

Networks

The Structure and Elasticity of Polyurethane Networks

4. The Effect of Additional Crosslinking on the Extraction and Elastic Behaviour of Model Polyoxypropylene-Urethane Networks Prepared in the Excess of Isocyanates

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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, $r_H = [\text{OH}]/[\text{NCO}]$; 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 1). The pendent isocyanate groups were deactivated by a reaction with methanol.

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

$$G_e = \sigma_e / (\lambda^2 - \lambda^{-1}) \quad (1)$$

where σ_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 1).

Results and discussion

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

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

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

Table 1. Effect of allophanates on the weight fraction of sol and on the concentration of EANC's

Sample	r_H	w_s	$G_r \cdot 10^4$ molcm ⁻³	α_I^a	α_A^a	K^a l mol ⁻¹	$\frac{T}{eg} \cdot 10^4$ molcm ⁻³	$\frac{V_A}{eg} \cdot 10^4$ molcm ⁻³	α_I^b	α_A^b	K^b l mol ⁻¹	$\frac{T}{eg} \cdot 10^4$ molcm ⁻³	$\frac{V_A}{eg} \cdot 10^4$ molcm ⁻³
Networks from $M_n = 708$													
1	0.64	0.012	4.83	0.861	0.558	1.12	8.03	9.57	0.859	0.540	1.03	8.20	9.26
2	0.69	0.006	6.52	0.902	0.516	1.40	9.03	9.86	0.899	0.496	1.26	9.21	9.46
3	0.70	0.003	7.01	0.930	0.540	2.19	9.78	11.27	0.928	0.521	1.96	10.00	10.85
4	0.73	0.002	8.25	0.944	0.500	2.40	10.19	10.74	0.941	0.480	2.10	10.42	10.27
5	0.75	0.001	9.65	0.963	0.488	3.45	10.72	10.96	0.960	0.468	2.95	10.97	10.47
6	0.80	0.002	10.38	0.947	0.362	1.52	10.39	7.56	0.944	0.339	1.29	10.60	7.05
7	0.86	0.006	10.00	0.914	0.175	0.37	9.20	3.14	0.911	0.149	0.29	9.36	2.67
8	0.90	0.003	9.81	0.941	0.144	0.43	10.20	2.78	0.937	0.117	0.32	10.40	2.26
Networks from $M_n = 2630$													
9	0.665	0.017	3.15	0.843	0.532	2.60	2.09	2.75	0.831	0.464	1.84	2.15	2.32
10	0.716	0.080	1.69	0.756	0.238	0.49	1.06	0.64	0.751	0.168	0.31	1.06	0.44
11	0.736	0.056	2.05	0.787	0.261	0.65	1.31	0.85	0.778	0.185	0.40	1.31	0.58
12	0.767	0.070	2.22	0.783	0.178	0.41	1.41	0.51	0.777	0.104	0.21	1.15	0.29
13	0.817	0.067	1.87	0.803	0.107	0.26	1.17	0.31	0.802	0.044	0.10	1.25	0.13
14	0.847	0.019	3.43	0.882	0.217	1.03	2.01	0.11	0.868	0.131	0.50	2.04	0.60
15	0.870	0.012	3.91	0.911	0.223	1.45	2.29	1.19	0.894	0.132	0.65	2.32	0.67
16	0.921	0.010	4.36	0.927	0.151	1.15	2.38	0.82	0.911	0.058	0.33	2.43	0.30

^aCalculated with $\alpha_H = 0.97$ for networks with $M_n = 708$ and with $\alpha_H = 0.93$ for networks with $M_n = 2630$;^bcalculated with $\alpha_H = 0.98$ for networks with $M_n = 708$ and with $\alpha_H = 0.96$ for networks with $M_n = 2630$.

molar concentrations of isocyanate and hydroxyl groups, respectively, and the subscript o is related to the initial concentrations). Because the formation of allophanates is a reversible reaction, we may write for the equilibrium constant K (Eq.(28), Ref.(6)).

$$KI_o = (\alpha_I - \alpha_H r_H) / [(2\alpha_H r_H - \alpha_I)(1 - \alpha_I)] \quad (3)$$

Also, relations have been derived for the weight fraction of sol, w_s , and the concentration of elastically active chains (EAMC) related to the gel $v_{eg} = v_{eg}^T + v_{eg}^A$ (Eqs (19 and (27) in Ref.(6), v_{eg}^T and v_{eg}^A , respectively, are the contributions by PPT and A).

The effect of allophanates on the weight fraction of sol

Both the reported and new values of the weight fraction of sol, w_s , as a function of r_H are given in Fig.1. along with the theoretical dependences (4) calculated assuming the formation of urethanes only (the calculation was carried out taking into account the measured number averages from functionality PPT (f_n); PPT was regarded as a mixture of a bi- and trifunctional component with the same M_n value). In the range of OH groups in excess the theory adequately describes the

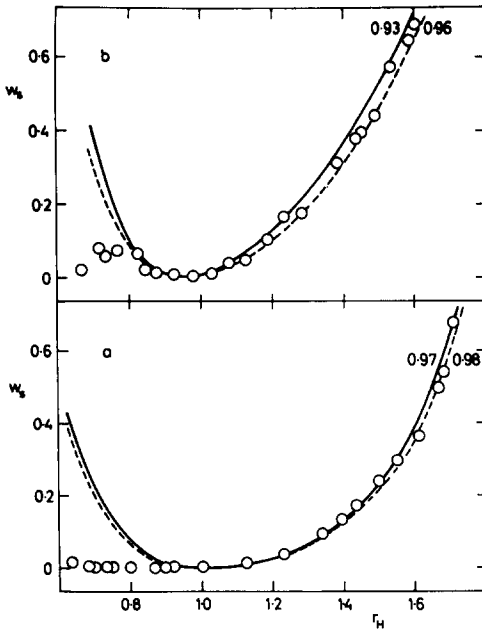


Fig.1. Dependence of the weight fraction of the sol w_s on $r_H = [OH]/[NCO]$
 a networks with $M_n = 708$;
 b networks with $M_n = 2630$;
 the numbers denote conversion of minority groups.

dependence of w_s on r_H , assuming that the intramolecular conversion of NCO groups α_I reaches 0.97-0.98 for networks of short PPT and 0.93-0.96 for those of long PPT. (Since, however, 2-3% of bonds are wasted in elastically inactive cycles (4), the overall conversions of NCO groups are higher just by these values.)

The w_s values in the range of NCO groups in excess were used in the calculation of the conversions α_I and α_A (by means of Eqs (2) and (19) in Ref.(4)), and from these, the values of the constant K were determined (Eq.(3), Table 1). This calculation was made on the assumption that the conversion of minority groups is the same in both regions (i.e., in the range $r_H < 1$, $\alpha_H = 0.97-0.98$ for $M_n = 708$ and $\alpha_H = 0.93-0.96$ for $M_n = 2630$).

For networks of short PPT the conversion values of isocyanates α_I (at $\alpha_H = 0.97$) vary in the range 0.86-0.96 (Table 1). The α_A values increase with decreasing r_H from 0.14 to 0.56. As expected, the increase of the conversion of minority OH groups to $\alpha_H = 0.98$ is reflected in a small decrease of α_I and α_A . For networks of long PPT the conversions α_I and α_A are generally lower than for those of short PPT.

In the experiments reported here it has not been checked whether the formation of allophanate groups has reached equilibrium. If this is assumed, then the equilibrium constant K varies in the range 0.1-3.4 l mol⁻¹ (Table 1). Model experiments of the formation of allophanates (8) in the reaction between butyl-N-phenylurethane and phenylisocyanate have led to estimated values of the equilibrium constants $K = 8.9$ l mol⁻¹ ($T = 50^\circ\text{C}$) and 6.5 l mol⁻¹ ($T = 70^\circ\text{C}$). In the case of organotin catalysis, the K values were found to be approximately 10⁻¹ l mol⁻¹ (9).

The effect of allophanates on the elastic behaviour

Assuming that the equilibrium modulus consists both of a chemical and of a topological contribution (of interchain constraints), we may write for the experimental modulus G_r in the Langley-Graessley approximation (10)

$$G_r = A \langle \alpha_o^2 \rangle v_{eg} + \langle \alpha_o^2 \rangle \epsilon T_{eg} \quad (4)$$

where $\langle \alpha_o^2 \rangle$ is the dilation factor (because the conditions of network preparation correspond to the conditions of measurement it has been assumed that $\langle \alpha_o^2 \rangle = 1$), ϵ is the proportionality constant, T_{eg} is the trapping factor, $A=1$ is the front factor for a phantom network with suppressed fluctuations of crosslinks, $A = 1/3$ is the front factor for a phantom network (11). With out networks, the best fit between theory and experiment was found in the range $r_H > 1$ (4), assuming $A = 1/3$ and $\epsilon = 5 \times 10^{-4}$ mol cm⁻³ (the v_{eg} and T_{eg} values were calculated from the theory in which only the formation of urethanes was considered (4)).

By means of the generalized theory (6) and using the conversions α_I and α_A (at a given α_H) determined from w_s , we

calculated the chemical contributions to the concentrations of EANC v_{eg}^T and v_{eg}^A (Table 1). As expected, v_{eg}^T and v_{eg}^A in networks of short PPT are higher than those of networks of long PPT. With increasing excess of NCO groups (decreasing r_H) the contribution of allophanate bonds increases; while in the range $r_H = 0.9-1$ v_{eg}^A is $\sim 10-20\%$ of v_{eg}^T , for networks in the range $r_H = 0.65-0.7$ $v_{eg}^A \approx v_{eg}^T$.

While the experimental values of G_r for networks of long PPT roughly correspond to the chemical contribution with $A=1$ (i.e., $G_r \sim v_{eg}^T + v_{eg}^A$) for networks of short PPT $(v_{eg}^T + v_{eg}^A) > G_r$ within the whole range (Table 1; a similar dependence has been observed earlier in the range $r_H > 1$). Analysis shows that also in the range $r_H < 1$ the dependence of G_r on r_H are best described by $A=1/3$ with the topological contribution $\Delta = G_r - (v_{eg}^T + v_{eg}^A)/3$. The dependence of Δ is roughly the same for networks of both PPT and decreases with NCO groups in excess (Fig.2).

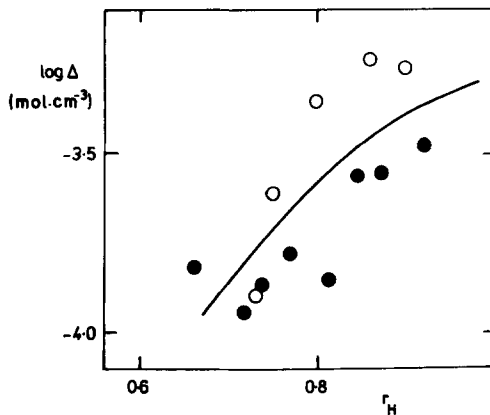


Fig.2. Dependence of the topological contribution to the modulus Δ (mol cm⁻³) on $r_H = [OH]/[NCO]$

○ networks with $M_n = 708$;
● networks with $M_n = 2630$.

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