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Experimental Evidence of the Volume Dependence of the Deformational Free Energy of Polymer Networks

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Summary

Analysis of reported data on the swelling and deformation of polymer networks shows that the volume -dependent term in the deformational free energy cannot be neglected. The analysis is based on a comparison between the equilibrium moduli of networks prepared at various dilutions and of the same degree of swelling and on a comparison between concentration dependences of the interaction parameter for a linear and a crosslinked polymer.

Determination of the Magnitude of the Volume Term

The equilibrium deformational and swelling behaviour of polymer networks is determined by the deformational free energy, ΔF_{def}, which for Gaussian netrorks may be written (JAMES and GUTH 1943, GRAESSLEY 1975, FLORY 1953, WALL and FLORY 1951, HERMANS 1947, FLORY 1976) in the form

$$\Delta F_{def}/RT = A\nu\,(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)/2 - B\nu_e \ln(\lambda_x \lambda_y \lambda_z) \qquad (1)$$

where R is the gas constant, T is temperature, λ is relative elongation with respect to the reference state ($= l/l_0$, l and l_0 are the deformed and initial sample length respectively), ν_e is molar concentrations of elastically active network chains (EANC).

The values of A and B were (DUŠEK and PRINS 1969) and still are (ALLEN 1976, FLORY 1979) an object of discussion. According to a recent theory forwarded by FLORY (1976, 1979), for a phantom network of Gaussian chains it holds that $B = 0$ and $A = (f_e - 2)/f_e$ (while for an imperfect phantom network f_e is the effective functionality of an elastically active junction (DUŠEK 1979) for a perfect phantom network f_e is the chemical functionality of a junction). For a phantom network with fully suppressed fluctuations of junctions it is expected that $A = 1$, $B = 2/f_e$.

Eq.(1) gives for the equilibrium shear modulus in the swollen state the relation

$$G = A\,\nu_{ed} v_2^{1/3} (v^0)^{2/3} (\overline{r_{nf}^2}/\overline{r_0^2}) RT \qquad (2)$$

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where v_2 is the volume fraction of the polymer in the swollen state, v^0 is the volume fraction of the polymer at network formation, ν_{ed} is the molar concentration of EANC in the dry state and $\overline{r^2_{nf}}$, $\overline{r^2_0}$ are the mean square end-to-end chain distances in the state of network formation and in the reference state, respectively. The swelling equilibrium of the network is determined by

$$\ln a_1 = \ln(1 - v_2) + v_2 + \chi v_2^2 + \nu_{ed} V_1 [A v_2^{1/3} (v^0)^{2/3} (\overline{r^2_{nf}}/\overline{r^2_0}) - B v_2] \quad (3)$$

where χ is the interaction parameter, V_1 is the molar volume of the solvent and a_1 is the activity of the solvent in the swollen network.

Assuming $\overline{r^2_{nf}}/\overline{r^2_0} = 1$, the volume term (B or B/A) may be determined by employing several procedures:

(1) Determination of A and B from equilibrium deformational and swelling data by using Eqs (2) and (3) which require the knowledge of ν_{ed} and $\chi(v_2)$; the most difficult step is an independent determination of ν_{ed} while adequately respecting the crosslinking process and of the possible contribution of trapped entanglements.

(2) Determination of χ and $B\nu_{ed}$ from measurements of the degree of swelling as a function of the activity of solvent, from the deformation behaviour using the $F(v_2)$ vs. v_2 plot (RIETSCH and FROEHLICH 1979, HORKAY et al. 1979). With respect to Eq.(3) we have

$$F(v_2) = [A\nu_{ed} V_1 (v^0)^{2/3} v_2^{1/3} + \ln(1 - v_2) + v_2 - \ln a_1]/v_2 = B\nu_{ed} V_1 - \chi v_2$$

the term comprising A may be obtained from measurement of the modulus using Eq.(2). For solvents with χ independent of v_2, the plot may rather be used in the determination of χ than $B\nu_{ed}$, because the intercept on the y-axis is very little sensitive to a change in B owing to the low $B\nu_{ed}$ compared with $F(v_2)$ for $v_2 > 0$.

(3) Determination of B/A from the fraction of the moduli G^1, G^2 of networks prepared at various dilutions characterized by the fractions v^{01} and v^{02} and various degrees of crosslinking so as to make the degree of swelling of networks the same. Using a procedure in principle suggested by MARK (1970), one obtains, by combining Eqs (2) and (3)

$$G^1/G^2 = [1 - B/A(v_2/v^{02})^{2/3}]/[1 - B/A(v_2/v^{01})^{2/3}] = X_t \quad (4)$$

The procedure is based on an assumption that the concentration dependence of χ is not affected by the network topology given by v^0 and by the degree of crosslinking.

(4) Comparison of the concentration dependence of the interaction parameter of a linear polymer, χ_l, and of a crosslinked polymer, χ_n, in a range where no important effect of crosslinking is expected makes possible a semiquantitative estimate of B/A.

Methods (2)-(4) do not require a separate determination of ν_{ed}, but method (2) is not suited for the determination of B.

Analysis of Experimental Data

Already the results obtained by Mark when employing method (3) and the analysis of swelling data (RIETSCH and FROELICH 1979) indicate that B/A is not negligibly small. On the other hand, some selected data treated by procedure (1) have been quoted as an example of a phantom network (FLORY 1979). However, experimental data do not always respect the two basic requirements for the validity of Eq.(1): (1) Gaussian deformation behaviour of the network, i.e. a negligibly small Mooney-Rivlin constant C_2, and (2) attainment of equilibrium. For this reason, we subjected available experimental data to critical evaluation, and only those satisfying the requirements just mentioned were used in the analysis carried out by means of methods (3) and (4).

(a) Moduli Ratio of Variously Diluted Networks

Usually, moduli of two networks having the same equilibrium degree of swelling are obtained by interpolating the G vs.v_2 dependences for networks with a different degree of crosslinking and prepared at different dilution. The analysis was performed involving data obtained by us earlier (HASA et al.1967, ULBRICH et al. 1977, 1978)(Table I). In these systems, great attention was concentrated on the attainment of equilibrium. If the equilibrium was not attained within experimentally available time intervals, extrapolation was made using the separation of the force $f(\lambda,t)$ into a time, $f_1(t)$, and deformation, $f_e(\lambda)$ dependent part,

$$f(\lambda,t) = f_e(\lambda)\, f_1(t) \qquad (5)$$

using the relation by CHASSET AND THIRION (1965)

$$f_1(t) = 1 + (t_0/t)^m \qquad (6)$$

in which t ,m are constants. For these systems also the other necessary condition, $C_2 \approx 0$, was satisfied.

Fig.1 shows the dependence of G^1/G^2 on X_t (Eq.4 for B/A = 1/2 and B/A = 1) from data in Table I, along with results published for polydimethylsiloxane networks (PDMS) (JOHNSON and MARK 1972, YU and MARK 1973, 1975). It is obvious that experimental data require predominantly the dependence of ΔF_{def} on volume (i.e. $B \neq 0$; if $B = 0$, then from Eq.(4) $G^1/G^2 = 1$), and that the experiment is better fitted by $B/A = 1$ than by $B/A = 1/2$).

(b) Concentration Dependence of χ

By combining the deformation and swelling experiment, it is possible to calculate $\chi(v_2)$ for various values of A and B using Eqs (2) and (3). For low ν_{ed}, i.e. for low v_2, the concentration dependence of χ should not be too much affected by the crosslinking alone and should approach the dependence for a linear polymer (DUŠEK 1974). The dependences were constructed by using three values of B/A:

(1) $B/A = 0$ corresponds to $B = 0$; the value of A is of no importance, because only the modulus G appears in Eq.(3).

TABLE I
The ratio of the equilibrium moduli of networks G^1/G^2 prepared with various amounts of diluent

v^{01}	G^1 MPa	v^{02}	v_2	$G^1/G^{2\,a)}$	X_t(B/A=1/2)	X_t(B/A=1)
Poly(N-ethylmethacrylamide) in water[1]						
0.822	0.140	0.701	0.156	1.00	0.98	0.94
0.637	0.099	0.701	0.148	1.01	1.02	1.04
0.443	0.059	0.701	0.110	1.26	1.07	1.38
0.345	0.008	0.701	0.047	(1.10)	1.06	1.14
Poly(N-ethylmethacrylamide) in dimethylsulphoxide[2]						
0.822	0.157	0.701	0.199	0.85	0.97	0.92
0.637	0.125	0.701	0.192	1.05	1.02	1.05
0.443	0.060	0.701	0.137	1.30	1.08	1.22
0.345	0.006	0.701	0.060	(1.10)	1.07	1.17
Poly(N-butylmethacrylamide) in dimethylsulphoxide[2]						
0.559	0.081	0.710	0.266	1.26	1.07	1.22
0.407	0.015	0.710	0.219	1.21	1.15	1.59
0.264	0.003	0.710	0.101	(1.40)	1.17	1.53
Poly(2-hydroxyethoxy-2-ethyl methacrylate) in water[3]						
0.80	0.016	1.00	0.149	(1.20)	1.03	1.07
0.80	0.059	1.00	0.217	1.25	1.04	1.10
0.80	0.087	1.00	0.238	1.17	1.04	1.11
0.80	0.138	1.00	0.266	1.21	1.05	1.13
0.60	0.007	1.00	0.107	(1.50)	1.05	1.13
0.60	0.036	1.00	0.180	1.33	1.08	1.23
0.60	0.053	1.00	0.207	1.17	1.09	1.28
0.60	0.081	1.00	0.227	1.30	1.10	1.32
0.40	0.006	1.00	0.105	(1.44)	1.12	1.32
0.40	0.023	1.00	0.157	(1.31)	1.17	1.52
0.40	0.041	1.00	0.183	1.43	1.19	1.66
0.40	0.058	1.00	0.206	1.34	1.22	1.82
0.40	0.086	1.00	0.229	1.34	1.24	2.01
0.20	0.008	1.00	0.107	(1.80)	1.32	2.27
0.20	0.015	1.00	0.125	(1.90)	1.38	2.79
0.20	0.021	1.00	0.142	(1.65)	1.43	3.56
0.20	0.026	1.00	0.156	(1.43)	1.48	4.65

1) ULBRICH et al. 1977, 2) ULBRICH et al. 1978, 3) HASA et al.1967

a) brackets denote cases where the G^2 value was determined by extrapolation

(2) B/A = 1/2 corresponds to $B = 2/f_e = 1/2$ (for a network close to a perfect one), and $A = 1$ (the case of fully suppressed fluctuations of junctions).

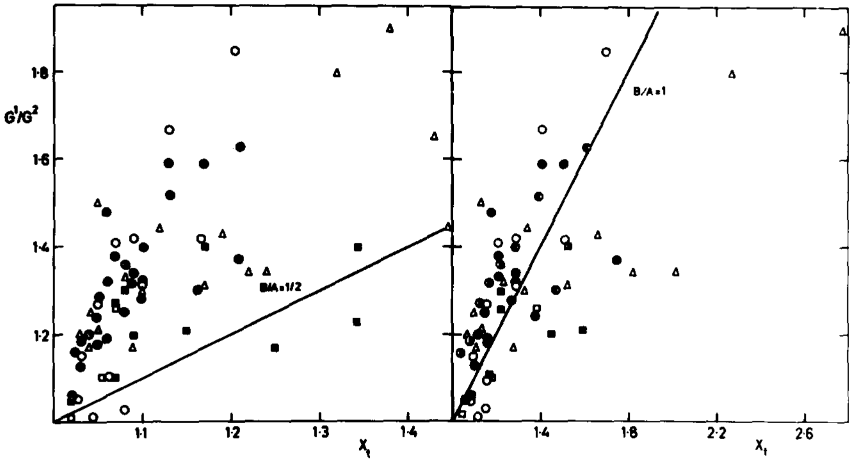

Fig.1 Comparison of the moduli G^1/G^2 of variously diluted networks with the theoretical prediction X_t (Eq.4)

○ dry polydimethylsiloxane (PDMS) (JOHNSON and MARK 1972), ● swollen PDMS (YU and MARK 1973), ⊗ PDMS in compression (YU and MARK 1975), □ poly(N-ethylmethacrylamide)-water (ULBRICH et al. 1977), ■ poly(N-ethylmethacrylamide)-dimethylsulphoxide (DMSOx) (ULBRICH et al. 1978), ◧ poly(N-butylmethacrylamide)-DMSOx (ULBRICH et al. 1978), Δ poly(2-hydroxyethoxy-2-ethylmethacrylate) -water (HASA et al. 1967), — theoretical prediction

(3) B/A = 1; ratio which better satisfied the deformation behaviour of dilute networks.

Data in Figs 2-4 were calculated from reported data on the degree of swelling and modulus; the published data of $\chi(v_2)$, originally calculated assuming B/A = 1/2, were recalculated. It may be seen from Figs 2-4 that the assumption B/A = 0 leads to the greatest divergency of the dependences of χ_1 and χ_n; for B/A = 1/2 the difference $\chi_n - \chi_1$ is the smallest. In addition to data in Figs 2-4, the concentration dependence of χ_n for the system fluoroelastomer Viton AHV -methylethylketone is also worth mentioning; this dependence is best extrapolated at B/A = 1 to $\chi = -0.005$ for $v_2 \approx 1$, determined by gas chromatography (FOGIEL 1975, McCATHERN and THOMPSON 1972).

Conclusion

Even under conditions where the equilibrium deformation and swelling behaviour closely approach an ideal behaviour given by the validity of the functional dependence of the deformational free energy defined by

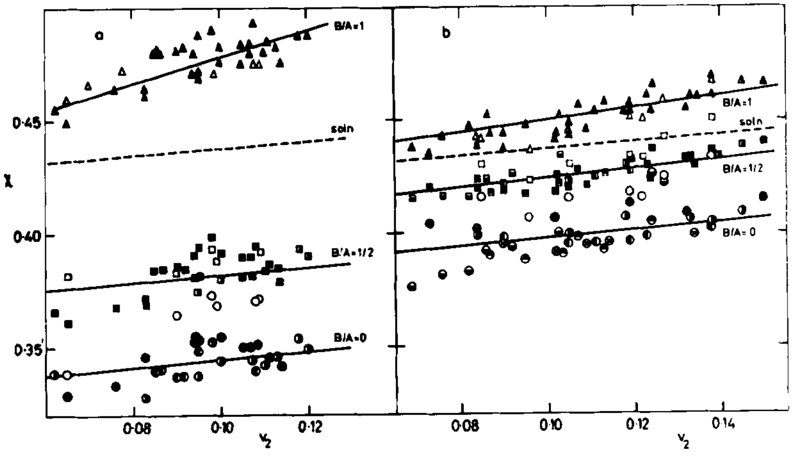

Fig.2 The dependence of the interaction parameter, χ, (Eq.3) on the volume fraction of the polymer in the swollen state, v_2, for polydimethylsiloxane networks in cyclohexane

(a) compression-dry state (YU and MARK 1975; $v^0 = 1$: ○, □, △; $v^0 = 0.58$: ●,■,▲; $v^0 = 0.45$: ◑,◨,◮; $v^0 = 0,4$: ⊗, ⊠, ▲; $v^0 = 0.28$: ◐,◧,◭; --- dependence found solutions (FLORY and SHIH 1972);
(b) extension-swollen state (YU and MARK 1973); $v^0 = 1$: ○ ,□,△; $v^0 = 0.75$: ●,■,▲; $v^0 = 0.62$: ◑,◨,◮; $v^0 = 0.55$: ⊗,⊠, ▲; $v^0 = 0.48$: ◐,◧,◭; $v^0 = 0.40$: ◒,⬒,△; $v^0 = 0.30$: ◓,⬓,▲;
--- dependence found for solutions (FLORY and SHIH 1972)

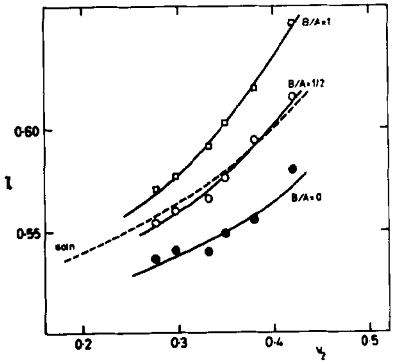

Fig.3 The concentration dependence of χ for polydimethylsiloxane networks in benzene

○,●,□ data on networks (St.PIERRE et al. 1959), --- dependence found for solutions (FLORY and SHIH 1972)

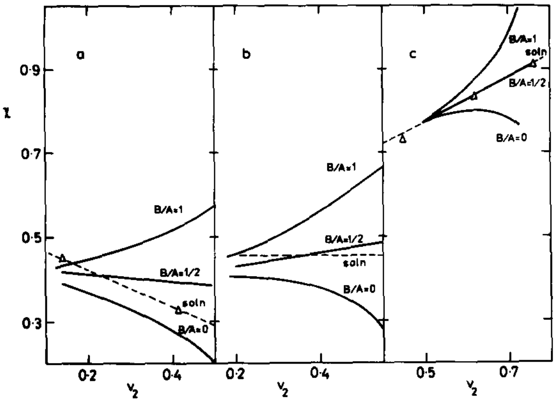

Fig.4 The concentration dependence of χ for polystyrene networks in various diluents
(a) in chloroform (BERANOVA and DUŠEK 1969), Δ polystyrene in solution (BAWN and WAJID 1956)
(b) in benzene (BERANOVA and DUŠEK 1969), --- polystyrene solutions (MARON and DANIELS 1968)
(c) in acetone (BERANOVA and DUŠEK 1969), Δ polystyrene solutions (BAWN and WAJID 1956).

Eq.(1), B/A and the volume dependence of ΔF_{def} cannot be regarded as negligible. As to the magnitude of B/A no unambiguous result could be obtained by the treatment of various systems and by using various methods. Values satisfying the experiment seem to be situated between 1/2 and unity.

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