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Physical Properties of Real Polymer Networks

New General Criteria for the Gel Point and the Principle of Macroscopic Uniformity

W. Klonowski

Polish Academy of Sciences, Medical Research Centre, 3, Dworkowa Str.,
PL-00-784 Warsaw 36, Poland*

SUMMARY: The physical properties of real polymer networks (i.e. networks with different kinds of defects) are calculated based on the probabilistic theory of crosslinked polymer systems developed by the author. In particular the recently proposed: (1)general criterion for the gel point (critical branching point) and (2)principle of macroscopic uniformity (PMU) are applied and discussed and a new principle of maximum is proposed.

Our theory is based on the assumption that physical properties of crosslinked polymers depend essentially on defects in the network structure (KLONOWSKI 1978, 1978-9, 1979a). From the statistics of defects one may infer physical properties of the system (KLONOWSKI 1979a-e). Theoretical analysis of network connectivity gives us the fractions, n_k , of different kinds of junctions, i.e. of junctions with different numbers, k , of free chain ends. Free chain ends are unavoidable defects in systems consisting of crosslinked primary macromolecules - they interrupt continuity of molecular tracts in the network. Fractions n_k are expressed as functions of the crosslinking index, l , and of the fraction, β , of junctions closing cycles (KLONOWSKI 1979c). By definition:

$$l = \frac{2\tilde{J}}{N} \qquad (1)$$

$$\beta = \frac{\tilde{J}_t}{\tilde{J}} \qquad (2)$$

where N - the total number of primary macromolecules,
$\tilde{J}$ - the total number of junctions in the system,
$\tilde{J}_t$ - the minimal number of junctions necessary to obtain the given state of crosslinking, i.e. necessary to form the same numbers of different molecular aggregates and the given network as in the system under consideration but in a "tree-like form", without any close cycles.
It is not possible to point out in the given crosslinked system which junctions closed cycles and which ones do not. Instead of it each junction is assumed to close

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* Present address: Professeur A.T.G. Klonowski Wlodzimierz, L'Université de Kinshasa, Faculté des Sciences, Departement de Physique, B.P. 190, Kinshasa XI, Zaïre

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any cycle with probability β and to form a molecular "tree" with probability $(1-\beta)$. So the division of all junctions into those closing cycles and those forming "trees" must be understood in the above probabilistic sense.

The theory gives possibility to calculate n_k if the distribution function, f_q, of junctions between primary macromolecules is known. If $N_q(l)$ is the number of primary macromolecules involved into q junctions each (for a given value of crosslinking index, l), then $f_q(l)$ denotes the fraction of such macromolecules

$$f_q(l) = \frac{N_q(l)}{N} \tag{3}$$

In reality only f_0 and f_1 are needed. For randomly crosslinked systems f_q may be assumed to have Poissonian form, i.e.

$$f_0 = e^{-l} \tag{4}$$

$$f_1 = le^{-l} \tag{5}$$

f_0 and f_1 may be also found from an experiment - for a monodisperse system (not necessarily random) one has

$$f_0 = w_s \tag{6}$$

$$f_1 = l\left[(1-\beta)w_d\right]^{\frac{1}{2}} \tag{7}$$

where w_s and w_d are respectively weight fractions of uncrosslinked primary macromolecules and of dimers, which of course all belong to the sol and so these fractions are usually easily measured; for polydisperse systems simple averaging over m.w.d. is necessary (KLONOWSKI 1979b). It may be of great practical importance that by making measurements on the sol one may deduced from the presented theory properties of the gel.

Having $f_q(l)$ one may calculate n_k from which different physical characteristics of the system may be calculated (cp.KLONOWSKI 1979a,c) as functions of the crosslinked index, l. Results of the calculations made for a monodisperse randomly crosslinked system with Poissonian distribution function (4)-(5) are shown on Fig.1.

One may also calculate the reduced crosslinking density (the notion introduced first time in KLONOWSKI 1979a,c)

$$L = \frac{2 \cdot J_{gef}}{N_{gef}} \tag{8}$$

where J_{gef} denotes the number of "gel-effective junctions" and N_{gef} - the number of "gel-effective primary macromolecules". A junction is said to be gel-effective if it forms a part of a molecular tract going from one topologically nearest neighbour junction (i.e. jun-

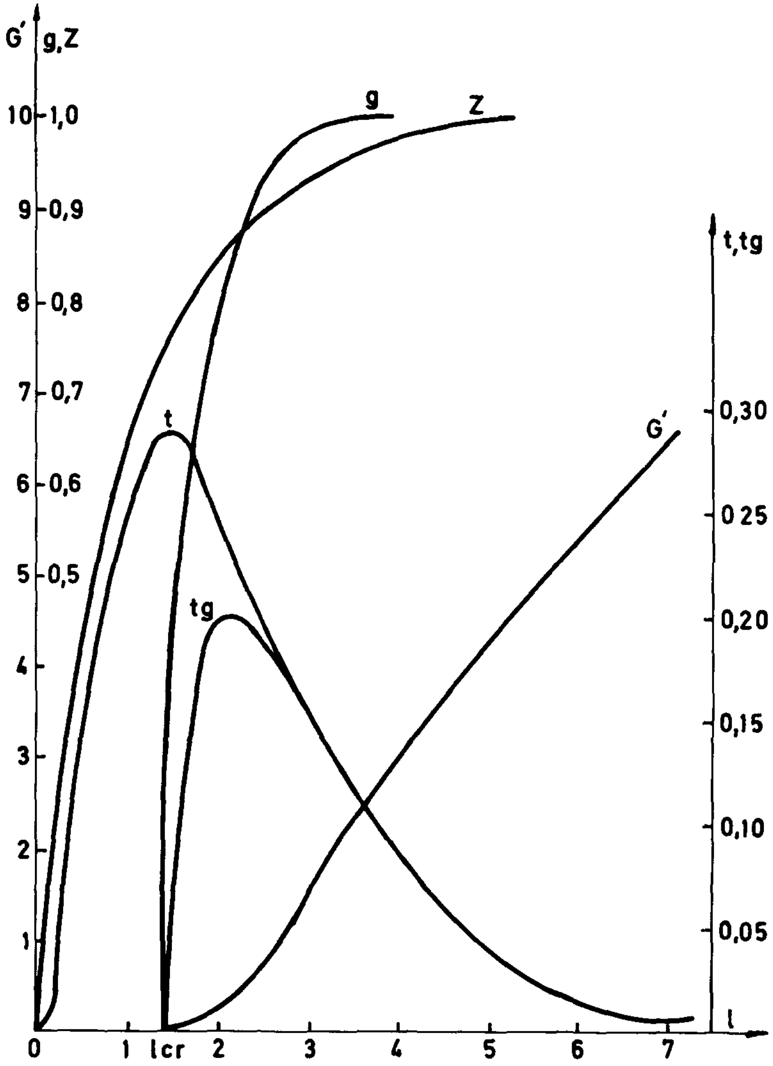

Fig. 1. Physical characteristics vs. crosslinking index, calculated for a monodisperse, randomly crosslinked system of pre-existing linear macromolecules, without closed cycles (β=0). Symboles denote respectively: g - gel fraction; z - fraction of primary macromolecules bearing at least one crosslink each; t - fraction of pendent chains in the whole system $[t = l(n_3+n_2)/2]$; t_g - fraction of pendent chains in the gel $[t_g = g \cdot t]$; $G' \equiv$ reduced modulus of elasticity $[G' = (2M_0/kTv_2) \cdot G]$ (where G - modulus, M_0 - molecular weight of a primary macromolecule, v_2 - volume fraction of polymer in the system, T - absolute temperature, k - Boltzmann constant).

ction connected with the considered one by the only one network chain), "the grand-father", to at least one another topologically nearest neighbour junction, "the descendant" ("son") of the junction under consideration, ("the father"), belonging to the different primary macromolecule than "the grand-father". Otherwise, a gel-effective junction is a junction forming molecular tree and such that each of two fragments of the tree it joints is not just a single primary macromolecule (pendent chain); of course junctions forming dimers, n_4 , are not gel-effective.

A primary macromolecule is said to be gel-effective if it is involved in at least one gel-effective junction, i.e. if it forms a part of molecular tracts and not just remaining uncrosslinked, forming a dimer or being a pendant chain (crosslinked only at one junction).

As it was mentioned above, division of all junctions into those closing cycles and those forming molecular trees has generally only probabilistic sense; the same concernes the division into gel-effective and not-gel-effective junctions.

The notion of the reduced crosslinking density is the base of the new general criterion for the gel point (KLONOWSKI 1979a,c):

$$L_{cr} = 2 \qquad (9)$$

Eq. (9) expresses physically obvious fact that to form "infinite" network each gel-effective primary macromolecule must be involved at least in two gel-effective junctions (KLONOWSKI 1979a). This criterion remains true for the systems being far from thermodynamic equilibrium and not necessarily random, including networks with closed cycles (KLONOWSKI 1978-9, 1979c). So it may be applied also for biophysical systems.

The reduced crosslinking density is a function of crosslinking index (through n_k). Eq. (9) is an implicit equation for critical crosslinking index, l_{cr}. The value of l_{cr} strongly depends on β and on polydispersity of the system (characterised, as usual, by the ratio $\bar{M}_w:\bar{M}_n$) , where $\bar{M}_w$ and $\bar{M}_n$ are weight- and number-average molecular weights, respectively). The greater is polydispersity the lower is l_{cr} (Fig.2).

For a macroscopically uniform system the principle of macroscopic uniformity must hold. This principle (PMU), introduced recently by the author (KLONOWSKI 1979c), states that to be macroscopically uniform the crosslinked system must characterise itself by the well defined value of β , i.e. it must have the well defined number of close cycles, such that the effective number of "descendants" per each junction is exactly 1. If it is not the case the Malthus's paradox arises. But the PMU is used not simply in order to cope the Malthus paradox; it renders possible to interpretate quantita-

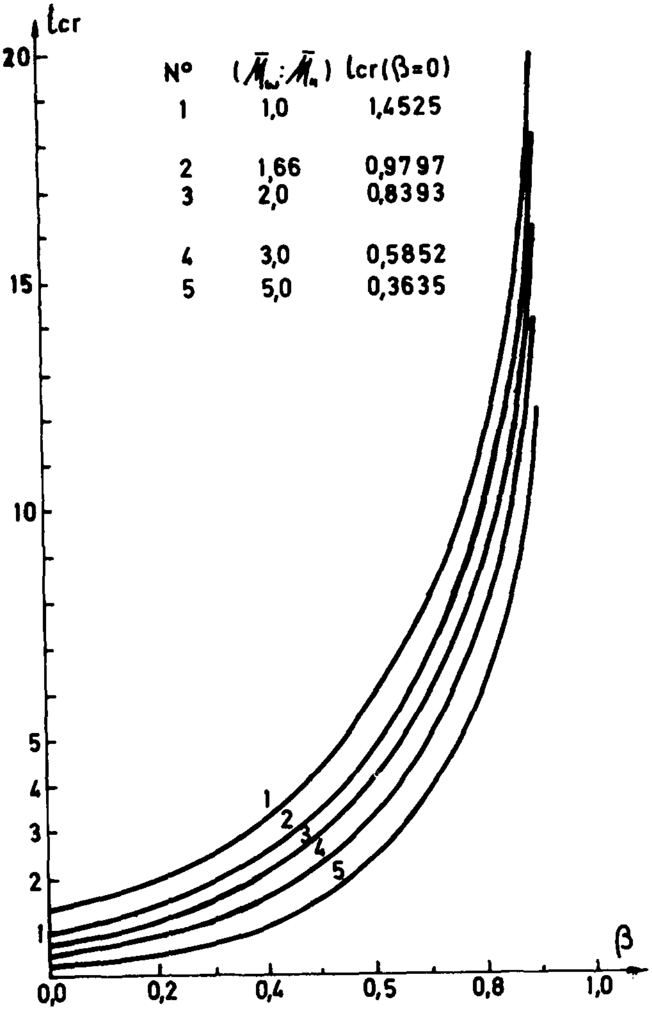

Fig.2. Critical crosslinking index, l_{cr}, vs. fraction of closed cycles, β, for different degrees of polydispersity, ($M_w:M_n$). The curve No.1 corresponds to monodisperse case, No.3 - to Flory's distribution of primary macromolecules.

tively the structure of a macroscopically uniform system, namely to calculate the appropriate value of b for any given value of crosslinking index, l. One obtains from PMU the following equation for b (eq.(10)) which may be easily solved numerically if f_0 and f_1, being themselves functions of l, are known :

$$(1-\beta)^3 + \left[3 - \frac{4(1-f_0)}{l}\right](1-\beta)^2 + \left[\frac{f_1^2}{l^2} - \frac{4(1-f_0)}{l}\right](1-\beta) + \frac{3f_1^2}{l^2} = 0 \qquad (10)$$

For randomly crosslinked systems (i.e. for Poissonian $f_0(l)$ and $f_1(l)$) one obtains $\beta=0$ in and below the gel point (Fig.3).

(N.b. There is a misprint in the equation expressing PMU , equivalent to the above eq. (10), in the work KLONOWSKI 1979c - the coefficient staying there before the term $(1-\beta)^2$ in the eq. [55] ought not to be squared.)

In developing the theory it is implicitly assumed that the same rules for the cyclization hold both for the gel and the sol, i.e. our b is a mean value for the whole system. It does not mean, however that in the presented theory the cyclization in the gel and in the sol is actually the same. The sol is composed mainly of uncrosslinked primary macromolecules, dimers and aggregates of low molecular weights; so, in the sol there is only a small fraction of all junctions present in the whole system and thus only a small fraction of all cycles. Of course cyclization is physically necessary only for gel. Nevertheless, in reality some cycles do occur also in sol. Thus another simple assumption, namely that there is no cyclization in sol, seems to be also an oversim-

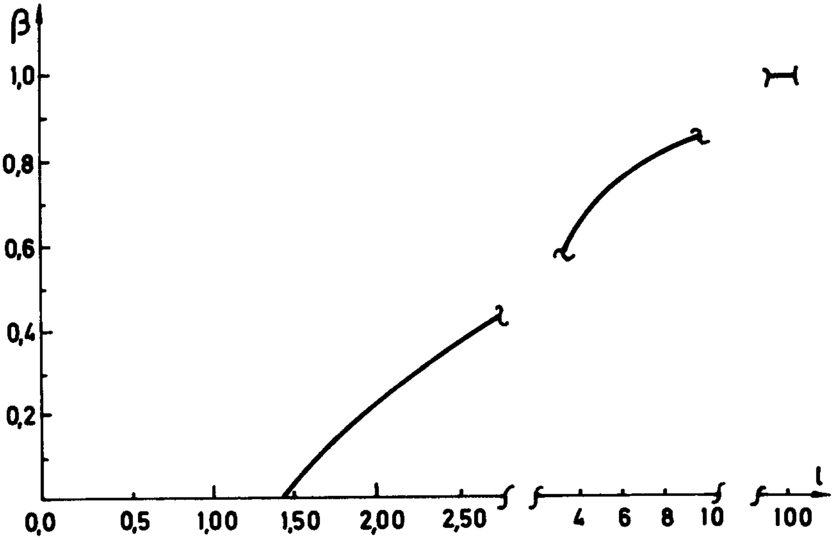

Fig.3. Fraction of closed cycles, β , found from the principle of macroscopic uniformity for monodisperse random system (i.e. with Poissonian f_0 and f_1, eqs.(4-5))

plification, which may lead to errors comparable with those produced by the assumption of the same β for the whole system. The theory in which this problem is taken into account more precisely is now under development. In the case of crosslinking of preexisting linear macromolecules the spatial non-uniformity of the system is not very pronounced even in the gel point. So, the principle of macroscopic uniformity ought to be well applicable to these systems (DE GENNES 1980).

If one assumes that β is independent of l, than the gel point (determined from eq.(9)) for greater values of b moves towards greater l and the reduced crosslinking density, L , behaves asymptotically as $(1-\beta)l$. If, however, the PMU is taken into account and β is changed appropriately when l increases, then the critical value , $L=L_{cr}=2$, is shown to be simultanously the maximal one (Fig.4). This way the new criterion for the gel point together with PMU give a new principle - the principle of the maximum of the reduced crosslinking densit in the gel point.

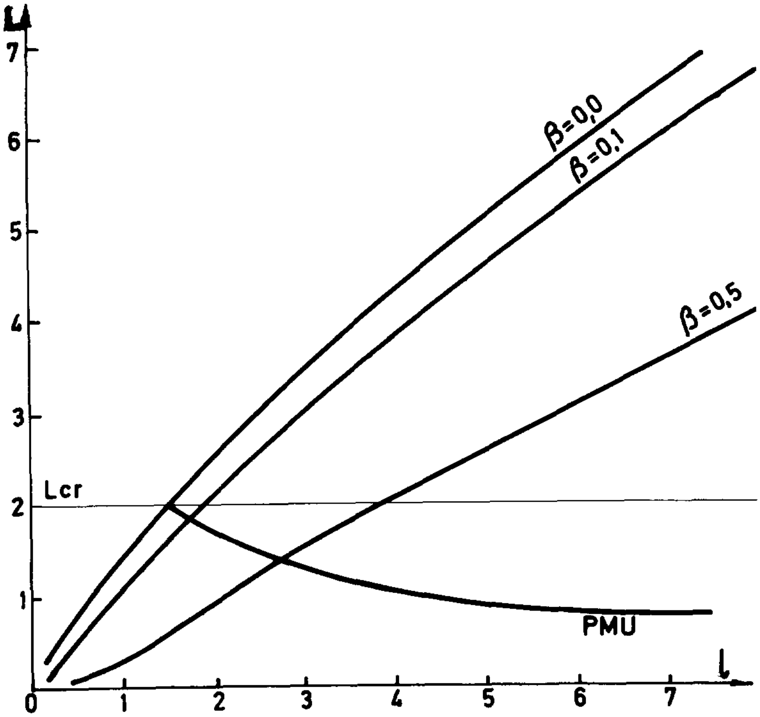

Fig.4. Dependance of the reduced crosslinking density, L, on the crosslinking index, l , for the different assumed constant values of β (indicated on the curves) and with PMU taken into account (the curve marked PMU, which below the gel point is identical with the curve for $\beta=0$) The intersections with the line L=2 indicate gel points.

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