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Statistical Treatment of Allophanate Crosslinking in the Formation of Polyurethane Networks

K. Dušek, M. Ilavský and L. Matějka

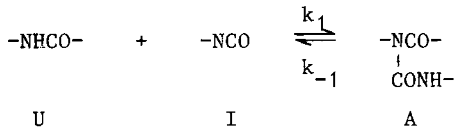
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences,
162 06 Prague 6, Czechoslovakia

Summary

Crosslinking of polyurethanes by a reaction of isocyanate groups with urethane groups leading to trifunctional allophanate branch points is treated statistically using the theory of branching processes. The occurrence of gelation in the diol - diisocyanate system and its dependence on the excess of isocyanate groups and the intensity of allophanate formation is discussed.

Introduction

The formation of allophanate groups is the most important side reaction accompanying the formation of polyurethanes. Allophanate (A) groups are formed from isocyanate (I) and urethane (U) groups



$$\underset{\text{U}}{\text{-NHCO-}} \quad + \quad \underset{\text{I}}{\text{-NCO}} \quad \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \quad \underset{\text{A}}{\begin{array}{c}\text{-NCO-}\\ | \\ \text{CONH-}\end{array}} \qquad (1)$$

It has been found (1) that (a) this reaction is reversible; the rate and equilibrium constants depend on the nature of the catalyst, and the stability of A decreases with increasing temperature, (b) the formation of A leads to additional crosslinking since A has a functionality of three. Allophanate formation is sometimes considered undesirable (branching and gelation in linear polyurethanes), but sometimes it has a beneficial effect as it improves the ultimate properties of polyurethane networks. Also, polyurethanes lightly crosslinked by A can be processed as thermoplastic rubbers at elevated temperatures when A groups dissociate and are re-formed at lower temperatures.

In spite of the importance of A formation, no quantitative study is available correlating the extent of A formation with branching, gelation and network formation. In this contribution, a theoretical approach to crosslink formation by A is presented, based on the theory of branching processes which was earlier applied to polyurethane networks when urethane formation was the only proceeding reaction (2-4).

Statistics of Formation of Urethane-Allophanate Networks

The hydroxyl groups (H) in the polyol and isocyanate (I) groups in diisocyanate are considered of equal and independent reactivity; cyclization is not taken into account. As is seen from Eq. (1), the urethane group is bifunctional (U = -HI-) whereas the allophanate group is trifunctional (A = $-\mathrm{H}\underset{|}{\mathrm{I}}\mathrm{I}-$) and is composed of two former I groups. Because the probabilities for I to be bound in A or U are different and only a single I-I bond is present in A ($\underset{|}{\mathrm{I}}\mathrm{-I-I-}\ldots$ is not allowed), one has to distinguish between reacted I units by adopting a different notation

$$\begin{aligned} &\mathrm{I\ (in\ urethane)} \longrightarrow \mathrm{U}\ , \\ &\mathrm{I\ (in\ -HI-\ of\ A)} \longrightarrow \mathrm{X}, \quad \mathrm{i.e.}\ \mathrm{A} = -\mathrm{H}\underset{\mathrm{Y-}}{\underset{|}{\mathrm{X}}}- \\ &\mathrm{I\ (in\ -I-\ of\ A)} \longrightarrow \mathrm{Y} \end{aligned} \tag{2}$$

The extent of A formation can be characterized in two ways - either by the fraction of reacted I groups in A (X+Y),

$$\alpha_A = \frac{2[(I_0 - I) - (H_0 - H)]}{I_0 - I} = \frac{2A}{I_0\alpha_I} = 2[1 - \frac{\alpha_H r_H}{\alpha_I}] \tag{3}$$

or by the fraction of reacted H groups in A,

$$\alpha'_A = \frac{I_0 - I - (H_0 - H)}{H_0 - H} = \frac{A}{H_0\alpha_H} = \frac{\alpha_A/2}{1 - \alpha_A/2} \tag{4}$$

In these equations, I, H, and A are the respective molar concentrations of isocyanate, hydroxyl, and allophanate groups, the subscript 0 refers to initial concentrations. The conversions are defined as $\alpha_I = (I_0 - I)/I_0$, $\alpha_H = (H_0 - H)/H_0$; r_H is the initial mole fraction $r_H = H_0/I_0$.

Probability generating functions. Let us consider the reaction of mono-, di-, and trifunctional, H-containing components in the polyol, their distribution in the mixture being characterised by the respective mole fractions n_{H1}, n_{H2}, and n_{H3} ($n_{H1} + n_{H2} + n_{H3} = n_H$), with diisocyanate ($n_{I2} = n_I$, $n_H + n_I = 1$). The probability generating functions (pgf) for the number of bonds issuing from H- and I-containing units in the root read as follows

$$F_{OH}(\underline{\theta}) = [n_{H1}(1 - \alpha_H + \alpha_H\vartheta) + n_{H2}(1 - \alpha_H + \alpha_H\vartheta)^2 + + n_{H3}(1 - \alpha_H + \alpha_H\vartheta)^3]/n_H \tag{5}$$

$$F_{0I}(\theta) = \{ 1 - \alpha_I + \alpha_I[(1 - \alpha_A)\theta_{UH} + (\alpha_A/2)(\theta_{XH}\theta_{XY} + \theta_{YX})]\}^2 \tag{6}$$

where $\vartheta = [(1 - \alpha_A)\theta_{HU} + (\alpha_A/2)\theta_{HX}]/(1 - \alpha_A/2)$.

The construction of F_{OH} and F_{OI} calls for the following comment: Bond directions are denoted with the substricts of the dummy variable θ of the pgf: θ_{MN} means that the bond connects a unit of type M on generation g with unit of type N on generation g+1. The coefficient at θ^{i}_{MN} has the meaning of probability of finding i such bonds issuing from unit M. Therefore, one has to consider for the reacted H group the bonds H→U and H→X and for the reacted I group the bonds U→H, X→H, X→Y, and Y→X.

The probability of finding specified bonds issuing from a unit on generation g to a unit on generation g+1 (g>0) depends on the type of unit on generation g-1. Thus, F_{MN} means a pgf for the unit N which is attached to (rooted on) unit M on generation g-1. The six pgf´s are obtained by the differentiation of F_{OH} or F_{OI}; $F_{MN} = A_{MN}(\partial F_{OK}/\partial \theta_{NM})$ (K = I or H) because the unit N is rooted on M via an N→M bond (looking out of N); A_{MN} is a normalizer so that $F_{MN}(1) = 1$ is obeyed:

$$F_{UH}(\underline{\theta}) = \phi_1 + \phi_2(1 - \alpha_H + \alpha_H\vartheta) + \phi_3(1 - \alpha_H + \alpha_H\vartheta)^2 \tag{7}$$

$$F_{XH}(\underline{\theta}) = F_{UH}(\underline{\theta}) \tag{8}$$

$$F_{HU}(\underline{\theta}) = f_{OI} = (F_{OI})^{1/2} = 1 - \alpha_I + \alpha_I[(1 - \alpha_A)\theta_{UH} + \\ + (\alpha_A/2)(\theta_{XH}\theta_{XY} + \theta_{YX})] \tag{9}$$

$$F_{HX}(\underline{\theta}) = \theta_{XY}f_{OI} \tag{10}$$

$$F_{YX}(\underline{\theta}) = \theta_{XH}f_{OI} \tag{11}$$

$$F_{XY}(\underline{\theta}) = f_{OI} \tag{12}$$

where $\phi_k = kn_{Hk}/\sum_k kn_{Hk}$.

The gel point. Gelation occurs when infinite continuation of bonds is possible. This condition is satisfied (5) if

$$\det(\delta^{KL}_{MN} - F^{KL}_{MN}) = 0 \tag{13}$$

where $F^{KL}_{MN} = (\partial F_{MN}/\partial \theta_{KL})_{\underline{\theta}=\underline{1}}$ and $\delta^{KL}_{MN} = 1$ if KL = MN and zero otherwise. In this case, the explicit form of the determinant is as follows

$$\begin{vmatrix} 1-F^{UH}_{UH} & -F^{UH}_{XH} & -F^{UH}_{HU} & -F^{UH}_{HX} & -F^{UH}_{YX} & -F^{UH}_{XY} \\ -F^{XH}_{UH} & 1-F^{XH}_{XH} & -F^{XH}_{HU} & -F^{XH}_{HX} & -F^{XH}_{YX} & -F^{XH}_{XY} \\ -F^{HU}_{UH} & -F^{HU}_{XH} & 1-F^{HU}_{HU} & -F^{HU}_{HX} & -F^{HU}_{YX} & -F^{HU}_{XY} \\ -F^{HX}_{UH} & -F^{HX}_{XH} & -F^{HX}_{HU} & 1-F^{HX}_{HX} & -F^{HX}_{YX} & -F^{HX}_{XY} \\ -F^{YX}_{UH} & -F^{YX}_{XH} & -F^{YX}_{HU} & -F^{YX}_{HX} & 1-F^{YX}_{YX} & -F^{YX}_{XY} \\ -F^{XY}_{UH} & -F^{XY}_{XH} & -F^{XY}_{HU} & -F^{XY}_{HX} & -F^{XY}_{YX} & 1-F^{XY}_{XY} \end{vmatrix} = \begin{vmatrix} 1 & 0 & -X_3 & -X_3 & -X_3 & -X_3 \\ 0 & 1 & -X_4 & -X_4 & -1-X_4 & -X_4 \\ -X_1 & -X_1 & 1 & 0 & 0 & 0 \\ -X_2 & -X_2 & 0 & 1 & 0 & 0 \\ 0 & 0 & -X_4 & -X_4 & 1-X_4 & -X_4 \\ 0 & 0 & -X_4 & -1-X_4 & -X_4 & 1-X_4 \end{vmatrix} \tag{14}$$

solution of Eqs. (13) and (14) yields

$$1 - 2X_4(1 + X_1 + 2X_2) - X_3(2X_2 + X_1) = 0 \tag{15}$$

where

$$X_1 = \frac{(\phi_2 + 2\phi_3)\alpha_H(1 - \alpha_A)}{1 - \alpha_A/2} , \qquad X_3 = \alpha_I(1 - \alpha_A) ,$$

$$X_2 = \frac{(\phi_2 + 2\phi_3)\alpha_H\alpha_A}{2(1 - \alpha_A/2)} , \qquad X_4 = \alpha_I\alpha_A/2 \quad .$$

At a given r_H, Eq.(15) yields critical values for a pair from α_H, α_I, and α_A; the critical value of the third quantity is given by Eq.(3).

Postgel stage. The extinction probabilities, i.e., probabilities that a given bond has a finite continuation, are given by the relation $v_{MN} = F_{MN}(\underline{v})$; hence

$$\begin{aligned} v_{XH} &= v_{UH} = \phi_1 + \phi_2(1 - \alpha_H + \alpha_H R) + \phi_3(1 - \alpha_H + \alpha_H R)^2 \\ v_{HU} &= v_{XY} = 1 - \alpha_I + \alpha_I[(1 - \alpha_A)v_{UH} + (\alpha_A/2)(v_{XH}v_{XY} + v_{YX})] \\ v_{HX} &= v_{XY}v_{HU} \\ v_{YX} &= v_{XH}v_{HU} \end{aligned} \tag{16}$$

where $R = [(1 - \alpha_A)v_{HU} + (\alpha_A/2)v_{HX}]/(1 - \alpha_A/2)$.

The set (16) of six equations can be reduced to two equations (17) and (18) which can be solved numerically to obtain v_{UH} and, subsequently, all other extinction probabilities:

$$v_{HU} = \frac{1 - \alpha_I + \alpha_I(1 - \alpha_A)v_{UH}}{1 - \alpha_I\alpha_A v_{UH}} \tag{17}$$

$$v_{UH} = \phi_1 + \phi_2(1 - \alpha_H + \alpha_H R) + \phi_3(1 - \alpha_H + \alpha_H R)^2 \tag{18}$$

with

$$R = \frac{(1 - \alpha_A)v_{HU} + (\alpha_A/2)v_{HU}^2}{1 - \alpha_A/2}$$

The sol is composed of units from which no bond continues to infinity. This happens if the probability of existence of a bond is weighted by the respective v. The weight fraction of sol, w_s, is thus given by the relation

$$\begin{aligned} w_s = {} & m_{H1}(1 - \alpha_H + \alpha_H R) + m_{H2}(1 - \alpha_H + \alpha_H R)^2 + m_{H3}(1 - \alpha_H + \alpha_H R)^3 + \\ & + m_{I2}\{1 - \alpha_I[(1 - \alpha_A)v_{UH} + (\alpha_A/2)(v_{XH}v_{XY} + v_{YX})]\}^2 \end{aligned} \tag{19}$$

where m_{Xi} is the weight fraction of the component Xi, $M_{Xi}n_{Xi}/\sum_{X,i} M_{Xi}n_{Xi}=m_{Xi}$, M_{Xi} is the molecular weight of Xi.

Concentration of elastically active network chains (EANC). Active junctions, i.e., those from which at least three bonds issue to infinity, contribute to the number of EANC´s. Not only the triol units but also a part of diisocyanate units in A groups may become active crosslinks. Hence, the number of EANC´s per starting unit (polyol + diisocyanate) in the system is given by the contributions $N_{eT} + N_{eI}$ which are functions of the coefficients of the respective generating functions T_H and T_I for the number of bonds with infinite continuation. These functions are obtained by substituting the quantity

$$z_{MN} = v_{MN} + (1 - v_{MN})\theta \tag{20}$$

in F_{OH} and F_{OI} for each θ_{MN}. Thus,

$$T_H(\theta) = F_{OH}(\underline{z}) = \sum t_{Hi}\theta^i \tag{21}$$

$$T_I(\theta) = F_{OI}(\underline{z}) = \sum t_{Ii}\theta^i \tag{22}$$

where the coefficients t_{Hi} and t_{Ii} are the probabilities that i bonds with infinite continuation issue from a polyol and diisocyanate unit, respectively. The diisocyanate unit is considered short and/or stiff so that it can become an active junction with three or four active bonds. As one half of the number of active bonds issuing from active junctions contributes to the number of EANC´s, N_e, and a junction is regarded active if it issues three or more active bonds, N_e is given by

$$N_e = N_{eH} + N_{eI} = (3/2)n_H t_{H3} + n_I(3t_{I3}/2 + 2t_{I4}) \tag{23}$$

As explained elsewhere (e.g. refs. 5,6), N_e is conveniently obtained from the derivatives of the pgf's T_H and T_I; thus

$$N_{eH} = (n_H/2)[T_H'(1) - T_H'(0) - T_H''(0)] \tag{24}$$

$$N_{eI} = (n_I/2)[T_I'(1) - T_I'(0) - T_I''(0)] \tag{25}$$

where the prime and double prime respectively denote the first and second derivatives of T with respect to θ. One can notice that the terms of T_H corresponding to mono- and bifunctional polyol must disappear (they cannot contribute to N_e) and the contribution N_{eH} is given by the relation

$$N_{eH} = \frac{3n_{H3}\alpha_H^3}{2}\left[\frac{(1 - \alpha_A)(1 - v_{HU}) + (\alpha_A/2)(1 - v_{HX})}{1 - \alpha_A/2}\right]^3 \tag{26}$$

The derivatives in Eq.(25) are

$$T_I'(1) = 2\alpha_I\{(1 - \alpha_A)(1 - v_{UH}) + (\alpha_A/2)[(1 - v_{XH}) + \\ + (1 - v_{XY}) + (1 - v_{YX})]\}$$

$$T_I'(0) = 2\tau_I(0)\tau_I'(0)$$

$$T_I''(0) = 2(\tau_I'(0))^2 + 2\tau_I(0)\alpha_I\alpha_A(1 - v_{XH})(1 - v_{XY})$$

where

$$\tau_I(0) = 1 - \alpha_I + \alpha_I[(1 - \alpha_A)v_{UH} + \alpha_A v_{YX}]$$

$$\tau_I(0) = \alpha_I[(1 - \alpha_A)(1 - v_{UH}) + (\alpha_A/2)(1 + v_{XH} + v_{XY} - 3v_{YX})]$$

The interrelations (16) between v's have been used to derive the last two relations.

The concentrations of EANC's per unit volume of unextracted (ν_e) or extracted (ν_{eg}) network are given by the relations

$$\nu_e = (N_e/\bar{M})d \qquad \text{or} \qquad \nu_{eg} = [N_e/\bar{M}(1 - w_s)]d \tag{27}$$

where $\bar{M}$ is the number-average molecular weight of the starting components, $\bar{M} = \Sigma\, M_{Hi}n_{Hi} + M_{I2}n_{I2}$, and d is density.

Discussion

The treatment explained above makes it possible to calculate the most important characteristics of polyurethanes when allophanate formation becomes important. It can easily be applied to polyols of functionality $f>2$, or to diols ($n_{H2}/n_H = 1$) which may be interesting, e.g., in examining the first stage of the two-stage process. A comparison with experimental data will be presented at a later date. Here, the gelation and network formation will be illustrated using an example of a diol and a diisocyanate.

The allophanate formation is a reversible reaction (Eq.(1)) and the equilibrium value of α_I is determined from the equilibrium constant K defined as

$$K = \frac{A}{UI} = \frac{I_0 - I - (H_0 - H)}{[2(H_0 - H) - (I_0 - I)]I} \tag{27}$$

or

$$KI_0 = \kappa = \frac{\alpha_I - \alpha_H r_H}{(2\alpha_H r_H - \alpha_I)(1 - \alpha_I)} \tag{28}$$

Eq.(28) is quadratic in α_I and its solution reads

$$\alpha_I = \{B - [B^2 - 4\kappa(2\kappa + 1)\alpha_H r_H]^{1/2}\}/2\kappa \tag{29}$$

where $B = \kappa(2\alpha_H r_H + 1) + 1$. The constant K for organotin catalysts is of the order 10^{-1} l/mole (1). Fig. 1a illustrates the interdependence of the

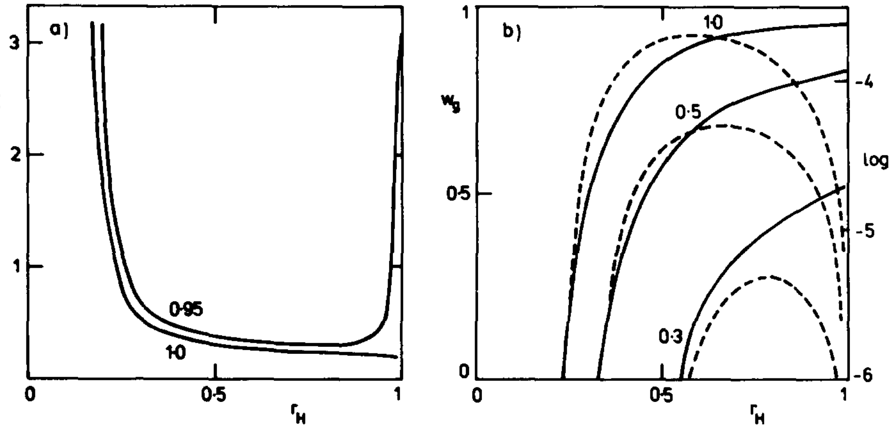


Fig.1. Critical values of K and r_H at gelation (a) and the dependence of both the gel fraction (w_g) and concentration of EANC´s (ν_{eg}) on the ratio r_H (b) for a system composed of a diol and a diisocyanate. $M_{I2} = 250$, $M_{H2} = 1000$, $I_0 = 2n_{I2}d/\bar{M}$; Fig. 1a: the value of α_H is indicated; Fig. 1b: —— w_g, ----- ν_{eg} (mol/ml), $\alpha_H = 1$, the value of K (l/mole) is indicated.

critical values of K and r_H at gelation and Fig. 1b shows a typical change in the gel fraction $w_g = 1 - w_s$ and ν_{eg}. While gelation is not much dependent on K within a certain range of excess I, ν_{eg} passes through a maximum although w_g increases monotonically. The finite value of w_g at $r_H = 1$ results because $\alpha_H = 1$; if $\alpha_H < 1$, w_g also passes through a maximum and goes to zero at $r_H = 1$. This is another example of an anomalous dependence of ν_{eg} on w_g, which can be observed when a single process introduces new branch points and increases the number of defects simultaneously. Here, the excess of I groups produces defects (dangling ends due to off-stoichiometric composition) and new crosslinks (allophanates) as well. Other examples are the coupled crosslinking and chain scission as in scission-determined crosslinking (7) or in transesterification of polyhydroxyesters (8).

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