Cross-Link Dimensions in Gelatin–Poly(acrylamide) Interpenetrating Hydrogel Networks†

P. R. CHATTERJI

Division of Organic Coatings & Polymers, Indian Institute of Chemical Technology, Hyderabad 500 007, India

Received September 14, 1990;
Revised Manuscript Received February 19, 1991

The average network dimensions of a cross-linked matrix (i.e., average dimension between two neighboring cross-link junctions) determine the swelling and mechanical behavior of the network.[1,2] Hence, it is possible in turn to deduce the network characteristics by monitoring the swelling and mechanical properties.[3,4] Flory and Rehner[5] have correlated the swelling behavior of a cross-linked matrix to M_x, the average molecular weight between two neighboring cross-link points:

$$-\ln(1-\upsilon_2) - \upsilon_2 - \chi_{12}\upsilon_2^2 = (\rho/M_x)V_s C_x^{2/3}(\upsilon_2^{1/3} - \upsilon_2/2) \quad (1)$$

where υ_2 is the volume fraction of the polymer in the gel swollen to equilibrium, χ_{12} is the polymer–solvent interaction parameter, ρ is the density of the solvent, υ_s is the molar volume of the solvent, M_x is the average molecular weight between cross-links, C_x is the concentration of the polymer expressed as the volume fraction in the cross-linked state.

For systems with a very high swelling ratio (i.e., very low υ_2 values), this expression can be simplified[5] to

$$q^{5/3} = M_x(\rho V_s^{-1})(1/2 - \chi_{12})C_x^{-2/3} \quad (2)$$

Poh et al.[6] and Adachi et al.[7] have used these equations to explain the swelling behavior of solution cross-linked natural rubber networks.

We have attempted to estimate the cross-link dimension in a series of gelatin–poly(acrylamide) full and semi interpenetrating polymer networks (IPNs) by using these equations. The details of the preparation of these gels have been reported in detail elsewhere.[8,9] In brief, the process involves the in situ polymerization of an acrylamide–bis(acrylamide) mixture in a gelatin medium followed by the cross-linking of the gelatin chains by soaking in 1% aqueous glutaraldehyde solution. This yields interpenetrating networks, with both macromolecules independently cross-linked. Semi-IPNs of the (PAam–Gelx) type and [PAamx–Gel] type were also prepared. See Table I for abbreviations used. Swelling studies were performed by immersing dry blocks in distilled water. The swollen gels were then lifted, patted dry, and weighed at definite intervals until equilibrium was achieved. From swollen and dry weights, the swelling ratios were calculated. The initial and final dimensions of the blocks were also measured in each case.

White[10] has reported earlier the pore size values of cross-linked poly(acrylamide) gels as a function of concentration. The computation of these average pore size values (ϕ) involved the use of the permeability coefficient (K_s) and specific water content (s) according to the equation

$$\phi = \frac{[8K_s]^{1/2}}{s} \quad (3)$$

In Figure 1, we have superimposed the M_x values we derived over White's pore size values for the corresponding concentrations. The swelling ratio (q) and the volume fraction (V_2) of the polymer in the hydrogel swollen to equilibrium were calculated as reported in the literature.[11] The polymer–solvent interaction parameter for cross-

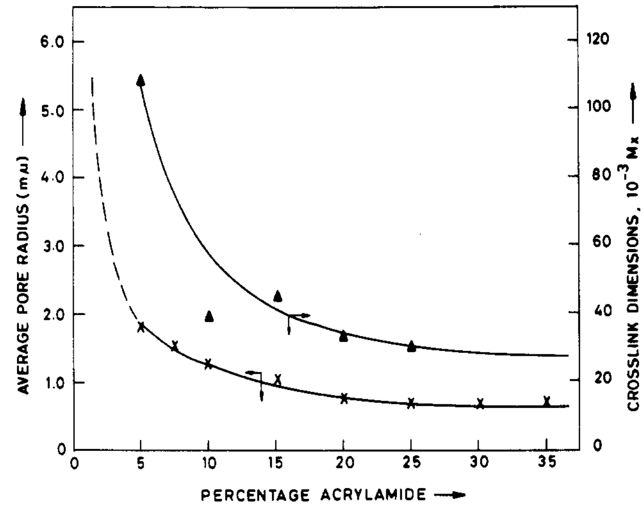

Figure 1. Average pore radii (from ref 7) and cross-link dimensions of poly(acrylamide) gels as a function of acrylamide concentration. (▲) M_x values from swelling data, (×) average pore radius.

Table I
Abbreviations and Symbols Used

Gelx–PAamx	full IPN where gelatin and poly(acrylamide) are fully independently cross-linked with glutaraldehyde and bis(acrylamide), respectively
Gelx–PAam	semi-IPN where only gelatin is cross-linked
Gelx–PAamx	semi-IPN where only poly(acrylamide) is cross-linked
SIPN	semiinterpenetrating polymer network, where only one component is cross-linked
FIPN	fully interpenetrating polymer network, where both components are independently cross-linked

Table II

no.	system		percentage (by weight) of PAam	percentage (by weight) of gelatin	$10^{-3}M_x$
I	PAamx		5		107.90
			10		39.22
			15	nil	45.50
			20		33.21
			25		30.00
II	full IPNs [PAamx–Gelx]	A	5	5	0.652
			5	10	1.496
			5	15	1.177
			5	20	1.713
			5	25	1.045
		B	10	5	2.71
			15	5	4.05
			20	5	
			25	5	4.83
III	semi-IPNs (PAam–Gelx)		5	5	0.326
			5	10	1.586
			5	15	1.028
			5	20	0.724
			5	25	0.945
IV	semi-IPNs (PAamx–Gel)	A	5	5	13.95
			5	10	10.90
			5	15	7.1
			5	20	1.2
			5	20	1.2
			5	25	1.6
		B	5	5	14.21
			10	5	13.7
			15	5	13.8
			20	5	10.2
			25	5	10.9

† IICT Communication No. 2518.

0024-9297/91/2224-4214$02.50/0

linked poly(acrylamide)–water systems has been reported to be 0.48.[12] We have used this value in our calculations.

The M_x values calculated from the equilibrium swelling data, given in Table II, provide significant insight into the molecular structure of a poly(acrylamide) network embedded in a gelatin matrix. Taking the M_x values of PAamx as the reference scale, the following inferences could be drawn. The full IPNs and semi-IPNs, where gelatin is in the cross-linked state and in excess over poly(acrylamide) content, have the lowest M_x values. In fact, the PAam–Gelx IPN system with low PAam content has M_x values comparable to the corresponding PAamx–Gelx system. There could be two explicit reasons for this. Primarily, the formation of collagen-like folds must necessarily bring the gelatin chains to close proximity. The other reason is the finite length of the glutaraldehyde oligomers, the cross-linker for gelatin.

The M_x values of PAamx–Gel semi-IPN systems are equally informative. The values are, in general, lower than those of pure PAamx gels even at low gelatin contents. With an increase in gelatin content, there is a steep fall. This could be due to the collagen folds getting reinforced by the overlapping poly(acrylamide) network, thus effectively reducing the M_x values.

References and Notes

(1) Baselga, J.; Hernandez, F. I.; Pierola, I. F.; Llorente, M. A. *Macromolecules* **1987**, *20*, 3060.
(2) Bansil, R.; Gupta, M. K. *Ferroelectrics* **1980**, *30*, 67.
(3) Geissler, E.; Hecht, A.-m.; Horkay, E.; Zrinyi, M. *Macromolecules* **1988**, *21*, 2594.
(4) Gnanuou, Y.; Hild, G.; Rempp, P. *Macromolecules* **1987**, *20*, 1662.
(5) Flory, P. J.; Rehner, J., Jr. *J. Chem. Phys.* **1943**, *11*, 521.
(6) Poh, B. T.; Adachi, K.; Nakamoto, T.; Kotaka, T. *Macromolecules* **1989**, *20*, 2563.
(7) Adachi, K.; Nakatomo, T.; Kotaka, T. *Macromolecules* **1989**, *22*, 3106.
(8) Kaur, H.; Chatterji, P. R. *Macromolecules* **1990**, *23*, 4868.
(9) Chatterji, P. R. *J. Appl. Polym. Sci.* **1990**, *40*, 401.
(10) White, M. L. *J. Phys. Chem.* **1960**, *40*, 401.
(11) Kudela, V. *Hydrogels in Encycl. Polym. Sci. & Engg.*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; John Wiley & Sons: New York, 1987; Vol. 7, p 783.
(12) Ilavasky, M.; Hrouz, J.; Stejskal, J.; Bouchal, K. *Macromolecules* **1984**, *17*, 2868.