The structure and elasticity of polyurethane networks: 1. Model networks of poly(oxypropylene) triols and diisocyanate

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The equilibrium mechanical and optical behaviour of networks prepared from poly(oxypropylene) triols (PPT) and 4,4′-diphenylmethane diisocyanate (MDI) at various initial molar ratios of reactive groups, $r_H = [OH]/[NCO]$, in the range $0.6 < r_H < 1.75$ have been investigated. The reaction proceeded at 80°C and in the presence of an organotin catalyst to a high conversion of minotirty groups (0.96–1.0). A comparison between experimental and theoretical (based on the theory of branching processes) dependences of the equilibrium modulus, G_e, on r_H or on the sol content, w_s, led to the following conclusions: (1) In the range $r_H \geq 1$ the theory adequately describes experimental dependences, while in the range $r_H < 1$ excess crosslinking takes place, obviously due to the formation of allophanate groups. (2) In PPT networks with a higher molecular weight ($M_n = 2630$), G_e is about twice the theoretical value for the front factor $A = 1$, which is interpreted as a contribution due to permanent interchain interactions. (3) In networks of lower PPT ($M_n = 708$), experimental G_e values lie between the theoretical ones calculated for $A = 1$ (affine deformation crosslinks) and $A = 1/3$ (phantom network). (4) The difference between the eperimental and theoretical moduli for $A = 1/3$ may be adequately described by using Langley's concept of trapped entanglement contribution (for networks of the longer triol quite satisfactorily, for those of shorter PPT with some systematic deviation) with the same proportionality constant. (5) For correlations between the experiment and theory a generalized plot of the reduced modulus of the weight fraction of the gel proved to be useful.

Keywords Polyurethane networks; poly(oxypropylene); allophanate; crosslinking theory; rubber elasticity; trapped entangelements

INTRODUCTION

The validity of formation and elasticity theories of polymer networks is most often tested by using networks prepared by endlinking of telechelic polymers[1–7]. The network density may be controlled in two ways: (a) by changing the size (length) of the telechelic polymer in networks with close to perfect structure and (b) by a controlled degree of imperfectness due to dangling ends caused by incomplete conversion of functional groups, produced for example by disturbing the stoichiometry in reactions of the alternating type. It has been stressed elsewhere[8,9] that the synthesis of perfect networks is virtually inaccessible experimentally, and a certain level of defects (residual unreacted groups, elastically inactive cycles, etc.) always persists. Even a low level of defects in these systems greatly affects the concentration of elastically active network chains (EANCs) and the equilibrium modulus, thus invalidating the simple way of obtaining the concentration of EANCs in perfect networks. There exist, however, effective statistical methods of calculation of structural parameters of imperfect networks that allow us to take into account all chemical features of the system, such as for example possible functionality distribution, possible differences in reactivities, etc.

The main issue in the testing of the theory of elasticity[10,11] consists of the correlation between the equilibrium modulus of elasticity G, and the calculated concentration of EANCs, ν_e, and in particular in the determination of the value of the so-called front factor A:

$$G = ART\nu_e \qquad (1)$$

where for phantom networks $A_{ph} = (f_e - 2)/f_e$, and for networks with fully suppressed fluctuation of crosslinks so that they are displaced affinely with macroscopic strain, $A_{af} = 1$ (f_e is the average functionality of elastically active crosslinks, close to 3 near the gel point and reaching the value of chemical functionality in perfect networks[12,13]). According to the theory, the A value for real networks varies between A_{ph} and A_{af}. In real networks there are no doubt numerous interactions between EANCs (entanglements). In the theory of Flory[10,11] these interactions are assumed to suppress the crosslink fluctuations only so that G (determined by covalent crosslinks) with $A = 1$ in equation (1) is the upper limit of expected G values. It has been suggested, however, that there exists an additive contribution to G by the so-called trapped entanglements due to chain uncrossability G_{ent} so that G can be expressed as[14,15]:

$$G = G_{ch} + G_{ent} = [(f_e - 2)/f_e]RT\nu_e + \varepsilon RTT_e \qquad (2)$$

where T_e is the so-called trapping factor characterizing the level of interactions between segments in EANCs, and ε is a constant. Hence, an investigation of the front factor value is crucial in order to find out how close the system is

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to the phantom behaviour, and also to see if an extra contribution G_{ent} is needed and a simple additivity according to relation (2) is valid.

Homogeneous polyurethane networks are one of the simplest model systems. Bicomponent networks consisting of macrotriol of the polyether type and diisocyanate, or of a corresponding macrodiol and triisocyanate are suitable, mainly because of their homgeneity, since no chemical clustering[9] of hard units, such as for example with a low molecular weight triol added, can occur in this case. Such systems have been used in the testing of the network formation and elasticity theories in many studies[16-27]. The results and conclusions obtained regarding the magnitude of the front factor differ considerably. Most of the systems ranked among bona fide perfect networks. For networks consisting of triisocyanates and poly(oxyethylene) (PEO) and poly(tetramethyleneoxy) (PTMO) diols, Mark[22] determined the front factor under conditions of phantom behaviour A_{ph} (obtained from the Mooney–Rivlin constant C_1) varying in the range 0.22–0.77 (the theoretical value being 1/3) with average value 0.39. Surprisingly, A_{af} for unswollen samples calculated from $C_1 + C_2$ (conditions expected for affine displacement of junctions) did not exceed A_{ph} much (increasing from 0.27 to 0.34 only). In networks consisting of triisocyanate and poly(oxypropylene) (POP) diol, the A_{ph} (from C_1 constant) and A_{af} (from $C_1 + C_2$) values were respectively 0.41 and (only) 0.5 (ref. 23), while for poly(caprolactone) diol networks[20] the respective values were $A_{ph} \simeq 0.7$ and $A_{af} = 0.8$–1.36 (ref. 24). A deeper analysis of these results is impeded by uncertainty in the level of existing network defects; hence, generally higher A_{af} and A_{ph} values can be expected if these defects are taken into account. Other authors[16,25] came to the conclusion that an extra contribution to the chemical network is necessary (owing to trapped entanglements), irrespective of whether A is considered for the phantom network or for the network with suppressed fluctuations of crosslinks. Stepto[20] avoided the problem of defects caused by elastically inactive cycles (EIC) by extrapolating the molecular weight between crosslinks, M_c (calculated using the equilibrium modulus), in networks prepared with various amounts of a diluent to a state corresponding to a ring-free network. $A \simeq 1$ was thus obtained, but this conclusion is somewhat weakened by a long extrapolation and by the assumption of linearity; also, the possible existence of residual unreacted functional groups has been disregarded.

Thus, the results just outlined do not provide any definite conclusion about the adherence of the theory of elasticity to polyurethane networks, the level of fluctuations of the junctions and the existence of an extra contribution due to permanent interchain interactions (equation (2)). We believe that the uncertainty in the defects in bona fide perfect networks is one of the causes underlying such discrepancies.

In this study, the crosslinking density was controlled by the molecular weight of poly(oxypropylene) triols as well as by molar ratios of OH and NCO groups, similarly to the study of epoxy networks[28-30]. In reactions of the alternating type, the excess of one or the other type of functionality makes the network structure looser by increasing the number of dangling chains. The excess of functional groups and the almost full conversion of minority groups makes these systems chemically inactive (in the case of NCO groups in excess only after their deactivation) and no changes can occur during the measurements. The weight fraction of the sol, w_s, may be used as an independent variable for the calculation of the concentration of EANCs. As has been proved earlier for epoxy networks[28-30], w_s correlates well with the independently determined conversion of functional groups. The Appendix presents a procedure based on the theory of branching processes for calculation of the necessary parameters including the trapping factor which appears in Langley's treatment of the trapped entanglements[14,15]. The study also offers a rather broad rheo-optical characterization of networks obtained from POP triols and 4,4′-diphenylmethane diisocyanate with OH and NCO groups in excess which may be found useful in practical applications of these systems. The absence of major polar interactions in these networks was indicated by for example a very narrow distribution of relaxation times in the main transition region which became broader only due to the broadening of the distribution of lengths of EANCs (excess of OH groups)[31].

EXPERIMENTAL

Materials

The samples were prepared from two poly(oxypropylene) triols (PPT) (Union Carbide Niax Polyols) from which water had been removed by azeotropic distillation with benzene; the content of the remaining residual water was 0.02 wt% in both cases. The number average molecular weights M_n determined by vapour pressure osmometry were 708 for triol Niax LHT-240 and 2630 for Niax LG-56. The concentration of OH groups was determined by a reaction with phenyl isocyanate in excess; the unreacted phenyl isocyanate was subsequently removed by a reaction with dibutylamine in excess, and the unreacted dibutylamine was determined by a potentiometric titration with HCl. The OH contents in the triol LHT-240 and in LG-56 were 6.94 wt% and 1.8 wt% respectively. These values were used in the determination of the number average functionality, $f_n = 2.89$ (LHT-240) and 2.78 (LG-56). By using the method of critical molar ratio necessary for gelation[27], the average f derived from the second distribution moment

$$f_w = \sum_f f^2 n_f \Big/ \sum_f f n_f$$

(where n_f is the molar fraction of molecules with f functional groups) was also determined. The f_w values for LHT-240 and LG-56 were 2.92 and 2.90±0.05. The measurement of the sol fraction in the networks reveals that the content of non-functional polymer must lie below 0.1% (*Table 1*). The results of a chromatographic analysis[32] also corroborate the assumption that the triols used, LHT-240 and LG-56, are composed of bi- and trifunctional polymers only (molar fractions n_3 are 0.89 and 0.78, respectively).

4,4′-Diphenylmethane diisocyanate (MDI) was distilled under reduced pressure, then crystallized twice from dry hexane and the solvent was removed at reduced pressure using an oil vacuum pump at room temperature. The purity of MDI determined using the dibutylamine method was 99.5%.

Sample preparation

PPT together with MDI was stirred for 15 min in a sealed glass vessel in an atmosphere of dried nitrogen at

Table 1 Mechanical and optical characteristics of polyurethane networks

Sample	r_H[a]	$G \times 10$[b] (MPa)	$C \times 10^4$[c] (MPa^{-1})	$C_1 \times 10$[d] (MPa)	$C_2 \times 10$[d] (MPa)	w_s[e]	$\bar{n}$[f]
PPT – LHT-240							
1	0.64	13.55	42.5	21.30	4.00	0.012	1.532
2	0.70	19.86	39.2	24.50	2.50	0.003	1.534
3	0.75	27.42	41.0	21.60	5.00	0.001	1.528
4	0.80	29.44	36.7	25.50	2.52	0.002	1.527
5	0.86	28.25	36.9	–	–	0.006	1.523
6	0.92	27.42	34.2	21.30	0.40	0.007	1.522
7	1.01	24.32	33.8	21.80	4.74	0.004	1.514
8	1.12	17.50	34.4	14.60	3.00	0.013	1.509
9	1.23	11.51	33.8	9.40	1.60	0.039	1.505
10	1.34	7.76	34.1	5.05	1.30	0.097	1.500
11	1.39	4.320	35.0	3.25	0.90	0.131	1.499
12	1.44	2.93	34.5	2.49	0.65	0.168	1.496
13	1.50	1.710	34.5	1.830	0.12	0.238	1.495
14	1.55	1.049	33.1	0.920	0.250	0.296	1.494
15	1.61	0.619	32.2	0.585	0.100	0.362	1.492
16	1.66	0.170	33.1	0.173	0.04	0.501	1.492
17	1.67	0.123	34.5	0.135	0.04	0.542	1.490
18	1.71	0.032	32.8	0.040	0.002	0.674	1.489
PPT – LG-56							
21	0.665	11.59	21.6	8.60	3.01	0.017	1.472
22	0.716	4.42	20.4	3.35	1.68	0.080	1.470
23	0.767	5.86	18.3	3.72	1.92	0.070	1.468
24	0.817	4.97	18.4	3.77	1.27	0.067	1.468
25	0.870	10.99	20.0	–	–	0.012	1.466
26	0.921	9.46	18.5	7.90	2.60	0.010	1.462
27	0.970	11.09	17.7	8.60	2.44	0.009	1.462
28	1.021	10.69	17.1	8.10	1.83	0.015	1.460
29	1.073	6.92	18.0	4.72	1.46	0.046	1.458
30	1.123	6.41	17.9	4.62	0.99	0.051	1.458
31	1.177	5.40	18.1	–	–	0.109	1.459
32	1.229	2.98	18.1	2.08	0.60	0.170	1.457
33	1.282	2.77	18.0	2.24	0.41	0.179	1.456
34	1.384	1.25	17.2	1.01	0.24	0.318	1.457
35	1.436	0.590	18.1	0.469	0.086	0.387	1.456
36	1.452	0.536	17.3	0.382	0.051	0.397	1.454
37	1.485	0.400	18.4	0.305	0.033	0.442	1.453
38	1.532	0.143	18.0	0.138	0.028	0.577	1.453
39	1.587	0.080	18.0	0.087	0.002	0.651	1.454
40	1.603	0.065	17.8	0.061	0.003	0.691	1.453

[a] Fraction r_H = [OH]/[NCO].
[b] G = equilibrium modulus measured on dry unextracted samples at T = 65°C.
[c] C = stress–optical coefficient.
[d] C_1 and C_2 = Mooney–Rivlin constants of unextracted networks.
[e] w_s = weight fraction of the sol.
[f] $\bar{n}$ = refractive index.

55°–60°C; 0.005 wt% of dibutyltin dilaurate was added at the end, the mixture was homogenized and dosed into closed Teflon moulds. The size of sheets thus obtained was $10 \times 10 \times 0.1$ cm^3. The polymerization proceeded for seven days at 80°C. With both PPT a series of networks was prepared with a variable molar ratio of OH and NCO groups, $r_H = [OH]/[NCO]$, in the range $0.64 < r_H < 1.71$ (*Table 1*). In the case of networks with $r_H < 1$, one half of the sheet was swollen in methanol in order to convert the unreacted NCO into urethane groups; the sheets were then dried to constant weight.

Extraction and swelling

The weight fraction of the sol, w_s, was determined by multiple extraction of the networks with benzene ($r_H \geq 1$) or chloroform ($r_H < 1$) at room temperature. The extracted samples were dried in vacuum using an oil pump at 60°C to constant weight. The w_s values given in *Table 1* are the average from at least two measurements. The densities of the network, ρ, were determined by the double weighing method in air and in water (for networks from LHT-240 $\rho = 1.14$ g cm^{-3}, with LG-56 $\rho = 1.04$ g cm^{-3}). The refractive indices of networks $\bar{n}$ were determined with an Abbé refractometer at 65°C (*Table 1*).

Photoelastic and stress–strain characteristics

The photoelastic measurement was carried out using an apparatus described earlier[33] which makes possible a simultaneous determination of the force f and optical retardation δ (and thus the birefringence $\Delta n = \lambda_0 \delta / 2\pi d$, where d is the deformed sample thickness and λ_0 is the light wavelength, $\lambda_0 = 5461$ Å). The dependence of stress $\sigma = f/A$ (A being the deformed cross-section of the sample) and birefringence Δn on elongations λ, $1 < \lambda < 1.1$, were measured each time after a relaxation of 120 s. The measurements were carried out with dry unextracted networks at 65°C, when equilibrium was reached in all networks after 120 s of relaxation. The initial equilibrium modulus G, the deformation–optical function A and the stress–optical coefficient $C = A/G$ were determined from:

$$\sigma = G(\lambda^2 - \lambda^{-1}) \quad (3)$$

$$\Delta n = A(\lambda^2 - \lambda^{-1}) \quad (4)$$

The stress–strain measurement in the range of high elongations of the samples was carried out with an Instron (table type TM-M) apparatus with the rate of deformation 0.02 min^{-1}. Dry unextracted networks at 65°C were used in the measurement, and the Mooney–Rivlin parameters C_1 and C_2 were thus determined using the relation:

$$\sigma = (C_1 + C_2/\lambda)(\lambda^2 - \lambda^{-1}) \quad (5)$$

Within experimental error ($\pm 4\%$) the same values of C_1 and C_2 constants were obtained if the deformation was decreased by the same rate.

RESULTS AND DISCUSSION

Calculated structural parameters, cyclization and superposition procedure

The structural parameters of the networks, the mass fraction of the sol, w_s, the concentration of elastically active network chains (EANCs) in the gel, ν_{eg}, and the trapping factor, T_e or T_{eg} (equations (A.15), (A.17)–(A.21)) have been calculated using the theory of branching processes (*Table 2*); the procedure is described in the Appendix. A system composed of mono-, di- and triol with the same and with independent reactivities of OH groups and of mono- and diisocyanate also with the same and with independent reactivities of NCO groups, is considered in the calculation. (Mono derivatives have been included into the consideration because their addition has been used to explain anomalies observed if NCO groups are in excess.) The procedure outlined in this study extends and supplements that described in ref. 26.

Cyclization was also neglected in the calculation for the following reasons. Although it is only weakly operative in these systems[18–21,27], its effect on w_s and particularly on ν_{eg} may be considerable. However, the independent variable used by us for determining the extent of the crosslinking reaction is the sol (gel) fraction from which the conversion of functional groups ξ was calculated. The conversion thus obtained concerns only the formation of intermolecular bonds, and (e.g. conversion of isocyanate groups ξ_I (*Table 2*)—calculated using equations (A.13)–(A.15) for an unknown ξ_I) it is somewhat smaller than the total conversion of isocyanate groups ξ_I'. The difference $\xi_I' - \xi_I$ corresponds to the fraction of bonds wasted in elastically inactive cycles.

Being able to determine the fraction of intermolecular bonds from w_s does not automatically mean that this conversion value may be used in the calculation of ν_{eg} and T_{eg}. The situation arising in the gel is much more complicated in that only elastically inactive cycles (EIC) must be considered, in contrast to the predominant active circuits, and in that EIC are not only formed but also activated in the gel. The problem of post-gel cyclization has been explained in greater detail in refs. 34 and 35, where an approximate procedure for its treatment has also been suggested. Even though the EIC fraction may increase[34] or decrease[35] with proceeding crosslinking, it is important that in this approximation the dependences of ν_{eg} on w_g calculated taking or not taking the existence of EIC into consideration are virtually identical. The adherence between the suggested theory[34] and reality is supported by a satisfactory agreement with the experiment near the gel point[27].

Table 2 Theoretical values of structural parameters of polyurethane networks in the range [OH]/[NCO] ⩾ 1

Sample	ξ_I[a]	$\nu_{eg} \times 10^4$[b] (mol cm^{-3})	$T_{eg} \times 10$[c]	$X \times 10^4$[d] (mol cm^{-3})	$G_r \times 10^4$[e] (mol cm^{-3})
PPT – LHT-240					
7	0.983	12.330	8.440	8.330	8.529
8	0.964	7.077	6.870	5.790	6.193
9	0.970	4.696	5.410	4.260	4.183
10	0.970	2.737	3.510	2.670	3.002
11	0.970	2.140	2.800	2.110	1.736
12	0.976	1.684	2.224	1.660	1.230
13	0.975	1.120	1.444	1.096	0.784
14	0.979	0.825	1.029	0.789	0.521
15	0.984	0.575	0.677	0.530	0.339
16	0.978	0.272	0.264	0.223	0.119
18	0.971	0.090	0.039	0.059	0.039
PPT – LG-56					
28	0.936	2.180	5.600	3.527	3.791
29	0.920	1.395	4.355	2.642	2.533
30	0.937	1.320	4.358	2.619	2.359
31	0.926	0.813	2.970	1.755	2.197
32	0.923	0.543	2.072	1.217	1.254
33	0.940	0.520	2.060	1.200	1.178
34	0.943	0.241	0.932	0.546	0.640
35	0.947	0.166	0.610	0.360	0.336
36	0.951	0.158	0.580	0.343	0.310
37	0.955	0.126	0.445	0.264	0.250
38	0.952	0.057	0.164	0.101	0.118
39	0.960	0.035	0.087	0.055	0.080
40	0.960	0.026	0.059	0.038	0.073

[a] ξ_I = conversion of NCO groups calculated from the weight fraction of the gel w_s by equation (A.15).
[b] ν_{eg} = concentration of EANCs calculated from equation (A.20) for conversion ξ_I.
[c] T_{eg} = trapping factor calculated from equation (A.21) for ξ_I.
[d] $X = \nu_{eg}/3 + \epsilon T_{eg}$ with $\epsilon = 5 \times 10^{-4}$ mol cm^{-3}.
[e] Experimental reduced modulus $G_r = G/w_g RT$.

The possibility of a considerable suppression of the effect of EIC on the ν_{eg} and T_{eg} indicates the advantage of plotting these parameters as a function of w_g when correlating theoretical dependences and experimental data. As has been shown by the analysis, however, in this plot variations of other variables, such as minor variations of conversion, of the initial molar ratio, reactivity of groups, etc., are also suppressed, which is why the preference of such a plot is stressed here. Even at major differences between parameters of the systems the dependences on w_g are close and parallel, so that they may be superimposed by a small vertical shift[26,28–30].

In the case under study, universal dependences are obtained when plotting $\log \nu_{eg}\bar{M}$ or $\log T_{eg}$ as a function of $\log w_g$, where $\bar{M}$ is the number average molecular weight of the initial system. The presence of the factor $\bar{M}$ at ν_{eg} can be understood, because ν_{eg} is the molar concentration related to a volume or weight unit, and for T_{eg} the weight of the components is unimportant (equation (A.21)).

Effect of the molar ratio of OH and NCO groups on the weight fraction of sol and optical behaviour

In *Figure 1* the w_s values have been plotted against the molar ratio of OH and NCO groups, r_H, and it is obvious that the branch for $r_H \geq 1$ adequately follows the theoretical dependence for a high conversion of NCO groups. However, in the range $r_H < 1$ the experimental w_s values are systematically lower compared with the theoretical ones, which suggests a higher density of crosslinks. We believe that the source of these crosslinks should be seen in a consecutive reaction between unreacted NCO groups and urethane groups which give rise to allophanate groupings. The reaction obviously takes place in spite of the use of a selective organotin catalyst.

In the range $r_H \geq 1$ where the fraction of the sol adequately obeys the assumed dependence on r_H, the calculated intermolecular conversions are $\xi_I = 0.97$–0.98 for LHT-240 and 0.92–0.96 for LG-56 (*Table 2*). Using the procedure described in ref. 34 and experimentally verified near the gel point[27], an approximate fraction of bonds wasted in EIC has been calculated (*Figure 2*); the fraction varies by about 2–3%. If these values are added to those of intermolecular conversion ξ_I, the total conversion of isocyanate groups ξ_I' is obtained, by varying by about 0.99–1.0 for networks from triol LHT-240 and by about 0.94–0.99 for networks of triol LG-56. Lower conversion may be expected for networks from triol of a higher molecular weight, because in these systems the concentration of functional groups is about one-third of that of systems from triol LHT-240. A rise in ξ_I' from 0.95 to 0.99 with increasing excess of OH groups in the system may also be expected, in accordance with rules of chemical kinetics.

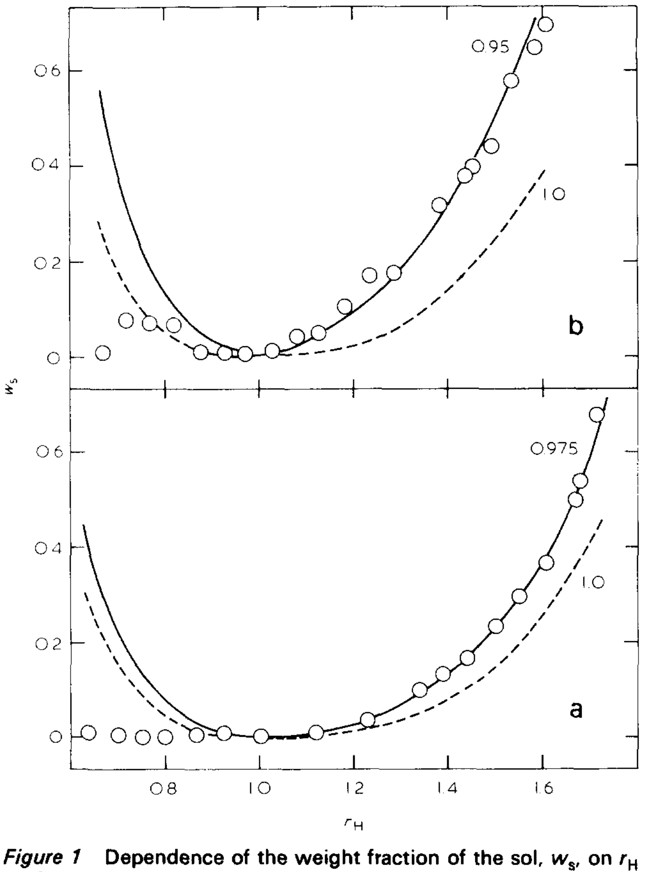

Figure 1 Dependence of the weight fraction of the sol, w_s, on r_H = [OH]/[NCO]. (a) Networks from LHT-240; (b) networks from LG-56. O, experimental data; ———, theory (equation (A.15) from the Appendix). Numbers indicate intermolecular conversion of minority groups

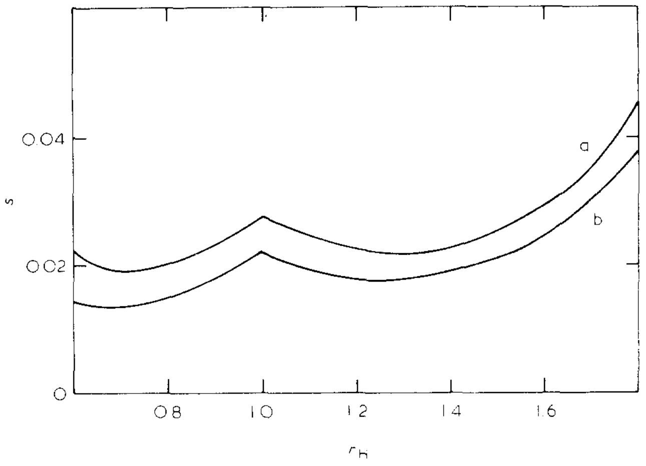

Figure 2 Dependence of the fraction of bonds lost in EIC, *s*, on r_H = [OH]/[NCO]. (a) Dependence for networks from LHT-240; (b) dependence for networks from LG-56

The stress–optical coefficient C is independent of initial composition in the range $r_H \geq 1$ while it increases with increasing excess of NCO groups in the range $r_H < 1$ (*Figure 3*). Although also the refractive index $\tilde{n}$ increases with increasing concentration of NCO groups (*Table 1*), the increase in $\tilde{n}$ does not compensate the increase in C, and the optical anisotropy of the statistical segment $\Delta\alpha$ calculated from:

$$\Delta\alpha = \tilde{n} \times 45kTC/[2\pi(\tilde{n}^2+2)^2] \qquad (6)$$

(where k is the Boltzmann constant and T is temperature) shows a dependence on r_H similar to that of C. Owing to the alternating mechanism, EZNCs consist of multiples of $(\frac{2}{3}\mathrm{PPT}+\mathrm{MDI})$; consequently, their composition does not

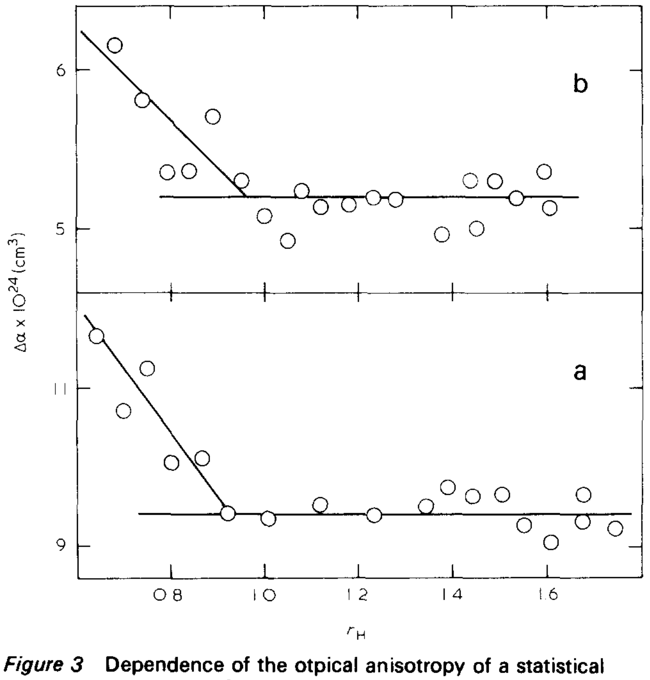

Figure 3 Dependence of the otpical anisotropy of a statistical segment, $\Delta\alpha$, on r_H = [OH]/[NCO]. (a) Networks from LHT-240; (b) networks from LG-56

depend on the excess of groups in the range $r_H \geqslant 1$, which leads to the expected independence of composition for both triols. A lower $\Delta\alpha$ for networks with LG-56 compared with networks with LHT-240 is also expected due to a lower content of polar urethane groups ($\Delta\alpha$ of poly(oxypropylene) is $2\times10^{-24}\,\mathrm{cm}^{-3}$ (cf. ref. 36)). The observed increase in $\Delta\alpha$ in the range $r_H < 1$ may be explained through the increasing participation of polar groups with a positive contribution to the birefringence; thus these results also support the idea of formation of allophanate groups in the case of NCO groups in excess.

Concentration of elastically active network chains and the theory of rubber elasticity

The dependences of ν_{eg} and T_{eg} on the composition given by r_H for $r_H \geqslant 1$ (ν_{eg} and T_{eg} were calculated using conversions ξ_I determined from w_s) and their comparison with the equilibrium modulus G allows us to find the magnitude of the front factor A and the likely contribution of interchain interactions, i.e. to test the validity of equations (1) or (2). Assuming that the chain dimensions in an undeformed state are close to the reference dimensions (measurements were performed on unextracted networks and the temperature of measurement, 65°C, was close to the preparation temperature 80°C), the experimental values of the modulus G may be reduced by using the expression

$$G_r = G/w_g RT$$

Figure 4 shows the reduced experimental values of both the modulus G_r and the Mooney–Rivlin constant C_{1r}(C_{1r} $= C_1/w_g RT$) plotted in dependence on r_H for networks from both PPT, along with the theoretical dependences of ν_{eg} both for $A=1$ and for $A=1/3$ (in our networks the elastically active crosslinks may be only trifunctional, and hence $A_{ph}=1/3$ independently of conversion). It can be seen that, owing to the low values of the parameter C_2, the character of the dependence of G_r and C_{1r} on r_H is virtually the same. The ratio $C_2/C_1 \simeq 0.1$–0.35 determined by us is somewhat lower than that determined earlier[16,25] for similar networks ($C_2/C_1 \simeq 0.5$), but approaches 0.3 reported by Walsh *et al.*[17] For networks with NCO groups in excess ($r_H < 1$) the experimental G_r are very high for both PPT, in accordance with the assumed formation of allophanates. In networks with OH groups in excess the expected decrease of G_r with increasing r_H may be observed. While for networks from short PPT the experimental points G_r lie between the phantom' ($A=1/3$) and 'affine' ($A=1$) behaviours, for networks from LG-56 the G_r values lie even above the dependence for $A=1$. Hence, in order to explain the dependence of G_r on r_H in networks of LHT-240, only a chemical contribution to the modulus would be sufficient (in equation (1) the parameter A would decrease with increasing r_H), but in networks of LG-56 an additional entanglement contribution appears to be necessary (cf. equation (2)).

Assuming that the chemical contribution to the reduced modulus is given by $\nu_{eg}/3$, the contribution of permanent interchain interactions $\Delta = G_r - \nu_{eg}/3$ (cf. equation (2)) as a function of r_H has been plotted in *Figure 5*. For a network of triol LG-56, the dependence of Δ on r_H is well described by the theoretical dependence of εT_{eg} (equation (A.21)) with $\varepsilon = 5\times10^{-4}\,\mathrm{mol\,cm}^{-3}$. For networks from triol LHT-240, the same ε value satisfies networks with a higher EANC concentration, but at

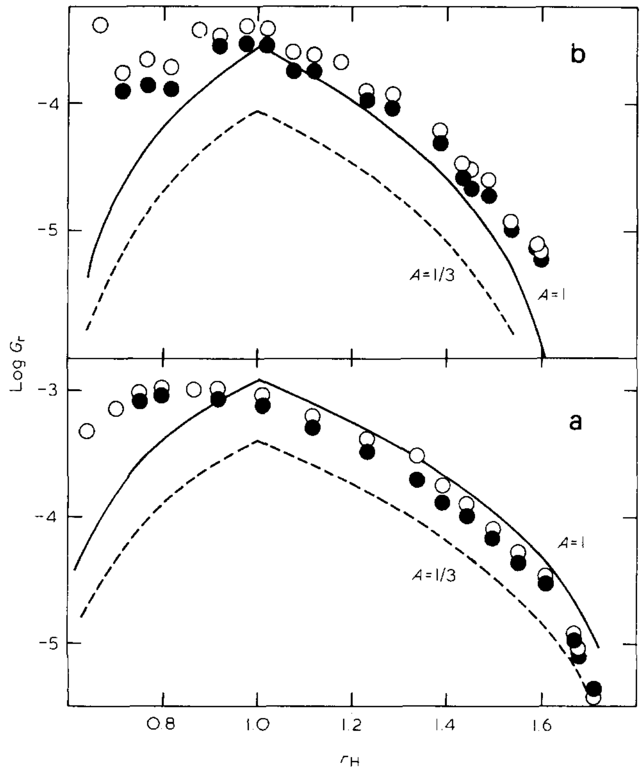

Figure 4 Dependence of the reduced equilibrium modulus, G_r (mol cm^{-3}, and of the reduced Mooney–Rivlin constant, C_{1r} (mol cm^{-3}), on r_H = [OH]/[NCO]. (a) Networks from LHT-240; (b) networks from LG-56. ○, G_r; ●, C_{1r}; ———, theory $A\nu_{eg}$ (ν_{eg} calculated from equation (A.20) for ξ_I values determined from w_s) with denoted values of the front factor A

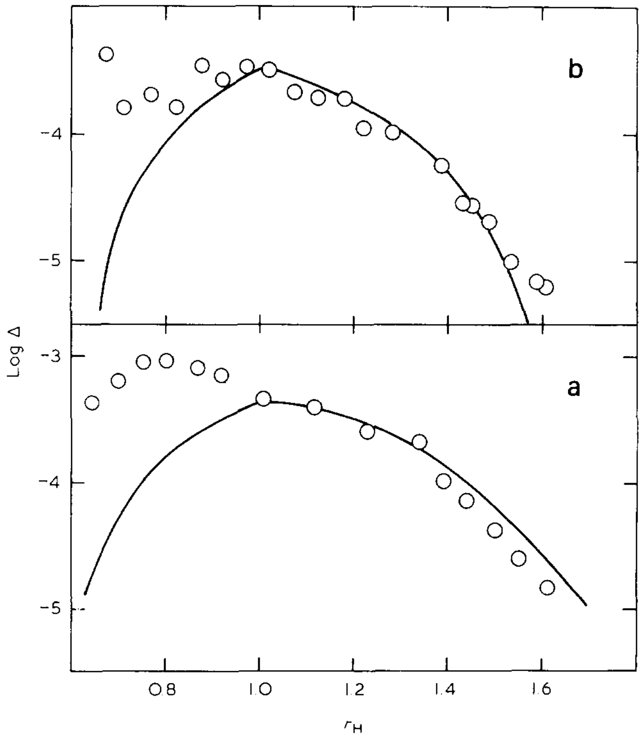

Figure 5 Dependence of the topological contribution, Δ (mol cm^{-3}), on r_H=[OH]/[NCO]. (a) Networks from LHT-240; (b) networks from LG-56. ———, theory εT_{eg} (T_{eg} given by equation (A.21)) for the conversion ξ_I determined from w_s) with ε = 5×10^{-4} mol cm^{-3}

higher r_H ratios ε decreases to 3×10^{-4} mol cm^{-3}. A simultaneous determination of A and ε by using the Langley–Graessley plot G_r/T_{eg} vs. ν_{eg}/T_{eg} fails as has been pointed out earlier[8], because the ν_{eg}/T_{eg} vs. r_H dependence passes through a minimum, and the available range of changes of ν_{eg}/T_{eg} is insufficient. Only if networks from both triols are taken into consideration are the values $A = 0.4 \pm 0.2$ and $\varepsilon = (4.5 \pm 1.0)\times10^{-4}$ mol cm^{-3} obtained.

A generalized plot of the concentration of EANCs, ν_{eg}, on the weight fraction of the gel, w_g

As has been stressed in the introduction, it is expected that in the generalized $\log G_r$ vs. $\log w_g$ plot the effect of inaccuracies in the determination of ξ_I or r_H will be reduced. In our case the effect of possible errors in ξ_I is not operative, because ν_{eg} and T_{eg} have been calculated directly from w_s. *Figure 6* shows the different behaviour of networks of both PPTs. While the G_r data of networks from LHT-240 are distributed between curves corresponding to $A = 1/3$ and $A = 1$, data for networks of LG-56 lie above the theoretical curve for $A = 1$. This positive contribution above the 'limiting' curve for $A = 1$ may be explained by the role played by permanent interchain interactions due to chain uncrossability.

Taking an assumption used in equation (2) that the chemical contribution to G_c is determined by $A_{ph} = 1/3$, the Δ vs. w_g dependences have been plotted in *Figure 7*. It is obvious that for networks with longer PPO chains the agreement between data and theory is good with $\varepsilon = 5\times10^{-4}$ mol cm^{-3}, while for networks with shorter polypropylene oxide sequences in EANCs, a decreasing ε would be needed. The Langley–Graessley approach to the contribution of trapped entanglements expressed in equation (2) also assumes that the proportionality factor εRT equals the plateau modulus of the corresponding linear polymer. No data for the corresponding linear polyurethanes are available, but an estimate of ε for polyoxypropylenes[37] leads to $\varepsilon \simeq 2\times10^{-4}$ mol cm^{-3}.

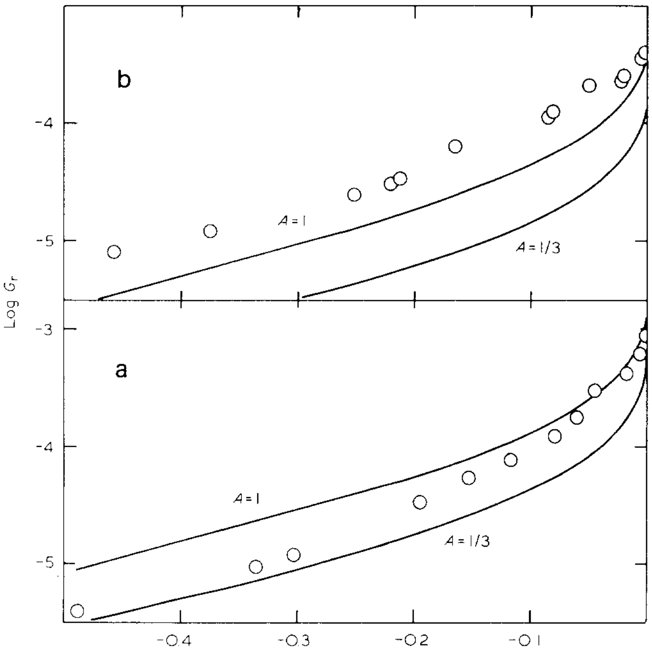

Figure 6 Dependence of the reduced modulus, G_r (mol cm^{-3}), on the weight fraction of the gel, w_g. (a) Networks from LHT-240; (b) networks from LG-56. ——, theory $A\nu_{eg}$ (ν_{eg} determined from equation (A.20) for ξ_1 from w_s) with denoted values of the front factor A

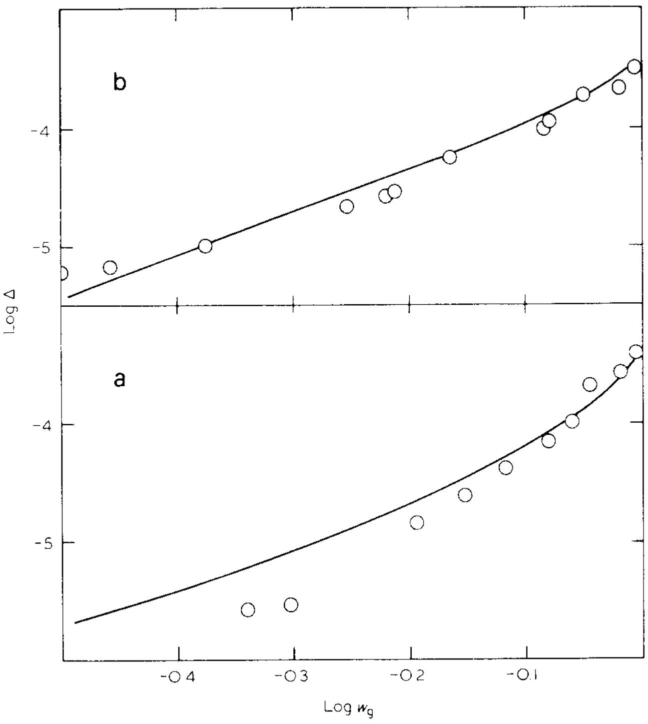

Figure 7 Dependence of the topological contribution, Δ (mol cm^{-3}), on the weight fraction of the gel, w_g. (a) Networks from LHT-240; (b) networks from LG-56. ———, theory given by εT_{eg} with $\varepsilon = 5\times10^{-4}$ mol cm^{-3} (T_{eg} from equation (A.21) for ξ_I determined from w_s)

It is somewhat difficult to draw clear-cut conclusions from the results presented above, for the following reasons. If we admit that the contribution to G given by the chain uncrossability is real (which is sufficiently documented by results obtained with LG-56 networks), then the additivity of contributions given by equation (2) with a constant $A = A_{ph}$ is still an assumption. It should be pointed out that the uncrossability of chains interferes with one of the basic postulates of the phantom behaviour (chains may interpenetrate without restriction). Therefore it is likely that fluctuations of the crosslinks are also affected by these interactions. Thus, even if additivity of both contributions were satisfied, A need not be constant and equal to A_{ph}. A higher A may be expected for networks with a higher crosslinking density, which might explain changes in ε. When interpreting the data, one must of course bear in mind that (a) the mean field conception of pair interactions between segments in EANCs given by the trapping factor T_{eg} is a zero approximation to the problem, and (b) there is some ambiguity in expressing T_{eg} for copolymer EANCs. If ε is compared with the plateau modulus of the corresponding linear polymer, the polymer should not be PPO, but the corresponding polyurethane.

CONCLUSIONS

Experimental results obtained on simple polyurethane networks and their comparison with a theoretical prediction show that:

(a) The equilibrium small strain modulus, or even the value of the Mooney–Riblin constant C_1, may be higher than the calculated value for $A=1$ and taking into account only the contribution of EANCs due to covalent bonds.

(b) Experimental values of the constant C_1 are always higher than those calculated for the chemical contribution only and for the front factor $A=A_{ph}=1/3$.

Hence, a contribution to the elastic retractive force in equilibrium caused by permanent interchain interactions due to chain uncrossability is very likely. Even though on the whole the Langley conception of trapped entanglements describes this contribution satisfactorily, the data obtained do not prove the validity the additivity of the chemical contribution with $A=A_{ph}$ and of the topological contribution due to chain uncrossability.

APPENDIX

Calculation of structural parameters of polyurethane networks

The following system has been considered: a mixture of mono-, di- and triol with equally reactive OH groups and no substitution effect, reacting with a mixture of mono- and diisocyanate with equally reactive NCO groups and no substitution effect. Formation of elastically inactive cycles[34] has not been considered. A somewhat simpler case has been treated in ref. 26. The theory of branching processes employing the cascade substitution and link probability generating functions (*PGF*) has been used.

The vectorial link *PGF* for units in the root (representing units in the whole system) is composed of two components F_{OH} and F_{OI}; they express the probabilities of bond formation of OH and NCO containing components, respectively:

$$F_{OH}(\theta_I)=[n_{H1}(1-\xi_H+\xi_H\theta_I)+n_{H2}(1-\xi_H+\xi_H\theta_I)^2+n_{H3}(1-\xi_H+\xi_H\theta_1)^3]/n_H \tag{A.1}$$

$$F_{OI}(\theta_H)=n_{I1}[(1-\xi_I+\xi_I\theta_H)+n_{I2}(1-\xi_I+\xi_I\theta_H)^2]/n_I \tag{A.2}$$

where ξ_H and ξ_I are molar conversions of OH and NCO groups, respectively, n_{H1}, n_{H2} and n_{H3} are molar fractions of molecules with 1, 2 and 3 OH groups, respectively, and n_{I1} and n_{I2} are molar fractions of molecules with 1 and 2 isocyanate groups, respectively. We have

$$n_H=n_{H1}+n_{H2}+n_{H3} \qquad n_I=n_{I1}+n_{I2} \qquad n_H+n_I=1$$

The coefficient of θ_I^k in the expansion of F_{OH} is equal to the probability of finding a unit issuing k bonds to isocyanate units. The meaning of the coefficient of θ_H^k in F_{OI} is analogous.

The molar fractions of groups belonging to the respective ϕ_i molecules of functionality i normalized with respect to the OH or NCO containing molecules are given by:

$$\phi_{Hi}=in_{Hi}/\sum_i in_{Hi} \qquad \phi_{Ii}=in_{Ii}/\sum_i in_{Ii} \tag{A.3}$$

the initial molar fraction of OH and NCO groups by:

$$\phi_H=\sum_i in_{Hi}\Big/\left(\sum_i in_{Hi}+\sum_i in_{Ii}\right) \qquad \phi_I=1-\phi_H \tag{A.4}$$

and the molar ratio of OH to NCO groups by:

$$r_H=[OH]/[NCO]$$

The relations between the initial molar fractions of molecules (components) and groups are:

$$n_{Hi}=\phi_H\phi_{Hi}/iS \qquad n_{Ii}=\phi_I\phi_{Ii}/iS \tag{A.5}$$

where

$$S=\phi_H(\phi_{H1}+\phi_{H2}/2+\phi_{H3}/3)+\phi_I(\phi_{I1}+\phi_{I2}/2)$$

and

$$\phi_H=r_H/(1+r_H) \qquad \phi_I=1/(1+r_H) \tag{A.6}$$

The components of the link *PGF* for units in the first and higher generations F_1 are obtained from F_0 by differentiation:

$$F_{1H}(\theta_I)=\phi_{H1}+\phi_{H2}(1-\xi_H+\xi_H\theta_I)+\phi_{H3}(1-\xi_H+\xi_H\theta_I)^2 \tag{A.7}$$

$$F_{1H}(\theta_H)=\phi_{I1}+\phi_{I2}(1-\xi_I+\xi_I\theta_H) \tag{A.8}$$

Since only the reaction between OH and NCO groups resulting in urethane groups is assumed to take place, the network build-up is of strictly alternating type, reflected in the structure of link *PGF*s: the F_H components are only a function of the dummy variable θ_I and the F_I of θ_H.

Critical conversion. The gel point condition, equation (A.9), is therefore given by derivatives of F_{1H} and F_{1I} with respect to θ at $\theta=1$ (cr. ref. 38):

$$F'_{1H}F'_{1I}=1 \tag{A.9}$$

i.e.

$$(\phi_{H2}+2\phi_{H3})\xi_H\xi_I\phi_{I2}=1 \tag{A.10}$$

Since $\xi_H r_H=\xi_I$, the explicit condition for the gel point reads:

$$(\xi_H)_c=[r_H\phi_{I2}(\phi_{H2}+2\phi_{H3})]^{-1/2} \tag{A.11}$$

The extinction probabilities governing the post-gelation stage of network formation[38] are determined by equations:

$$v_H=F_{1H}(v_I) \qquad v_I=F_{1I}(v_H) \tag{A.12}$$

After substitution from equations (A.7) and (A.8) and elimination of the trivial root $v=1$, one obtains:

$$1-v_1=\frac{\phi_{12}(\phi_{H2}+2\phi_{H3})\xi_1\xi_H-1}{\phi_{12}\phi_{H3}\xi_1\xi_H^2} \tag{A.13}$$

$$1-v_H=(1-v_I)/\phi_{I2}\xi_I \tag{A.14}$$

The extinction probabilities v_H and v_I are probabilities that a bond leading to a hydroxyl and isocyanate unit, respectively, has only a finite continuation (the respective subtree is finite).

The sol fraction. The sol is composed only of such units that issue bonds with finite continuation only. Therefore, the respective probabilities that a bond is formed, ξ_H and ξ_I, are weighted by the extinction probabilities, v_I and v_H. The weight fractions of the sol, w_s, and gel, w_g, are thus:

$$w_s=1-w_g=m_{H1}X+m_{H2}X^2+m_{H3}X^3+m_{I1}Y+m_{I2}Y^2 \tag{A.15}$$

where $X = 1 - \xi_H(v_1 - 1)$, $Y = 1 + \xi_1(v_H - 1)$, and m_A is the weight fraction of the component A:

$$m_{H1} = n_{H1} M_{H1}/\bar{M} \qquad (A.16)$$

etc., where

$$\bar{M} = n_{H1}M_{H1} + n_{H2}M_{H2} + n_{H3}M_{H3} + n_{I1}M_{I1} + n_{I2}M_{I2}$$

is the initial number-average molecular weight and M_A is the molecular weight of the component A.

Elastically active network chains. The number of elastically active network chains, N_e, is derived from the number of elastically active crosslinks, i.e. crosslinks issuing at least three infinite paths[39]. In the case under consideration, only the triol (H3) units can become elastically active and only if all OH groups have reacted and all issuing bonds have a continuation to infinity; each such bond contributes by 1/2 to the number of EANCs. Thus,

$$N_e = (3/2)n_{H3}\xi_H^3(1 - v_I)^3 \qquad (A.17)$$

The concentration of EANCs in unit weight of the sample v_e' is:

$$v_e' = N_e/\bar{M} \qquad (A.18)$$

and in unit weight of gel:

$$v_{eg}' = N_e/\bar{M}w_g \qquad (A.19)$$

The respective quantity per unit volume v_e is obtained by multiplying by density ρ or ρ_g:

$$v_e = N_e\rho/\bar{M} \qquad v_{eg} = N_e\rho_g/\bar{M}w_g \qquad (A.20)$$

The trapping factor. The trapping factor T_e in Langley's[14] approach to the trapped entanglement contribution is proportional to the probability of contacts between pairs of segments located in EANCs. T_e is normalized to the situation in the respective perfect network. In the case under consideration, it is a network formed at $r_H = 1$ and $\xi_H = \xi_I = 1$ and, moreover, not containing any monofunctional component, $\phi_{H1} = \phi_{I1} = 0$. The question whether to include active crosslinks (active triol units) into interactions between segments of EANCs or not has been analysed elsewhere[29]. The positive answer is physically clear because each active unit of macrotriol contributes by its arms to segments of EANCs.

On denoting the concentration (per building unit in the system) of units with two bonds having infinite continuation (units in EANCs between active branch points) by $C_{I2(2)}$, $C_{H2(2)}$ and $C_{H3(2)}$ and of units in the active branch points by $C_{H3(3)}$, the trapping factor T_e becomes:

$$T_e = N^{-1}[C_{I2(2)} + C_{H2(2)} + C_{H3(2)} + C_{H3(3)}]^2 v_0^2 \qquad (A.21)$$

and

$$T_{eg} = T_e/w_g$$

where the bracketed number in the subscript means the number of bonds with infinite continuation; v_0 is the initial volume fraction of the components if dilution is applied (in the experiments described below $v_0 = 1$) and N is the normalizer mentioned above.

The concentrations C can easily be obtained from a *PGF* for the number of bonds with infinite continuation. Thus for the OH components the *PGF* $T_H(\theta)$ is obtained by substitution of θ_I in $F_{OH}(\theta_I)$ (equation (A.1)) by $v_I + (1 - v_I)\theta$ and

$$T_H(\theta) = F_{OH}(\Theta) = \sum_i t_{H(i)}\theta^i \qquad (A.22)$$

where

$$\Theta = v_I + (1 - v_I)\theta$$

In the *PGF* $T_H(\theta)$, the coefficient $t_{H(i)}$ of θ^i acquires the meaning of the probability of finding an H-type unit with i bonds having infinite continuation (ties). For the calculation of the trapping factor T_e, coefficients $t_{H(2)}$ and $t_{H(3)}$ are relevant. Since $T_H(1) = 1$, $T_H(0) = t_{H(0)}$ and the value of the first derivative $T_H'(0) = t_{H(1)}$, it is easy to see that:

$$t_{H(2)} + t_{H(3)} = 1 - T_H(0) - T_H'(0) \qquad (A.23)$$

$t_{H(2)}$ sums the contributions from diol and triol units: $t_{H(2)} = t_{H2(2)} + t_{H3(2)}$. The coefficients t_H count the contributions to EANCs in the number of building units, e.g. in the number of poly(oxypropylene) oligomers irrespective of the number of monomer units (segments) per building unit (their degree of polymerization). Hence, in order to obtain the concentrations C, one has to multiply the respective t_H by the number of interacting segments in EANCs per unit, P_H. Using relation (A.23), one obtains:

$$C_{H2(2)} = n_H P_{H2} t_{H2(2)} = P_{H2} n_{H2} \xi_H^2 (1 - v_1)^2 \qquad (A.24)$$

$$C_{H3(2)} = n_H P_{H3}' t_{H3(2)} = 3P_{H3}' n_{H3}[\xi_H^2(1 - v_1)^2 + \xi_H^3 v_1 (1 - v_I)^2] \qquad (A.25)$$

$$C_{H3(3)} = n_H P_{H3} t_{H3(3)} = P_{H3} n_{H3} \xi_H^3 (1 - v_1)^3 \qquad (A.26)$$

P_{H2}, P_{H3} and P_{H3}' obviously depend on the molecular mass of the components but also on their shape. In this work, we assumed the three-arm star structure for the trifunctional component and also for the bifunctional component in which one arm does not bear the OH group (these assumptions can be modified, if necessary). Then

$$P_{H2} \doteq (2/3)M_{H2}/M_{OH} \qquad P_{H3} = M_{H3}/M_{OH}$$
$$P_{H3}' = (2/3)M_{H3}/M_{OH}$$

where M_{OH} is the molecular weight of the monomer unit (propylene oxide), $M_{OH} = 58$.

A similar reasoning for diisocyanate units gives the concentration $C_{I2(2)}$:

$$C_{I(2)} = P_{I2} n_{I2} \xi_I^2 (1 - v_H)^2 \qquad (A.27)$$

The number of interacting segments of a diisocyanate unit must be taken relative to the polyol segment. For 4,4'-diaminodiphenylmethane diisocyanate we assumed four interacting segments ($P_{I2} = 4$), each of which is equivalent in size to a PPO segment. However, a variation of the number of equivalent segments in diisocyanate units affects the value of T_e only very slightly.

Thus, equations (A.24)–(A.27) yield explicitly the concentrations C entering equation (A.21) for the trapping factor. The normalizer N is obtained by introducing conditions corresponding to a perfect network: $n_{H1} = n_{I1} = 0$; $r_H = 1$, $\xi_H = \xi_I = 1$; i.e. $v_H = v_I = 0$.

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