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Studies on Mechanical and Swelling Behaviour of Polymer Networks on the Basis of the Scaling Concept

1. Experiments on Chemically Cross-Linked Poly/Vinyl Acetate/Gels in Swelling Equilibrium with Toluene

M. Zrinyi and F. Horkay

Department of Chemistry, National Institute of Occupational Health,
Nagyvárad tér 2, 1096 Budapest, Hungary

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SYNOPSIS: The scope of the present paper is to discuss the mechanical properties of poly/vinyl acetate/ /PVAc/ gels on the basis of scaling laws. The effect of different factors - the initial polymer concentration, the relative average molecular mass of the primary chains and the ratio of the pendent chains - has been studied.

INTRODUCTION

Until 1972 the only way to describe the behaviour of polymer solutions and gels was based on mean field ideas due to the works of Flory and Huggins [FLORY 1953]. This situation has changed by the discovery of rigorous analogy between chain statistics and magnetic phase transitions. De Gennes has shown that the magnetic problem solves the excluded volume problem of a single chain and Des Cloiseaux has extended this treatment to the many chain problem which is encountered in good solvent [DAOUD et al. 1975 and DE GENNES 1979]. He derived a scaled equation of state for the osmotic pressure /π/

$$\pi N^{3\nu} = \Phi(cN^{3\nu-1}) \qquad (1)$$

where N is the number of repeating units of the polymer, c is the polymer concentration and ν is the excluded volume exponent, theoretically $\nu \cong 3/5$. The scaling function, Φ, has the form [DAOUD et al. 1975]

$$\Phi(cN^{3\nu-1}) = \begin{cases} cN^{3\nu-1} & \text{if} \quad cN^{3\nu-1} \ll 1 \\ (cN^{3\nu-1})^{x} & \text{if} \quad cN^{3\nu-1} \gg 1 \end{cases} \qquad (2)$$

where x equals to $3\nu/(3\nu-1)$.

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For a network in equilibrium with pure solvent

$$\Delta\mu_{mix} + \Delta\mu_{net} = 0 \tag{3}$$

where $\Delta\mu_{mix} = -\pi V_1$, $\Delta\mu_{net} = EV_1$, V_1 means the partial molar volume of the solvent, and E is the elastic modulus. According to the classical theory of rubber elasticity $E = RTnq_o^{-2/3} d^{-1/3} c_e^{1/3}$, where n is the molar concentration of the elastically effective chains in the dry network, q_o is the memory term, d is the density of the polymer and RT has its usual meaning.
Taking into account Eqs.(1) and (3) one obtains

$$EN^{3\nu} = \Phi\,(cN^{3\nu-1}) \tag{4}$$

There are two possible cases:
/i/ The equilibrium concentration, c_e, of the polymer in the swollen network is equal to the overlap concentration, c^*, of the macromolecules having the same molecular mass as the network chains /c^* theorem/ [MUNCH et al. 1977 and CANDAU et al. 1979].
In this case c_e is proportional to $N^{1-3\nu}$ and thus the value of the scaling function is constant and Eq.(4) can be reduced to the form:

$$E = Ac_e^{3\nu/(3\nu-1)} \tag{5}$$

The constant, A, is in relationship with the functionality of the junction points.
/ii/ For the case $c_e > c^*$, there is no known relationship between c_e and N; and $cN^{3\nu-1}$ is no longer constant. Combining Eqs.(2) and (4) we arrive at Eq.(5) again.
Recent experimental studies [MUNCH et al. 1977] on polystyrene networks swollen in benzene have supported the validity of Eq.(5).

The main purpose of this work has been to study the applicability of c^* theorem and the scaling behaviour of mechanical and swelling properties of swollen networks of different kind, through the relationships (3), (4) and (5).

EXPERIMENTAL

The PVAc gels were prepared according to a previously described method [NAGY et al. 1978 and HORKAY et al. 1980], by the acetylation of poly/vinyl alcohol/ /PVA/ networks.

TABLE 1

List of the PVA gels

DC \ c_o, w%	12	9	6	3
50	+	+	+	+
100	+	+	+	+
200	+	+	+	–
400	+	+	+	–

DC: molar ratio of the monomers to the cross-linking agent

c_o: the polymer concentration at which the cross-links were introduced.

In addition we have synthesized several series of networks at c_o=9 w%. Five series of PVA gels were prepared from linear polymer chains with rather different primary molecular mass ($22300 < M_w < 345500$) and six series from polydisperse samples. The latter were obtained by mixing different amount of monodisperse fractions. The ratio of M_w/M_n for these samples was varied from 1.1 to 4.4. For detailed description see ref. [HORKAY, NAGY 1980].
Unidirectional compression measurements were performed on PVAc gels swollen to equilibrium in toluene at 298 K, in an apparatus sensitive to ±0.0001 N and ±0.006 mm, respectively [HORKAY et al. 1980].
The number of monomer units of the network chains were calculated from DC data, taking into account the number of pendent chains.

RESULTS AND DISCUSSION

In order to check the applicability of the c* theorem for our systems we have plotted $EN^{3\nu}$ against $c_eN^{3\nu-1}$ for all the different PVAc gels swollen in toluene and polystyrene networks /PS/ swollen in benzene /Fig. 1/. One can see that $c_eN^{3\nu-1}$ is not constant as the c* theorem predicts. Different networks have different $c_eN^{3\nu-1}$ values indicating higher or smaller degree of interpenetration of the network chains. The experimental data obtained for chemically different systems support the universality of the scaled equation of state of Des Cloiseaux. The exponent, x, of Eq.(2) is close to the theoretical value 9/4, and the prefactor does not differ considerably for the PVAc-toluene and the PS-benzene systems. The consequence of the above discussed relation can be seen on Fig. 2. The fact that the ratio of pendent chains to the network chains does not yield any significant deviation from the scaling law is inconsistent with the recent finding for PS networks [BASTIDE et al. 1979].

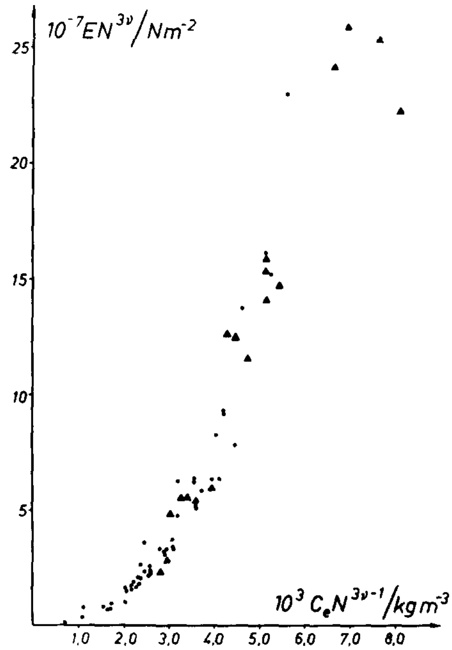

Fig. 1: Scaled equation of state for PVAc-toluene ● and PS-benzene ▲ gels. (PS-benzene data were taken from ref. [MUNCH et al. 1977].)

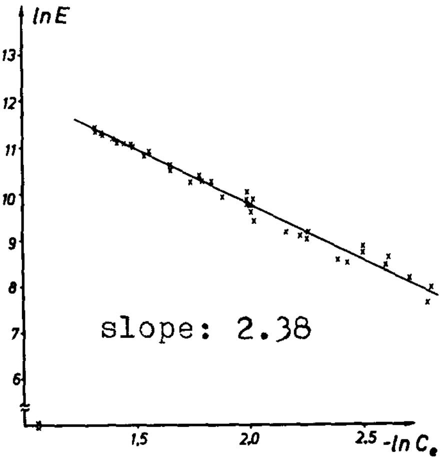

Fig. 2: The effect of the topology on the lnE-lnc function. (All the experimental points are represented by × independent of the conditions of the gelation process.)

We expected that a network structure formed at higher initial polymer concentration has a higher degree of interpenetration, thus $c_e M_c^{0.8}$ should increase with increasing polymer concentration as it can be seen on Fig. 3. (M_c is the average molecular mass of the network chains.) The degree of interpenetration has been fixed by the cross-linking process in the form of network defects /e.g. entanglements, loops/, which make their influence felt on both mechanical and swelling properties.

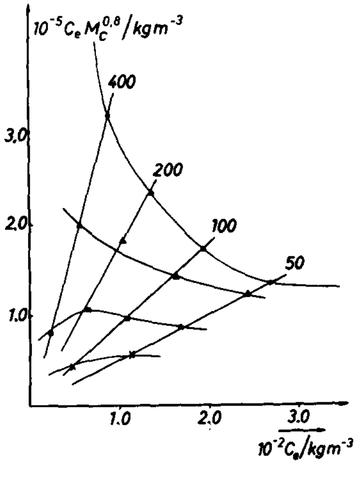

Fig. 3: Dependence of $c_e M_c^{0.8}$ on c_e at various initial polymer concentration /c_o: 12 ● ,9 ▲ ,6 ■ ,3 × / and different DC indicated on the figure.

Accepting the idea proposed by de Gennes [DE GENNES et al. 1976] in a network swollen in good solvent the average distance between chains connecting either chemical cross-links or entanglements can be identified with the screening length, ξ , characteristic of a solution of entangled linear polymer of high molecular mass at the same concentration as that of the network. Thus

$$c_e \sim M_\xi/\xi^3 \qquad (6)$$

where M_ξ is the molecular mass of the network chains belonging to two adjacent contact points. Taking into account that the elastic modulus is proportional to the density of the contact points, one gets

$$M_\xi \sim c_e/E \qquad (7)$$

For an ideal network $M_\xi = M_c$, and by increasing the interpenetration the values of M_ξ and thus c_e/E decreases. On the Table 2 the effect of the initial polymer concentration (at fixed DC) on c_e/E can be seen.

TABLE 2

The influence of the topology on the number of repeating units connecting two adjacent contact points

	$10^3\ c_e/E$, $kgNm^{-5}$			
c_o \ DC	50	100	200	400
12	2.5	3.9	6.7	17.4
9	3.3	5.2	8.5	20.3
6	4.9	10.9	26.5	42.8
3	11.2	29.7	--	--

The results are in agreement with Fig. 3.
In order to test the validity of Eqs.(3) and (5) the elastic modulus of the networks and the osmotic pressure of the solution of the linear chains are plotted as a function of $c^{9/4}$ /Fig. 4/. Dotted line is the sum of the two quantities. It can be seen that π and E has the same concentration dependence; only the prefactor is different.

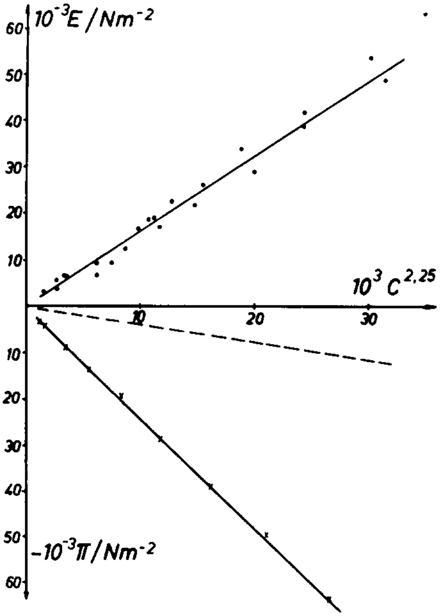

Fig. 4: Scaled form of Eq.(3) for PVAc-toluene systems. (Osmotic pressure data were taken from ref. [VINK 1973].)

These results support the suggestion of de Gennes, that the only parameter which control the elastic and swelling properties of a network in a good solvent is the screening length. This quantity is and its dependence on the concentration is not affected by the cross-linking process and the topology of the network systems investigated.

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