Studies on Mechanical and Swelling Behaviour of Polymer Networks on the Basis of the Scaling Concept
2. Test of the Scaling Law for the Elastic Modulus of Chemically Different Network Systems

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SUMMARY
    The elastic moduli of different network systems, swollen in good diluents have been determined by uni-directional compression measurements. The systems studied obey a simple scaling law independently of the preparation conditions and the chemical nature of the diluents. The exponents and prefactors for different polymer-diluent systems have been summarized. The effect of solvent quality on the equilibrium swelling degree of the gels has been discussed.

INTRODUCTION
    As has already been verified by several authors the scaling theories established for polymer solutions can also be applied to permanent network systems in equilibrium with a pure diluent. De Gennes has shown that the equilibrium polymer concentration, c_e, of a swollen network can be expressed in terms of the overlap concentration, c^*, of the solution of a polymer having the same molecular mass as the network chains (c^* theorem, DE GENNES 1979)

$$c_e = k(z)c^* \qquad (1)$$

where $k(z)$ is a constant depending on the functionality, z, of the cross-links.
    The overlap concentration depends on the polymerization index, N, the Flory-Huggins interaction parameter, χ, and the density of the polymer, d_2, through the relation

362

$$c^* = N^{-4/5} d_2 (1-2\chi)^{-3/5} \qquad (2)$$

In the case of an ideal network the overlap concentration is given by an alternative form of Eq.(2)

$$c^* = \frac{M_c}{R^3} \qquad (3)$$

where M_c is the average molecular mass and R is the radius of gyration of the network chains. For real networks the situation is somewhat different because of the presence of network defects (e.g. entanglements, loops, pendent chains). Most of these defects decrease the effective distance and, consequently, the molecular mass of the chains between the junction points. Although the c^* theorem is still valid the effective molecular mass, M_ξ, of the network chains connecting two neighbouring junction points can no longer be calculated from the polymerization index (CANDAU et al. 1981, ZRINYI and HORKAY 1980).

It has been shown that the elastic modulus, E, possesses the following properties:

/i/ For a given network system it is proportional to the number of elastic chains, n, in the swollen network

$$E \propto n \propto \frac{c_e}{M_\xi} \qquad (4)$$

thus there is a linear relationship between E and c_e in different diluents.

/ii/ For chemically identical but topologically different networks the c^* theorem, which takes into account the dependence of the equilibrium concentration on M_ξ ($c_e \propto M_\xi^{-4/5}$), yields a simple relationship between the elastic moduli and the equilibrium concentration of the networks

$$E = A_c c_e^m \qquad (5)$$

The exponent, m, is a function of the excluded volume exponent, ν,

$$m = \frac{3\nu}{3\nu-1} \qquad (6)$$

In good solvent conditions: $\nu=3/5$ and $m=9/4$
In poor (theta) solvent conditions: $\nu=1/2$ and $m=3$
The prefactor, A_c, of Eq.(5) depends on the functio-
nality of the junction points, the Flory-Huggins
interaction parameter and the density of the polymer.
This latter can be eliminated by using volume fractions
of the polymer, v_2, as concentration and Eq.(5) can be
written as follows

$$E = Av_2^m \tag{7}$$

where

$$A = K(z)(1-2\chi)^{3/4} \tag{8}$$

In Eq.(8) K(z) is another constant.
The aim of the present work has been to study the
scaling behaviour of chemically different network
systems and establish the influence of the solvent
quality on their equilibrium properties.

EXPERIMENTAL
Polyvinyl alcohol (PVA) and poly(vinyl acetate)
(PVAc) networks were prepared by a method described
earlier (HORKAY and NAGY 1980). Some characteristics of
the PVA gels prepared in water are listed in Table 1.

TABLE 1

Characteristics of the PVA gels

Symbol	M_w	M_w/M_n	DC			
I	22300	1.2	50	100	200	---
PD I	69500	2.7	50	100	200	---
PD II	184000	4.7	50	100	200	400
PD III	298300	2.7	50	100	200	400
V	345500	1.2	50	100	200	400

M_w and M_n are the mass and the number average molecular
mass of the primary chains, DC means the molar ratio of
the monomer units to the cross-linking agent. Systems
denoted by PD I, PD II and PD III were obtained by
mixing different quantities of fractions I and V.
Cylindrical gel specimens of equal height and dia-
meter were prepared at 9 w% initial polymer concent-
ration in a suitable frame. The PVAc networks were
prepared by total acetylation of the PVA gels.

Unidirectional compression measurements were carried out at 298 K using an apparatus sensitive to ± 0.0001 N and ± 0.006 mm, respectively (HORKAY et al. 1980). Force-deformation data were determined for the PVA and PVAc networks in swelling equilibrium with different diluents (systems: PVA/water, PVAc/toluene and PVAc/acetone).

The absence of volume change and barrel-distortion was checked by studying the shape of the deformed gel cylinders.

The experimental data were analysed on the basis of the relationship

$$ f = 2C_1 (\Lambda_x - \Lambda_x^{-2}) + 2C_2 (\Lambda_x - \Lambda_x^{-2}) \Lambda_x^{-1} \qquad (9) $$

where f is the force of retraction at deformation ratio Λ_x, which means the ratio of the compressed length of the gel sample to the length at rest. C_1 and C_2 are constants characterizing the network systems. For the PVA and the PVAc gels the value of C_2 was found to be zero. The elastic moduli of the gels were calculated from $2C_1$ data through the relation:

$$ E = 2C_1 F^{-1} d_2^{1/3} \qquad (10) $$

where F is the swollen unstrained cross-section.

RESULTS AND DISCUSSION

In order to establish the relationship between the equilibrium polymer concentrations of the network systems swollen in different diluents we have plotted the c_e(acetone) values as a function of c_e(toluene) (Fig. 1). Eq.(1) and Eq.(2) predict that the ratio of the equilibrium concentrations for the same networks is a function of the χ values.

$$ \frac{c_e(\text{acetone})}{c_e(\text{toluene})} = \frac{c^*(\text{acetone})}{c^*(\text{toluene})} = \frac{(1-2\chi_a)^{-3/5}}{(1-2\chi_t)^{-3/5}} \qquad (11) $$

The data reported on Fig. 1 suggest that the ratio of the swelling degrees in different diluents is affected by the extent of the chemical modification of the chains. The experimental points for gels with identical DC values are on the same straight lines. The slope of the lines increases with an increase in the amount of cross-linking agent added to the systems, which means that the χ parameter considerably depends on DC. We note that the scaling theory considers χ as an energetic contribution while χ is mainly dominated by structural effects due to

the external degrees of freedom of chains, which may be
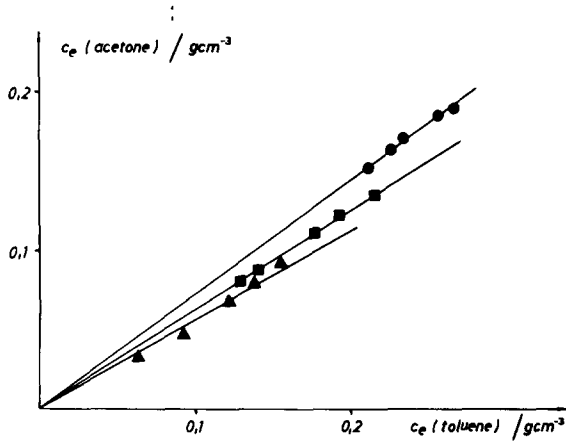strongly influenced by the cross-linking process.

Fig. 1. The effect of the solvent quality on the
equilibrium concentration of the gels. DC: ● 50, ■ 100, ▲ 200

In order to examine the validity of Eq.(4) we have
plotted E/c_e values determined in acetone against those
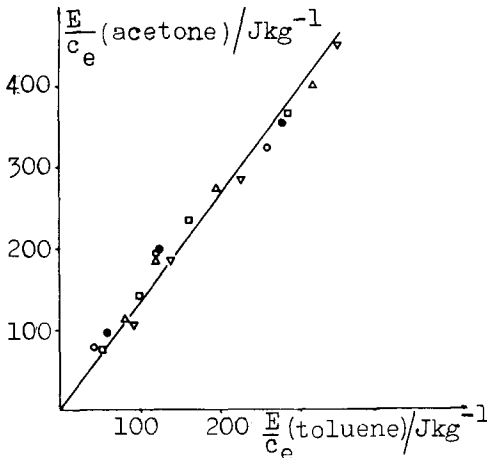obtained in toluene (Fig. 2). According to the theory
E/c_e is a function of
the molecular mass of
the network chains
between the neighbouring
junction points only,
thus the slope of the
function E/c_e(acetone)
vs. E/c_e(toluene) should
be equal to 1. For the
studied systems a
straight line was found
with a slope of 1.3. The
deviation from the theo-
retical value may be
attributed to the pre-
sence of entanglements.
For a given network an
increase in the swelling
ratio (e.g. swelling in
a better solvent) should
cause entanglement points
to act more and more like
permanent cross-links. A
similar effect has been
reported for poly(dimethyl
siloxane) networks swollen
in toluene and heptane,
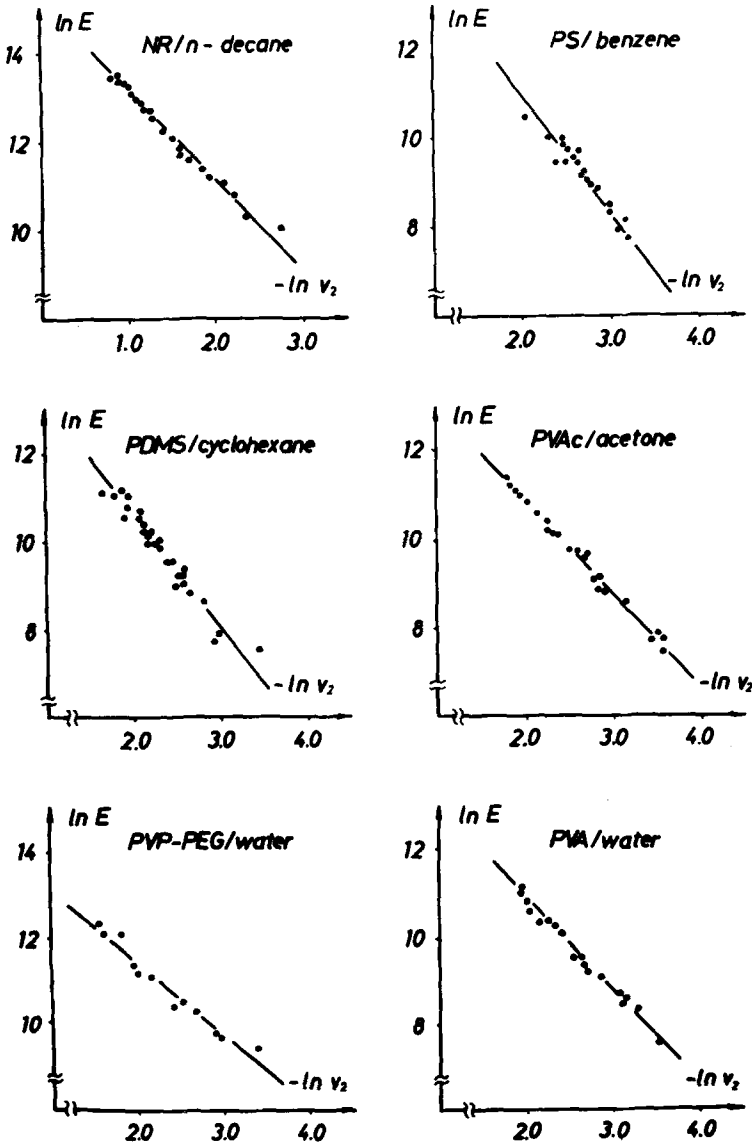respectively (MUNCH et al.
1977, CANDAU et al. 1981).

Fig. 2. E/c_e(acetone)vs.
E/c_e(toluene) for PVAc
gels. Samples: ○ I, ● PD I,
◻ PD II, △ PD III, ▽ V.

Fig. 3. Scaling law for the elastic moduli of six chemically different network systems. The values of E are given in Nm^{-2} units. The meanings of symbols and the references they have been taken from are detailed in Table 2.

TABLE 2

The calculated values of m and A

System	m	10^{-6} A	No.	r	REFERENCES
NR/n-decane	2.06	4.5	33	0.992	BRISTOW, G. M.: J. Appl. Polymer Sci. 9, 1571 (1965)
PIP/n-decane	2.68	8.9	14	0.996	BRISTOW, G. M.: J. Appl. Polymer Sci. 9, 1571 (1965)
PDMS/cyclohexane	2.57	7.9	29	0.964	COHEN, R. E., SEVERSON, S. D., YU, C. U. and MARK, J. E.: Macromolecules 10, 663(1977)
PDMS/toluene	2.84	8.2	15	0.892	BELKEBIR-MRANI, A., BEINERT, G., HERZ, J. and REMPP, P.: Eur. Polym. J. 13, 277 (1977)
PVAc/toluene	2.38	2.9	53	0.986	ZRINYI, M. and HORKAY, F.: Polymer Bulletin, 3, 665 (1980)
PVAc/acetone	2.09	3.5	23	0.994	HORKAY, F., NAGY, M. and ZRINYI, M.: Acta Chim. Acad. Sci. Hung. in press,(1981)
PS/benzene	2.28	4.2	22	0.955	MUNCH, J. P., CANDAU, S., HERZ, J. and HILD, G.: J. Physique, 38, 971 (1977)
PDEGMA/water	3.10	7.1	21	0.991	HASA, J., ILAVSKÝ, M. and JANÁČEK, J.: Coll. Czech. Chem. Commun., 32, 4156 (1967)
PVP-PEG/water	1.67	2.7	12	0.980	GOOD, W. R. and CANTOW, H.-J.: Polymer Bulletin 1, 857 (1979)
PVA/water	2.11	3.5	18	0.993	this work

No.: number of systems investigated, r: correlation coefficient
NR: natural rubber, PIP: cis-1,4-polyisoprene, PDMS: poly(dimethyl siloxane),
PVAc: poly(vinyl acetate), PS: polystyrene, PDEGMA: poly(diethyleneglycol monomethacrylate)
PVP-PEG: poly-vinyl-pyrrolidone cross-linked with polyethylene glycol oligomers
PVA: polyvinyl alcohol.

In addition Fig. 2 shows that the influence of DC has no longer been experienced. It is worth mentioning that the molecular mass and molecular mass distribution of the primary chains, thus the ratio of the pendent chains has no any significant effect on the equilibrium swelling degree. According to our experiments the parameters which control the swelling ability of a network are the polymer-solvent interaction parameter and the concentration of the elastically active chains.

In order to test the applicability of Eq.(7) we have plotted $\ln E$ as a function of $-\ln v_2$ for our systems and for other systems available from the literature (Fig. 3). It can be seen that all the systems obey a scaling law independently of the preparation conditions. The slight DC dependence of χ values does not affect the prefactors (see PVAc/acetone and PVA/water systems on Fig. 3). Preliminary calculations have shown that the change of prefactors by the altered χ values are within the experimental error. We have calculated the values of the exponent, m, and the prefactor, A, by linear regression for 10 chemically different systems. These data are summarized in Table 2. It can be seen that the m values are definitely larger than 2 predicted by the mean field theory and increase with the decrease of solvent quality. We note that the values of A for PVAc/acetone and PVAc/toluene systems (the same networks in different diluents) are in agreement with the prediction of Eq.(8), that is swelling in better solvent gives greater prefactor.

The fact that the exponents for gels swollen in water significantly differ from each other may be attributed to the presence of specific interactions. It is rather surprising that a linear dependence with comparatively good correlation coefficient has been found even for PVP-PEG/water gels in spite of their non-uniform (composite) character. At these systems the lengths of the PEG chains used as cross-linking agent were varied in wide range $(600 < M_w < 4000)$ (GOOD and CANTOW 1979) and thus a considerable effect of it on the χ values could have been expected.

REFERENCES

CANDAU, S., PETERS, A. and HERZ, J.: J. Polym. Sci. in press, (1981)
DE GENNES, P. G.: Scaling Concepts in Polymer Physics, Cornell University Press, Ithaca and London, (1979)
GOOD, W. R. and CANTOW, H.-J.: Polymer Bulletin, 1, 857 (1979)
HORKAY, F. and NAGY, M.: Polymer Bulletin, 3, 457 (1980)
HORKAY, F., NAGY, M. and ZRINYI, M.: Acta Chim. Acad. Sci. Hung. 103, 387 (1980)
MUNCH, J. P., LEMARÉCHAL, P., CANDAU, S. and HERZ, J.: J. Physique, 38, 1499 (1977)
ZRINYI, M. and HORKAY, F.: Polymer Bulletin, 3, 665 (1980)