Polymer Bulletin 8, 359-366 (1982)

Polymer Bulletin

The Structure and Elasticity of Polyurethane Networks

2. Model Networks from Poly(Oxypropylene)Triols, Diisocyanate and a Monofunctional Component

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Summary

If isocyanate groups are in excess networks prepared from poly(oxypropylene)triols (PPT) and 4,4′-diphenylmethanediisocyanate (MDI) in the presence of an organotin catalyst have higher values of the equilibrium modulus G and of the gel fraction w_g compared with theoretical predictions in which only the formation of urethane bonds is considered. If however, the NCO groups in excess were reacted with monofunctional phenyl isocyanate keeping the molar ratio $[OH]/[NCO] = 1$ constant, networks with a wide range of crosslinking density were obtained, for which the G and w_g values were in a good accord with the theory. The probable cause of departures in the PPT-MDI systems with NCO groups in excess consists in the formation of allophanate groups. An analysis of the equilibrium elastic behaviour of these networks has shown that the trapped entanglement contribution to the equilibrium modulus is likely to occur.

Introduction

The properties of model polyurethane networks prepared from poly(oxypropylene)triols (PPT) and 4,4′-diphenylmethane diisocyanate (MDI) are in the range $[OH]/[NCO] \geqslant 1$ in a good agreement with calculations based on the theory of branching processes and taking into account the formation of urethane bonds only (DUŠEK and ILAVSKÝ 1982, ILAVSKÝ and DUŠEK 1982). Also the viscoelastic and dielectric behaviour corresponds to the assumed simple structure (HAVRÁNEK et al. 1982). With the NCO groups in excess, however, higher values of the equilibrium modulus G and of the gel fraction, w_g, than those predicted by theory were observed (cf. also Figs 1 and 3). Although a specific organotin catalyst was used and the reaction temperature did not exceed 80°C, it is likely that allophanate groups were formed by a reaction between NCO and the urethane group.

In order to verify this assumption, we prepared networks in approximately the same range of G and w_g so that the effect of stoichiometric imbalance on crosslinking density was replaced by the effect of the addition of a monofunctional component;

hence, the ratio $r_{HT} = [OH]_{PPT}/[NCO]_{MDI}$ was variable, but the total ratio $r_H = [OH]/[NCO]$ was kept constant and was always unity. Cyclohexanol and phenyl isocyanate with the same reactivity of the OH and NCO groups as in PPT and MDI respectively were chosen as monofunctional compounds. A statistical calculation of network parameters applicable to this system has been offered in the Appendix to a paper by ILAVSKÝ and DUŠEK (1982). The results of photoelastic measurements were also used to test the applicability of recent theories of the rubber elasticity of polymer networks.

Experimental

Network preparation: The networks were prepared by employing the same procedure as earlier (ILAVSKÝ and DUŠEK 1982). Poly(oxypropylene)triols Union Carbide LHT-240 and LG-56 had the respective number average molecular weights M_n=708 and 2630, the respective number average functionalities f_n=2.89 and 2.78 and the residual water content 0.02 wt.%. MDI was redistilled and recrystallized twice from hexane. Cyclohexanol (COL), analytical purity grade, was freed from water by heating with CaO and purified by fractional distillation in the presence of 2 wt.% Na (b.p. 68.5-69°C at 2 kPa). Phenyl isocyanate (PI) was purified by rectification (b.p.58-59°C at 2 kPa).

Networks consisting of PPT-MDI-COL or PI in the range $0.6 < r_{HT} < 1.7$ and with r_H=1 were prepared in closed Teflon moulds at 80°C within seven days with 0.005 wt.% dibutyltin dilaurate as the catalyst (Table 1).

Extraction: The weight fraction of the sol w_s was determined by a multiple extraction of networks in chloroform at room temperature. The extracted samples were dried in the vacuo at 60°C to constant weight; the w_s values in Table 1 are an average from measurements carried out on at least two samples.

Measurements: Rheooptical measurements of unextracted networks were performed using an apparatus described earlier (ILAVSKÝ and DUŠEK 1976) at 340 K in the range of relative elongations $1 < \lambda < 1.1$. The equilibrium shear modulus G, strain- optical function A and stress-optical coefficient C=A/G were determined from

$$\sigma = G\,(\lambda^2 - \lambda^{-1}) \qquad (1)$$

$$\Delta n = A\,(\lambda^2 - \lambda^{-1}) \qquad (2)$$

where σ is stress related to a deformed cross-section, and Δn is birefringence (Table 1).

Results and Discussion

Sol content. Unlike the systems PPT-MDI (r_H=r_{HT}=0.65-1.7),

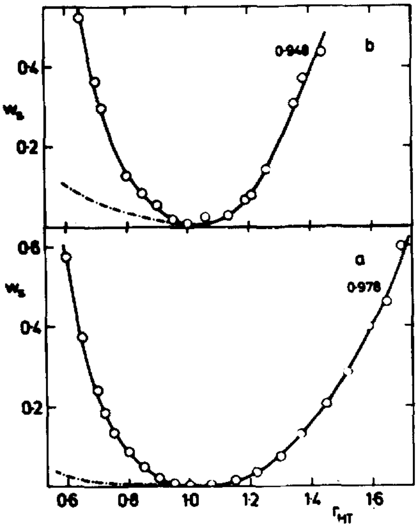

Fig. 1

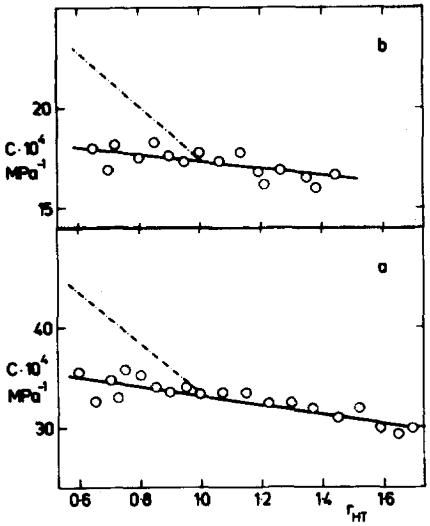

Fig. 2

Fig. 1 Dependence of the weight fraction of sol w_s on $r_{HT} = [OH]_{PPT}/[NCO]_{MDI}$

a - networks made from LHT-240, b - networks made from LG-56, ○ experiment, ——— theory (Eq.(A-15) from the paper ILAVSKÝ and DUŠEK 1982), numbers at curves denote conversion of minority groups, .-.-.- experimental data for PPT-MDI networks without the monofunctional component (cf. ILAVSKÝ and DUŠEK 1982)

Fig. 2 Dependence of the stress-optical coefficient C on $r_{HT} = [OH]_{PPT}/[NCO]_{MDI}$

a - networks made from LHT-240, b - networks made from LG-56, -.-.- data for PPT-MDI networks without the monofunctional component (cf. ILAVSKÝ and DUŠEK 1982)

a distinct minimum of the sol content at $r_{HT}=1$ can be observed in systems with a monofunctional component ($r_{HT}=0.65-1.7$, $r_H=1$) as predicted by the theory (ILAVSKÝ and DUŠEK 1982). Also the left branch of this dependence ($r_{HT}< 1$, COL added) satisfies the theory, similarly to the right branch ($r_{HT}> 1$, PI added) (Fig. 1). The best fit between experimental data and the theory corresponds to the conversion values of minority groups consumed by intermolecular bonds in networks made of triols LHT-240 and LG-56 $\xi \approx 0.978$ and ≈ 0.948 respectively (Table 1) (about 2-2.5 % of bonds are wasted by elastically inactive rings (DUŠEK and VOJTA 1977), so that the total conversions of groups are 0.99-1.0 and 0.96-0.99 respectively).

Stress-optical coefficient. In PPT-MDI networks at $r_H < 1$ the stress-optical coefficient C increased with increasing excess of NCO groups. This increase was interpreted by an increase in the concentration of polar groups in elastically active chains (EANC) due to the formation of allophanates; in networks with a monofunctional component and $r_H = 1$ no such increase could be observed (Fig. 2). A slight drop in C with increasing r_{HT} may be due to a change in the structure of side chains attached to EANC's: at $r_{HT} < 1$ side chains composed of one branch of PPT followed by a MDI unit and terminated with a COL unit predominate; at $r_{HT} > 1$, the side chain is shorter - the PPT branch is directly terminated with an PI unit. The lower C of networks composed of the larger PPT is given by the lower content of polar urethane groups in EANC's consisting of multiples of 2/3 PPT + MDI.

Elastic behaviour of networks. The equilibrium elastic behaviour was analyzed with respect to the value of the front factor A and to the possible contribution of trapped entanglements. For the equilibrium modulus G one may assume additivity of the chemical (G_c) and entanglement (G_e) contributions to the modulus G

$$G = G_c + G_e = A\,\nu_e RT + \varepsilon T_e RT \qquad (3)$$

where ν_e is the concentration of EANC's, R is the gas constant, T is temperature and where a conception of interacting segments in EANC's has been used for G_e (LANGLEY 1968, PEARSON and GRAESSLEY 1980); T_e is the trapping factor and ε is the proportionality constant. According to prediction (FLORY 1979), for a "phantom" network with free fluctuation of crosslinks $A = A_{ph} = 1/3$, while for a network with fully suppressed fluctuation of crosslinks A=1. Both the concentration of EANC's ν_e (or values related to the gel, ν_{eg}) and T_e (T_{eg}) were calculated by employing the procedure described in the Appendix of a paper by ILAVSKÝ and DUŠEK (1982) using the conversions of minority groups calculated from the sol content w_s (Table 1).

A plot of the reduced modulus

$$G_r = G/RTw_g = A\nu_{eg} + \varepsilon T_{eg} \qquad (4)$$

(measurements of the modulus G were carried out using nonextracted samples) as a function of r_{HT} shows that while for networks composed of the shorter triol the experimental data lie between the limiting cases for A=1/3 and A=1, for networks made of the larger triol in the range r_{HT} = 0.8 - 1.2 they lie above the theoretical curve for A=1, if the topological contribution G_e was not considered (ε=0) (Fig. 3). On assuming, however, that in Eq.(4) A=1/3, the difference $\Delta = G_r - \nu_{eg}/3$ is found to satisfy, the theoretical dependence of T_{eg} on r_{HT} (Fig.4) with

Table 1

Elasticity Characteristics

Sample	r_{HT}	$G*10$ MPa	w_s	ξ	$\nu_{eg}*10^4$ $molcm^{-3}$	$T_{eg}*10$	$X*10^4$ $molcm^{-3}$	G_r*10^4 $molcm^{-3}$
Networks from LHT - 240								
1	0.60	0.35	0.575	0.983	0.244	0.050	0.106	0.288
2	0.65	1.14	0.376	0.981	0.749	0.237	0.368	0.638
3	0.70	2.38	0.240	0.979	1.530	0.626	0.824	1.094
4	0.72	3.70	0.184	0.983	2.080	0.912	1.150	1.584
5	0.75	3.96	0.135	0.983	2.800	1.340	1.604	1.599
6	0.80	7.97	0.087	0.975	3.860	2.090	2.334	3.049
7	0.85	9.80	0.048	0.972	5.330	3.170	3.365	3.596
8	0.90	15.00	0.019	0.978	7.660	4.760	4.941	5.341
9	0.95	19.70	0.007	0.974	9.500	6.320	6.328	6.929
10	1.00	25.70	0.001	0.971	11.60	8.190	7.970	8.996
11	1.07	19.50	0.002	0.989	10.30	7.150	7.014	6.825
12	1.15	13.60	0.014	0.980	7.020	5.300	5.001	4.818
13	1.22	10.00	0.034	0.978	5.090	3.940	3.674	3.616
14	1.30	6.91	0.074	0.975	3.370	2.600	2.426	2.606
15	1.37	3.88	0.130	0.972	2.21	1.660	1.569	1.558
16	1.45	1.91	0.205	0.973	1.40	0.975	0.956	0.839
17	1.52	0.83	0.286	0.975	0.887	0.558	0.576	0.406
18	1.59	0.34	0.400	0.975	0.485	0.260	0.292	0.198
19	1.65	0.20	0.461	0.983	0.345	0.165	0.198	0.129
20	1.70	0.08	0.598	0.981	0.172	0.064	0.089	0.069
Networks from LG - 56								
21	0.65	0.08	0.524	0.964	0.088	0.058	0.058	0.061
22	0.70	0.38	0.365	0.955	0.207	0.204	0.171	0.209
23	0.72	0.97	0.298	0.957	0.306	0.347	0.276	0.483
24	0.80	2.33	0.130	0.952	0.756	1.200	0.854	0.935
25	0.85	3.44	0.083	0.945	1.060	1.940	1.306	1.310
26	0.90	5.00	0.055	0.935	1.34	2.78	1.840	1.848
27	0.95	7.60	0.020	0.944	2.01	4.400	2.873	2.709
28	1.00	10.00	0.010	0.937	2.42	5.80	3.719	3.528
29	1.06	8.14	0.024	0.940	1.87	4.65	2.951	2.913
30	1.13	6.10	0.030	0.961	1.69	4.07	2.605	2.197
31	1.19	4.37	0.068	0.955	1.14	2.84	1.802	1.638
32	1.21	4.02	0.080	0.950	1.01	2.54	1.610	1.526
33	1.26	1.59	0.145	0.945	0.645	1.60	1.017	0.650
34	1.35	0.46	0.313	0.933	0.255	0.547	0.359	0.234
35	1.38	0.26	0.372	0.933	0.185	0.366	0.245	0.145
36	1.44	0.15	0.437	0.942	0.129	0.227	0.157	0.090

r_{HT} molar ratio $[OH]_{PPT}/[NCO]_{MDI}$; w_s weight fraction of sol; ξ molar conversion of minority groups consumed in the formation

Table 1 (continued)

of intermolecular bonds calculated from w_s; ν_{eg} concentration of EANC's in gel; T_{eg} trapping factor for gel; $X = \nu_{eg}/3 + \varepsilon T_{eg}$ with $\varepsilon = 5 \times 10^{-4}$ molcm^{-3}; G_r reduced modulus $G_r = G/w_g RT$, G experimental equilibrium small-strain modulus. ξ, ν_{eg}, T_{eg} calculated from w_s (cf. Appendix of ILAVSKÝ and DUŠEK 1982); G, G_r and w_s experimental values

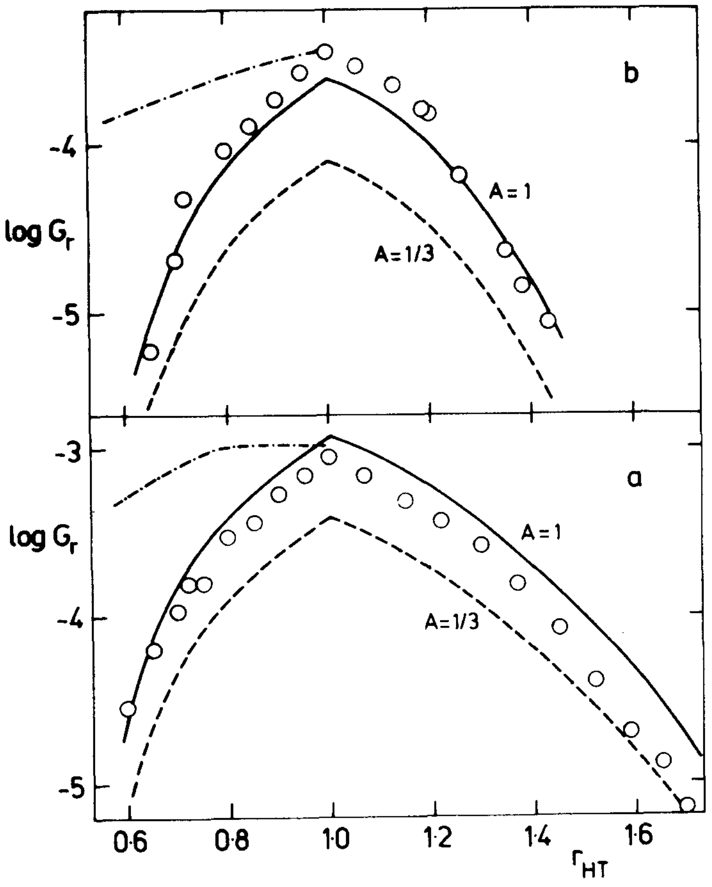

Fig. 3 Dependence of the reduced modulus G_r (molcm^{-3}) on $r_{HT} = [OH]_{PPT}/[NCO]_{MDI}$

a - networks made from LHT-240, b - networks made from LG-56, ○ experiment; —— , --- theory $A\nu_{eg}$ (Eq.(A-20) in the paper by ILAVSKÝ and DUŠEK 1982) with front factor values A indicated; -.-.- data for PPT-MDI netwoks without the monofunctional component (cf. ILAVSKÝ and DUŠEK 1982)

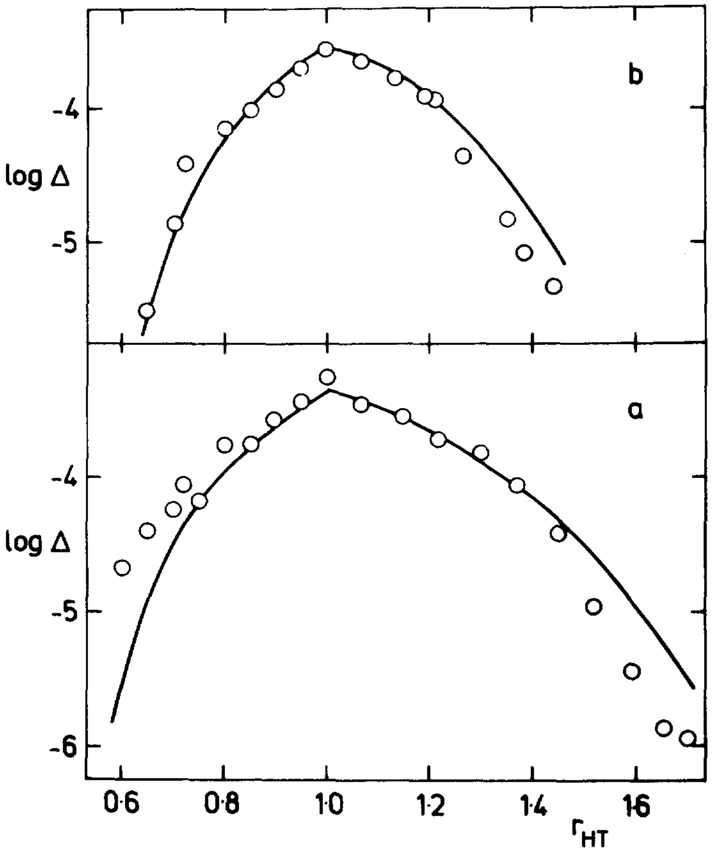

Fig. 4 Dependence of the topological contribution Δ(molcm^{-3}) on r_{HT} = $[OH]_{PPT}/[NCO]_{MDI}$
a - networks made from LHT-240, b - networks made from LG-56, ○ experiment, —— theory εT_{eg} (T_{eg} given by Eq.(A-21) in the paper by ILAVSKÝ and DUŠEK 1982) with the constant $\varepsilon = 5 \times 10^{-4}$ molcm^{-3}

$\varepsilon = 5 \times 10^{-4}$ molcm^{-3} (similarly to PPT-MDI networks for $r_H > 1$). However, the agreement of εT_{eg} with Δ is better for networks from the larger triol than from the smaller one. Similar conclusions may be reached by analyzing the G_r vs. w_g plot which smoothes out the experimental dependences by reducing the effect of experimental errors (DUŠEK et al. 1977, DUŠEK and ILAVSKÝ 1980, DUŠEK and ILAVSKÝ 1982).

Conclusions

A pronounced maximum of G and the good correlation between experimental and theoretical w_g and G dependences as a function of r_{HT} (for $r_{HT} > 1$ and $r_{HT} < 1$ alike) for PPT-MDI networks with a monofunctional component and constant $r_H = 1$ shows that deviations observed earlier for PPT-MDI networks in the absence of the monofunctional component and at $r_H < 1$ were due to additional crosslinking, obviously as a consequence of the formation of allophanate groups. Similar conclusions follow from the analysis of the dependences of stress-optical coefficient on r_{HT}. An analysis of the elastic behaviour demonstrates that the contribution to the equilibrium modulus due to permanent topological constraints between EANC´s is probable.

Acknowledgment. The authors are indebted to Mrs.R.Mejstříková for careful assistance in experimental work.

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Received September 11, accepted September 14, 1982