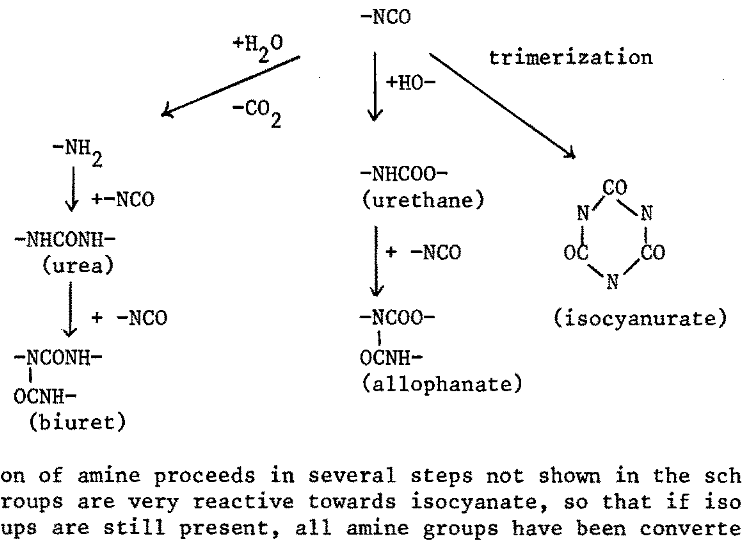
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences,
CS-162 06 Prague 6, Czechoslovakia

Summary

Using the theory of branching processes, conditions for gelation and relations for the sol fraction and concentration of elastically active network chains have been derived for polyurethane systems where also urea, biuret and allophanate units are formed. The application of the theory is illustrated by gelation in diol-diisocyanate-water systems in which urea and biuret units are formed.

Introduction

The formation of polyurethanes from polyols and polyisocyanates is accompanied by a number of side reactions which usually are the source of additional crosslinking (1). The most important reactions are given in the scheme which follows:



The formation of amine proceeds in several steps not shown in the scheme. The amine groups are very reactive towards isocyanate, so that if isocyanate groups are still present, all amine groups have been converted to urea and biuret units. The trimer is stable, whereas the possibly existing isocyanate dimer is unstable and cannot be considered as a permanent grouping in polyurethane products.

It was found earlier (2,3) that in the presence of organotin catalysts, absence of water and at temperatures below 100°C the reaction between the hydroxyl and isocyanate groups to give urethane was the only reaction, provided the initial molar ratio $r_H = [OH]_0/[NCO]_0 \geq 1$. In the excess of isocyanate, considerable additional crosslinking was detected, which was explained by the formation of allophanates (4,5).

Model experiments in alcohol-monoisocyanate systems (6) revealed that, in the case that traces of water are present, additional crosslinking due to biuret formation was much faster and intensive than the formation of allophanates. Since traces of water are always present in commercial polyols, chain extension by urea units and additional crosslinking due to biuret formation are of importance. The theoretical treatment of network formation due to allophanate formation was presented earlier (4) and compared with experiments (5).

In this contribution, the theory of network formation under participation of urethane, urea, biuret and also allophanate units is developed. Possible trimerization is not considered.

Theory

The network build-up is treated theoretically using the statistical theory of branching processes which employs the probability generating functions (Refs.2,4 and also 7,8).

The following assumptions have been used:

(1) the polyol has f OH (H) groups of equal and independent reactivity,

(2) the diisocyanate has two NCO (I) groups of equal and independent reactivity,

(3) intramolecular reactions do not occur.

Postulate (2) can be relaxed and the dependence of reactivities of NCO groups (like that in tolylene diisocyanates) can be taken into account without much difficulty, but relaxation of postulate (3) would be more difficult (cf.Ref.8).

In the treatment of allophanate crosslinking, the build-up of structures occurred from polyol and isocyanate units specially labelled (4). Isocyanate groups with one kind of label were engaged in urethane units, whereas allophanate units were assembled from NCO groups with different labels. The advantage of such treatment consists in that the concentration of all isocyanate groups (including unreacted groups) is constant during the reaction.

When a greater number of units of different kinds takes part in the network build-up, the former procedure becomes somewhat complicated. Therefore, an alternative way of network build-up was used in this case, in which structural units - urethane, urea, biuret and allophanate units - were used as building blocks.

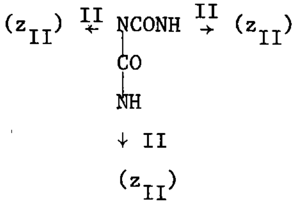
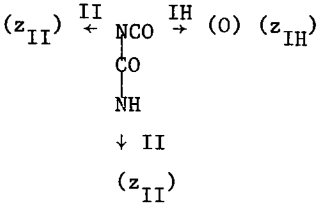
For this purpose, the diisocyanate units are split into two monoisocyanate units by cutting the connections between them and the points of cut are labelled (I). Then, the branched or crosslinked structures are reconstituted by connecting the labelled points of cut with themselves. The reacted OH groups of the polyol are connected with urethane or allophanate units.

The variables of the probability generating functions z are related to the types of the bonds. Table 1 enumerates the structural units involving isocyanate groups used in the generation.

The probability generating functions for the type and number of bonds issuing from these units (placed in the root of the probability tree) are as follows

$$F_{OH}(\mathbf{z}) = (1 - \alpha_H + \alpha_H z_{HI})^f \qquad (1)$$

Table 1 Structural units in a polyurethane

Unit	Designation	Structure, type of bond, pgf variable	Molar fraction
unreacted isocyanate	R	$OCN \overset{II}{\rightarrow} (z_{II})$	r
urethane	S	$(z_{II}) \overset{II}{\leftarrow} NHCO \overset{IH}{\rightarrow} (0)\ (z_{IH})$	s
urea	T	$(z_{II}) \overset{II}{\leftarrow} NHCONH \overset{II}{\rightarrow} (z_{II})$	t
biuret	U	 $(z_{II}) \overset{II}{\leftarrow} \underset{\substack{\vert \\ CO \\ \vert \\ NH \\ \downarrow II \\ (z_{II})}}{N}CONH \overset{II}{\rightarrow} (z_{II})$	u
allophanate	W	 $(z_{II}) \overset{II}{\leftarrow} \underset{\substack{\vert \\ CO \\ \vert \\ NH \\ \downarrow II \\ (z_{II})}}{N}CO \overset{IH}{\rightarrow} (0)\ (z_{IH})$	w
unreacted hydroxyl		$-OH$	$1 - \alpha_H$
reacted hydroxyl		$-O \overset{HI}{\rightarrow} (z_{HI})$	α_H

$$F_{OI}(\mathbf{z}) = (r + s z_{IH} + t z_{II} + u z_{II}^{2} + w z_{II} z_{IH}) z_{II} \ , \qquad (2)$$

where r + s + t + u + w = 1 and the subscripts at F, H and I, indicate the polyol and isocyanate component, respectively. The pgf's for the number of bonds issuing from units in the generation g>0 are obtained by differentiation

$$F_{IH}(\mathbf{z}) = \left(\frac{\partial F_{OH}(\mathbf{z})}{\partial z_{HI}}\right) \Bigg/ \left(\frac{\partial F_{OH}(\mathbf{z})}{\partial z_{HI}}\right)_{\mathbf{z}=1} = (1-\alpha_H+\alpha_H z_{HI})^{f-1} \qquad (3)$$

$$F_{HI}(\mathbf{z}) = \left(\frac{\partial F_{OI}(\mathbf{z})}{\partial z_{IH}}\right) \Bigg/ \left(\frac{\partial F_{OI}(\mathbf{z})}{\partial z_{IH}}\right)_{\mathbf{z}=1} = (s+w z_{II}) z_{II}/(s+w) \qquad (4)$$

$$F_{II}(\mathbf{z}) = \left(\frac{\partial F_{OI}(\mathbf{z})}{\partial z_{II}}\right) \Big/ \left(\frac{\partial F_{OI}(\mathbf{z})}{\partial z_{II}}\right)_{\mathbf{z}=\mathbf{1}} = \frac{r+sz_{IH}+tz_{II}+uz_{II}^{2}+wz_{II}z_{IH}+z_{II}(t+2uz_{II}+wz_{IH})}{r+s+2t+3u+2w} \qquad (5)$$

The meaning of subscripts in $F_{AB}(z)$ is the following: F_{AB} is the pgf for the number of bonds issuing from a unit B in generation g>0 rooted in generation g-1 by the bond BA.

The gel point condition reads

$$D = \det(\delta_{AB}^{CD} - F_{AB}^{CD}) = 0 \qquad (6)$$

where $\delta_{AB}^{CD} = 1$ for AB=CD and zero otherwise and $F_{AB}^{CD} \equiv (\partial F_{AB}(\mathbf{z})/\partial \mathbf{z}_{CD})_{\mathbf{z}=\mathbf{1}}$. Using Eqs.(3)-(5) for obtaining the derivatives, one gets for D

$$D = \begin{vmatrix} 1 & 0 & -F_{II}^{IH} \\ -F_{IH}^{HI} & 1 & 0 \\ 0 & -F_{HI}^{II} & 1 - F_{II}^{II} \end{vmatrix}$$

with $F_{II}^{IH} = (s+2w)/M$, $F_{IH}^{HI} = (f-1)\alpha_H$, $F_{HI}^{II} = (s+2w)/(s+w)$.

$F_{II}^{II} = (2t+6u+2w)/M$, $M = r+s+2t+3u+2w$

so that Eq.(6) yields

$$1 - F_{II}^{II} - F_{IH}^{HI}F_{HI}^{II}F_{II}^{IH} = 1 - \frac{2t+6u+2w}{M} - (f-1)\alpha_H \frac{(s+2w)^2}{(s+w)M} = 0 \qquad (7)$$

In the case that only allophanate units are formed, i.e. t = u = 0, gelation condition (7) is equivalent to that given by Eq.(15) of Ref.3. The equivalence can be proved, if one takes into account that

$$\frac{s + 2w}{r + s + 2w} = \alpha_I \quad \text{and} \quad \frac{2w}{r + s + 2w} = \alpha_I\alpha_A \quad ,$$

where α_A is the conversions of excess isocyanate groups into allophanate groups

$$\alpha_A = \frac{2(I_0 - I) - (H_0 - H)}{I_0 - I}$$

and

$$\alpha_I = \frac{I_0 - I}{I_0}$$

The pgf´s (1)-(5) give access to pregel and postgel structural parameters of the system such as molecular weight averages, or sol fraction and concentration of elastically active network chains. Here, the derivation of postgel parameters will be outlined.

Post-gel stage: The postgel structural parameters are determined by extinction probabilities, defined by

$$v_{AB} = F_{AB}(\mathbf{v}) \tag{8}$$

Thus, we have

$$v_{IH} = (1 - \alpha_H + \alpha_H v_{HI})^{f-1} \tag{9}$$

$$v_{HI} = (s + wv_{II})v_{II}/(s + w) \tag{10}$$

$$v_{II} = \frac{r+sv_{IH}+tv_{II}+uv_{II}^2+wv_{II}v_{IH}+v_{II}(t+2uv_{II}+wv_{IH})}{r+s+2t+3u+2w} \tag{11}$$

and one looks for the roots between 0 and 1. Specifically, one substitutes for v_{IH} and v_{HI} from Eqs.(9) and (10) into Eq.(11).

The sol fraction, w_s, is obtained from the relation

$$w_s = m_H F_{OH}(\mathbf{v}) + m_I F_{OI}(\mathbf{v}) \quad , \tag{12}$$

where m_H and m_I are the mass fractions of components H and I, and $F_{OH}(\mathbf{v})$ and $F_{OI}(\mathbf{v})$ are obtained from $F_{OH}(\mathbf{z})$ and $F_{OI}(\mathbf{z})$, respectively, by making substitution $z_{AB} \to v_{AB}$. The mass fractions, m, are given by

$$m_I = \frac{M_R N_R + M_S N_S + M_T N_T + M_U N_U + M_W N_W}{M_H N_H/f + M_R N_R + M_S N_S + M_T N_T + M_U N_U + M_W N_W} \tag{13}$$

$$m_H = 1 - m_I \quad ,$$

where M_X and N_X are the molecular weights and numbers of moles of component X, respectively, and N_H refers to hydroxyl groups. For the case under consideration,

$$M_R = M_S = M_{DI}/2$$

$$M_T = M_{DI} - 28$$

$$M_U = 3M_{DI}/2 - 28$$

$$M_W = M_{DI}$$

where for urea and biuret units the weight loss due splitting-off CO_2 and addition of H_2O has been considered. If the effect of this weight loss can be neglected, then

$$m_I = \frac{N_I M_{DI}/2}{N_H/f + N_I M_{DI}/2} = \frac{M_{DI}/2}{r_H M_H/f + M_{DI}/2} \quad , \tag{14}$$

where M_{DI} and M_H are, respectively, the molecular weight of the diisocyanate and polyol, and $r_H = N_H/N_I$ is the initial molar ratio of hydroxyl to isocyanate groups.

The number of elastically active network chains (EANC) is derived from the number of elastically active branch points. The latter quantity can be derived from the pgf´s T(z) for the number of bonds with infinite continuation issuing from a monomer unit. These pgf´s are obtained using the following substitution

$$T_H(z) \equiv \sum_{i=0} \tau_{Hi} z^i = F_{OH}(z_{XY} = v_{XY} + (1 - v_{XY})z) \qquad (15)$$

$$T_I(z) = \sum_{i=0} \tau_{Ii} z^i = F_{OI}(z_{XY} = v_{XY} + (1 - v_{XY})z) \qquad (16)$$

The number of EANC´s per structural unit, N_e, is given by the number of bonds with infinite continuation issuing from elastically active branch points, i.e., such branch points from which at least three paths issue to infinity:

$$N_e = (1/2)[n_H' \sum_{i=3} i\tau_{Hi} + n_I' \sum_{i=3} i\tau_{Ii}] \qquad (17)$$

where $n_H' = (N_H/f)/(N_H/f+N_R+N_S+N_T+N_U+N_W)$, $n_I' = 1 - n_H'$.
The sums in Eq.(17) are obtained by the expansion of pgf´s (15) and (16). For f<3, the contribution by the polyol is zero, for f=3

$$\sum_{i=3} i\tau_{Hi} = 3\tau_{H3} = \alpha_H^3(1 - v_{HI})^3 \qquad (18)$$

In the isocyanate containing structures, only biuret (U) and allophanate (W) are trifunctional and can contribute to N_e

$$\sum_{i=3} i\tau_{Ii} = u(1 - v_{II})^3 + w(1 - v_{II})^2(1 - v_{IH}) \qquad (19)$$

Equation (17) overestimates N_e at higher contents of allophanate and/or biuret groups, because the connections between branch points U and W become short and do not contribute to rubber elasticity. However, the derivation of N_e can be modified to take into account this feature.

Discussion

The calculation of the gelation condition, the sol fraction and concentration of EANC´s requires either analytical data on concentrations of the respective units as a function of time or conversion, or the kinetic and equilibrium constants for the respective reactions.

The application of the theory can be demonstrated by prediction of the gelation condition in a simplified diol-diisocyanate systems in the presence of water when allophanate formation does not occur. Gelation due to allophanate formation was discussed in Ref.3.

For the purpose of illustration, the following simplifying conditions have been imposed on the diol-diisocyanate-water system:

(1) Formation of urethane is the fastest reaction: at $r_H<1$, α_H is always 1.

(2) Reaction with water starts after all OH groups have reacted.

(3) In the reaction of isocyanate groups with water, urea is formed first and this reaction is quantitative.

(4) The concentrations of free isocyanate R, urea T and biuret U are governed by the equilibrium

$$K_B = \frac{U}{T\ R} \tag{20}$$

(5) No allophanate is formed and no cyclization is operative.

Under these conditions, one can distinguish two régimes depending on the initial molar concentration of water, X,

(a) $I_0 - H_0 = \Delta \leq 2X$

Urea is formed and no free isocyanate is left for the formation of biuret: $U = 0$, $T = \Delta/2$.

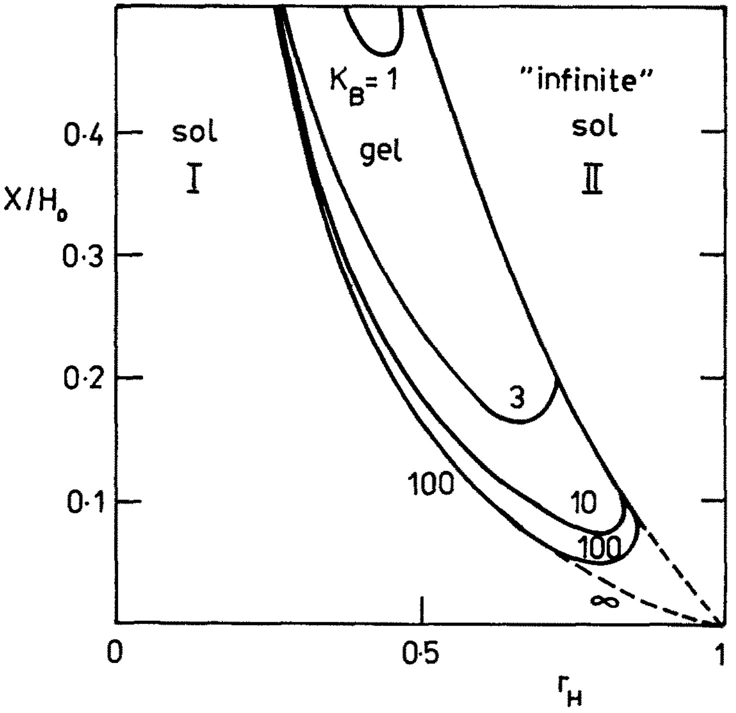


Figure 1. Gelation limits in an idealized system diol-diisocyanate-water calculated for the values of the equilibrium constant K_B indicated. I_0 = 1 mol/l; X/H_0 initial molar ratio Water/OH groups, $r_H = H_0/I_0$; region I: infinite polymer composed of diol units endlinked with urethane and urea units; region II: polymer branched with biuret units having dangling chains terminated with isocyanate groups.

(b) $I_0 - H_0 > 2X$

then

$$K_B = \frac{U}{(U - X)(\Delta - 2T - 3U)} = \frac{U}{(U - X)(\Delta - U + 2X)} \tag{21}$$

which gives U as a function of X for the given Δ and T = U - X.

Figure 1 shows the dependence of X on r_H necessary for gelation. There exist two soluble regions separated by the region where the gel exists. The right-hand side sol region ($\Delta<2X$) represents an "infinite" polymer because all excess isocyanate has reacted with water and has been converted to chain extending urea units. No chain ends are available. The left-hand side sol region represents a branched polymer (due to biuret formation) with many dangling chains terminated by unreacted NCO groups. The right-hand side sol becomes finite, if $\alpha_H<1$, but it is very sensitive towards any branching which will cause gelation. So, one can possibly expecte gelation also in this region, if the conditions (1)-(4) are not obeyed.

Comparison with experimental results will be published at a later date.

References

1 M. Saunders and K.C. Frisch, "Polyurethanes Chemistry and Technology", Pt.I. Interscience, New York 1963
2 M. Ilavský and K. Dušek, Polymer 24, 1323 (1983)
3 M. Ilavský and K. Dušek, Polym. Bull. 8, 359 (1982)
4 K. Dušek, M. Ilavský and L. Matějka, Polym. Bull. 12, 33 (1984)
5 M. Ilavský, K. Bouchal and K. Dušek, Polym. Bull. 14, 495 (1985)
6 M. Špírková, M. Kubín and K. Dušek, J. Macromol. Sci., Pt.A.-Chem., in press
7 K. Dušek, Adv. Polym. Sci. 78, 1 (1986)
8 K. Dušek, in "Telechelic Polymers", E.Goethals, Ed., CRC Press, Boca Raton, FL, in press

Accepted March 25, 1987 C