Polymer Bulletin 24, 665–670 (1990)

Polymer Bulletin

© Springer-Verlag 1990

Is a collapse phenomenon predicted by the constrained junction fluctuation network theory?

M. Zrínyi* and F. Horkay

Department of Colloid Science, L. Eötvös University, Pázmány sétány 2, H-1117 Budapest, Hungary

The concentration - temperature dependence of loosely cross-linked neutral networks being in equilibrium with pure diluent is studied. It is shown, that the constrained junction fluctuation network model, introduced by Flory and Erman, precludes the possibility of a first order like gel-collapse transition. A simple equation is proposed to describe the dependence of equilibrium swelling degree on the temperature. Experimental results performed on poly(vinyl acetate) networks swollen to equilibrium in isopropyl alcohol are also presented.

Introduction

The collapse phenomenon has aroused a great deal of interest in the past few years and the collapse of neutral gels has continued to be the subject of some dispute. For the first time Dusek and Patterson have predicted that, under certain condition a first order like transition can occur and two gel phases can appear or disappear by changing the temperature or the quality of the solvent [2,3]. On the basis of similar arguments Tanaka has concluded that a collapse can take place when the cross-linking density exceeds a critical value [4]. Khoklov has found that the stiffness of network chains plays a decisive role [5] .

For neutral gels the collapse transition has not been observed experimentally as yet. Poly(acryl-amide) and chemically modified poly-(acryl-amide) gels were found to have a sudden change in swelling degree within a narrow range of polymer solvent interaction, but it turned out that the observed collapse is due to electrostatic interaction or formation of heterogeneous structures [6]. A filler induced collapse was also observed [7]. The importance of Coulombic interaction in collapse transition was emphasised by Ilavsky [8].

From theoretical point of view, all the analysis, dealing with the interpretation of the phenomenon were based on either the phantom-, or the affine network models.

Due to the great improvement in the experimental testing of network theories, it turned out that the affine- and phantom models can not describe the mechanical and thermodynamical behaviour of real networks correctly [1,9,10].

Flory and Erman have introduced the constrained junction fluctuation model in order to overcome the difficulties arising from non-Gaussian effects [1,9].

---

*To whom offprint requests should be sent

The main purpose of the present paper is to investigate the swelling behaviour of loosely cross-linked networks on the basis of Flory-Erman theory. The dependence of swelling degree on the temperature is studied in the vicinity of theta temperature.

The swelling equilibrium

According to Flory and Erman the condition of equilibrium with pure diluent can be written as follows:

$$\xi \bar{V}_1 q_o^{-2/3} \Phi^{1/3} v_d^{-1} \left[1+K(\lambda^2) \right] + \ln(1-\Phi) + \Phi + \chi \Phi^2 = 0 \qquad (1)$$

where Φ is the volume fraction of the polymer in the gel,

χ represents the Huggins parameter,

q_o stands for the isotropic deformation which takes into account the effect of concentration on the network formation process,

ξ denotes the cyclic rank of the network,

V_1 is the partial molar volume of the swelling agent and

v_d means the volume of the dry polymer

The term $K(\lambda^2)$ in the elastic chemical potential involves

$$K(\lambda^2) = \frac{B}{1+B} \frac{\partial B}{\partial(\lambda^2)} + \frac{Bg}{(1+Bg)} \frac{\partial(Bg)}{\partial(\lambda^2)} \qquad (2)$$

$$B = (\lambda - 1)(1 + \lambda - \zeta \lambda^2)(1+g)^{-2} \qquad (3)$$

$$g = \lambda^2 [\kappa^{-1} + \zeta(\lambda - 1)] \qquad (4)$$

$$\lambda = q_o^{-1/3} \Phi^{1/3} \qquad (5)$$

where κ is the measure of severity of the constraints imposed by the neighbouring chains on the network junctions. The parameter ζ was introduced to take into account the effect of deformation on the distribution function of the network chains. It was found less important than κ, and since it is generally quite small, it can be neglected.
It is worth to mention that in the phantom network limit ($\kappa \to 0$), $K(\lambda\ ) = 0$. In case of an affine network ($\kappa \to \infty$, $K(\lambda\ ) = 1 - \lambda^{-2}$.
Since we are dealing with highly swollen networks ($\Phi \ll 1$) therefore it seems to be straightforward to substitute the mixing contribution of

the chemical potential its third order series, and generalised in order to take into account both, the effect of chain stiffness as well as the concentration dependence of Huggins parameter :

$$a\,\Phi^{1/3}\,[1 + K(\lambda^2)] - u\,\Phi^2 - w\,\Phi^3 = 0 \qquad (6)$$

where a stands for $\xi \bar{V}_1 q_o^{-2/3} v_d^{-1}$, u denotes (1/2 - χ) and w refers to the third virial coefficient of monomer interactions.
If we approximate the concentration dependence of Huggins parameter with the following equation,

$$\chi = \chi_o + \chi_1 \Phi \qquad (7)$$

then u and w become 1/2- χ_o and χ_1 - 1/3, respectively.
We suppose that only u depends on the temperature. The possible temperature dependence of quantities like V_1/v_d, q_o and w are neglected. In the vicinity of theta temperature, Θ, as shown by Flory [11] , u can be expressed by the reduced temperature,τ :

$$u = \Psi\,(\,1 - \Theta/T\,) = \Psi\,\tau \qquad (8)$$

where Ψ is the a constant and τ is defined as $\tau = (T-\Theta)/T$.
At Θ-temperature Eq. 6 can be written as follows:

$$a\,\Phi_\Theta^{1/3}\;[1 + K(\,\lambda_\Theta^2)\,] = w\,\Phi_\Theta^3 \qquad (9)$$

Combyning Eqs. 7,8 and 9 and introducing reduced variables:

$$\tilde{\Phi} = \Phi/\Phi_\Theta \qquad \text{and} \qquad \tilde{T} = \tau/\Phi_\Theta \qquad (10)$$

one obtains:

$$\frac{1 + K(\lambda^2)}{1 + K(\lambda_\Theta^2)}\left(\tilde{\Phi}\right)^{-5/3} - \left(\tilde{\Phi}\right) = c\,\tilde{T} \qquad (11)$$

where the parameter $c = \Psi/w$ characterizes the polymer- solvent system. c is independent of the cross-linking density.

One can see that in the phantom network limit, both $K(\lambda^2)$ and $K(\lambda_\Theta^2)$ approach zero and one obtains our previous result [12]:

$$(\tilde{\Phi})^{-5/3} - (\tilde{\Phi}) = c\,\tilde{T} \qquad (12)$$

Eq.12 predicts an universal dependence if the reduced concentration and the quantity $c\tilde{T}$ are used.
In the affine network limit, the quantity $(1-K(\lambda^2)/(1-K(\lambda_\Theta^2))$ does not disappear and an universal dependence can not be any longer expected. It is obvious that the same holds true for the intermediate network behaviour as well.
The shape of $\tilde{\Phi}$ - $c\tilde{T}$ curves are influenced by the structural parameters, via $K(\lambda^2)$ and $K(\lambda_\Theta^2)$.

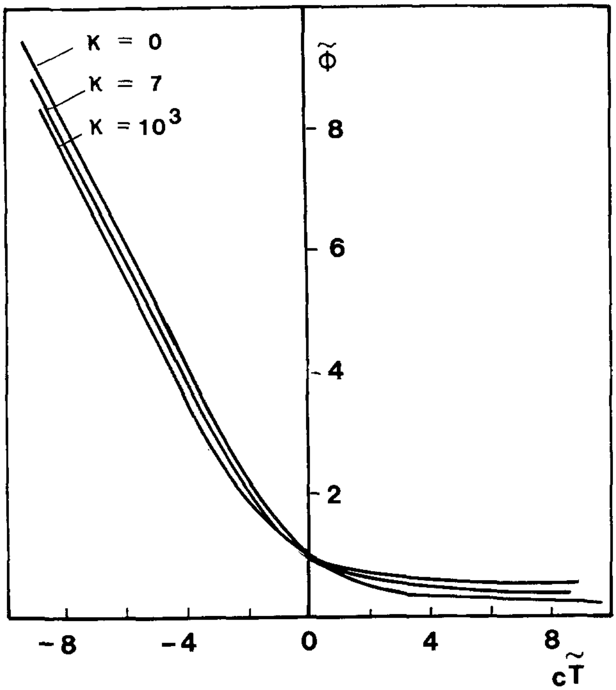

Fig.1 The reduced concentration as a function of reduced temperature. The curves were calculated with the aid of Eq.11. For the calculation $q_o = 8.33$ and $\Phi_\Theta = 0.23$ were used. The value of constrained junction fluctuation parameter is indicated on the figure.

Fig. 1 shows how the severity of constrained parameter (κ) makes its influence felt on this dependence. It can be concluded that the deviation due to different values of κ, is not very significant in the vicinity of Θ - temperature, and in the poor solvent regime.

Above the Θ-temperature —due to the small value of $\tilde{\Phi}$, the difference between the phantom and affine behaviour is rather significant.
In this range $\Delta\tilde{\Phi}/\tilde{\Phi} \sim 0.5$, whereas in the $T \ll \Theta$ region $\Delta\tilde{\Phi}/\tilde{\Phi}$ is much smaller.
It must be emphasised that the general monoton decreasig character of $\tilde{\Phi}$ - $c\tilde{T}$ dependence can not be altered by the parameters, q_q , a, w and $\varkappa$, that is the appearance of collapse transition is precluded by the constrained junction fluctuation model.

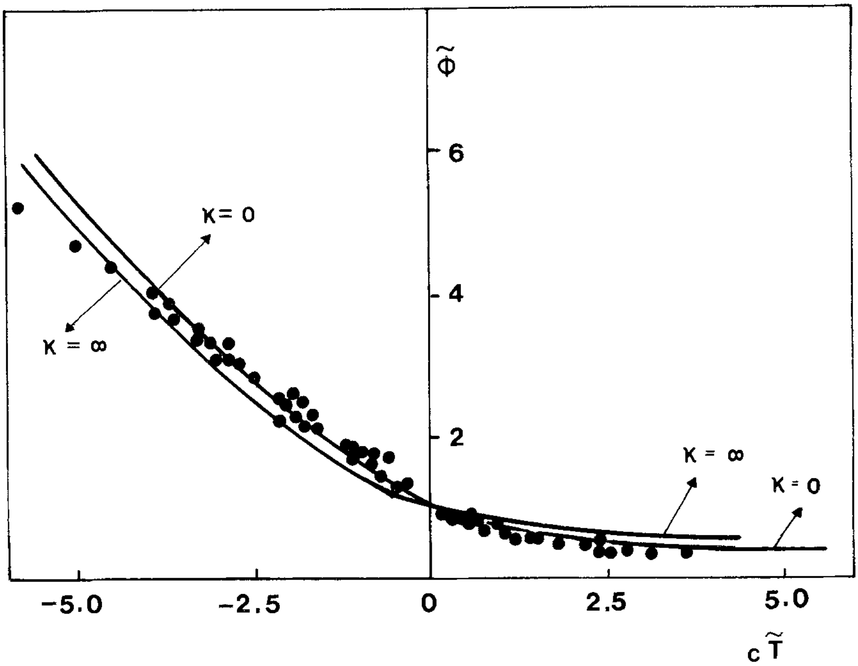

Fig.2 Scaled concentration versus the scaled temperature for different poly(vinyl-acetate) networks swollen to equilibrium in isopropyl alcohol.

In Fig.2 experimental results performed on poly(vinyl acetate) networks swollen to equilibrium in isopropyl alcohol are compared with Eq.11.
A detailed description of experiments can be found in ref. 12.
The equilibrium swelling degrees and concentrations of nine PVAc network-homologues were determined at eight different temperatures, 30, 37, 45, 50, 52, 55, 60 and 70 C°, respectively. The Θ temperature of PVAc/isopropyl alcohol gels were found to be 52 C°. The concentration of gels measured at T=Θ temperature varied between $0.146 \le \Phi_\Theta \le 0.365$.
It was found that c=0.1

In Fig.2 one sees that within experimental accuracy, all points (72) seem to be gathered in the same curve, which slightly differs from those predicted by the affine- and phantom models.

It can also be seen that none of the gels show the macroscopic collapse phenomenon within the studied temperature range. For all the gels a continuous monotonically decreasing curve was obtained.

Summary

We have studied the temperature dependence of equilibrium concentration of loosely cross-linked swollen networks on the basis of the constrained junction fluctuation model. It has been shown that the phantom limit exhibits a scaling behaviour. On the basis of Flory—Erman model an universal function can not be constructed and a first-order like collapse transition can not be expected. Experimental results obtained for chemically cross-linked PVAc networks swollen to equilibrium in isopropyl alcohol show no collapse phenomenon.

Acknowledgement. This research has been supported by a grant (OTKA 1204/86) of Hungarian Academy of Sciences.

References:

1) B.Erman and P.J.Flory, Macromolecules, 15, 800 (1982)
2) K.Dusek and D.Patterson, J.Polym. Sci., Polym. Phys. Ed. 6, 1209 (1968)
3) K.Dusek and W.Prins, Adv. Polym. Sci., 6, 1 (1969)
4) T.Tanaka, Phys. Rev. Lett., 40, 820 (1978)
5) A.R.Khoklov, Polymer, 21, 376 (1980)
6) V.F.Janas, F.Rodriguez and F.Cohen, Macromolecules, 13, 977 (1980)
7) M.Zrinyi, H.-G.Kilian, K.Dierksen and F.Horkay, in preparation
8) M.Ilavsky, Polymer, 22, 1678 (1981)
9) J.E.Mark and B.Erman, Rubberlike Elasticity a Molecular Primer, John Wiley & Sons, NY, Chichester, Brisbane, Toronto, Singapure (1988)
10) H.-G.Kilian, Polymer, 22, 209 (1981)
12) M.Zrinyi and F.Horkay, Macromolecules, 22, 394 (1989)

Accepted August 3, 1990 C