Networks

The Structure and Elasticity of Polyurethane Networks


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Summary

Model networks prepared from polyoxypropylenetriols (PPT) and diphenylmethane diisocyanate (MDI) in an excess of NCO groups were found to contain unusually small amounts of sol, $w_s$, and to have high values of the equilibrium modulus, suggesting an additional crosslinking, probably due to the formation of trifunctional allophanate crosslinks. A comparison of the $w_s$ values with the theory of branching processes in which the formation of both urethanes and allophanates is considered allowed us to determine the possible extent of the allophanate reaction, and to calculate the concentration of elastically active chains contributed by PPT and allophanate crosslinks.

Polyurethane networks based on poly(oxypropylene)triols (PPT) and diphenylmethane diisocyanate (MDI) were used as model systems for the testing of network formation and of the elastic behaviour (1-5). In these networks the network density was varied by varying the length of PPT and the initial mole ratio of reactive groups, $r_H = \frac{[OH]}{[NCO]}$; the reaction was conducted up to the highest possible conversion of minority groups in the presence of an organotin catalyst. In the range $r_H \geq 1$, a good fit was found for both the weight fraction of gel, $w_g$, and for the equilibrium modulus $G_e$, and the theoretical prediction, assuming that only urethane groups were formed (4). The viscoelastic and dielectric behaviour of networks also corresponded to the simple model character of these networks (3).

On the other hand, in the range of NCO groups in excess, higher $w_g$ and $G_e$ values than those predicted by theory taking into account only the formation of urethane bonds were systematically observed. It was assumed that such deviations exist as a consequence of additional crosslinking most probably caused by the formation of trifunctional allophanate groups by a reaction of isocyanate groups in excess with urethane groups. This assumption was supported by the results obtained with networks in which the crosslinking density was varied by the addition of a monofunctional isocyanate or alcohol, and the ratio $r_H$ was maintained unity; it was found that in these systems no additional crosslinking took place (5). The contribution to additional crosslinking by other side
reactions such as biuret formation seems to be unimportant due to a low concentration of water and strictly anhydrous conditions during preparation. By using the theory of branching processes, a statistical description of the build-up polyurethane networks was generalized by including the formation of allophanate groups (6).

In this contribution we analyze experimental results reported earlier and recent results obtained with PPT-MDI networks in the range $r_H < 1$ using a generalized branching theory (6). As a result, it was possible to estimate the likely extent of the allophanate reaction under conditions used in the preparation of PPT-MDI networks.

Experimental

Sample preparation: The networks were prepared (4) from two poly(oxypropylene)triols (PPT) having different molecular weights $M_n$ (Union Carbide Niax Polyols: LHT-240, $M_n = 708$, average functionality $f_n = 2.89$ and LG-56, $M_n = 2630$, $f_n = 2.78$) and 4,4'-diphenylmethanediisocyanate (MDI). PPT were dried by azeotropic distillation with benzene, so that the residual water content was 0.02% in both cases. The cross-linking proceeded at 80°C eight days in teflon moulds; 0.005 wt.% dibutyltin dilaurate was used as the catalyst. Networks with the initial mole ratio $r_H = [OH]/[NCO]$ in the range $0.6 < r_H < 1.7$ were obtained; a few new samples were prepared in the range $r_H < 1$.

Equilibrium modulus, extraction: The weight fraction of sol, $w_s$, was determined by multiple extraction of networks in benzene and chloroform at room temperature (Table I). The pendant isocyanate groups were deactivated by a reaction with methanol.

The equilibrium modulus was measured with a rheooptical apparatus (7) at 70°C in uniaxial elongation $\lambda$ ($\lambda = l/l_0$, $l$ and $l_0$ respectively being the deformed and initial length of the sample). The equilibrium shear modulus $G_e$ was determined from

$$G_e = e^e/(l^2 - l^{-1})$$

where $e^e$ is stress related to the deformed cross-section of the sample. The reduced modulus $G_r = G_e/[(1-w_s)RT]$ was determined from $G_e$ (Table I).

Results and discussion

Assuming that the trifunctional allophanate group (A) is composed of two isocyanate groups (I), a relation (Eq. (3), Ref. (6))

$$\alpha_A = 2(1 - \alpha_H r_H/\alpha_I)$$

was derived for the fraction of reacted I groups in allophanate $\alpha_A$, where $\alpha_H = (H_0 - H)/H_0$ and $\alpha_I = (I_0 - I)/I_0$ (I and H are the