Polymer Bulletin 13, 91-96 (1985)

Polymer Bulletin

Modelling

Importance of Junction Functionality in Highly Crosslinked Polymers

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Summary

A modification of a theoretical model for the determination of the number average molecular weight between crosslinks, $\overline{M}_c$, is presented for the case of multifunctional junction functionalities in highly crosslinked, macromolecular systems.

Determination of $\overline{M}_c$ of Highly Crosslinked Polymers

The molecular weight between crosslinks, $\overline{M}_c$, is of primary interest in the analysis of the crosslinked structure of polymeric networks. In a recent review [MARK, 1982] several methods of determining $\overline{M}_c$ and related parameters for polymer networks were discussed. The two main techniques for determination of $\overline{M}_c$ are equilibrium swelling experiments and tensile rubber elasticity experiments.

A primary technique for the determination of $\overline{M}_c$ involves experimental determination of the equilibrium polymer volume fraction of the macromolecular network in a thermodynamically good solvent at a specific temperature [PEPPAS and MERRILL, 1976] and knowledge of the thermodynamic interaction parameter, χ, for the polymer/solvent pair. This information allows the application of the FLORY-REHNER (1943) analysis with the determination of $\overline{M}_c$ according to equation (1).

$$\frac{1}{\overline{M}_c} = \frac{2}{\overline{M}_n} - \frac{(\bar{v}/V_1)[\ln(1 - v_{2,s}) + v_{2,s} + \chi\, v_{2,s}^2]}{[v_{2,s}^{1/3} - \frac{v_{2,s}}{2}]} \tag{1}$$

Here $\overline{M}_n$ is the number average molecular weight of the original chains before crosslinking, $v_{2,s}$ is the polymer volume fraction of the swollen network, χ is the thermodynamic interaction parameter of the polymer/solvent pair at $v_{2,s}$ and T, $\bar{v}$ is the specific volume of the polymer, and V_1 is the molar volume of the swelling agent.

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The previous equation applies to swollen networks of crosslinked polymers where the crosslinks were introduced in the solid state. For polymers crosslinked in solution, equation (1) is modified to give equation (2) according to PEPPAS and MERRILL (1976).

$$\frac{1}{\overline{M}_c} = \frac{2}{\overline{M}_n} - \frac{(\bar{v}/V_1)[\ln(1 - v_{2,s}) + v_{2,s} + \chi\, v_{2,s}^2]}{v_{2,r}[(\frac{v_{2,s}}{v_{2,r}})^{1/3} - \frac{1}{2}(\frac{v_{2,s}}{v_{2,r}})]} \qquad (2)$$

In this equation $v_{2,r}$ represents the polymer volume fraction of the gel immediately after crosslinking but before swelling.

Equations (1) and (2) were derived with the assumption of a Gaussian chain distribution in the network. A Gaussian distribution usually requires that the number of bond vectors exceed 100. There are, however, many situations of highly crosslinked networks, where this assumption is not valid. These highly crosslinked macromolecular networks must be analyzed using newer non-Gaussian distribution models. Many non-Gaussian distribution models exist today including models by FIXMAN and ALKEN (1973), KOVAC (1978), PEPPAS and LUCHT (1979), and GALLI and BRUMAGE (1983).

The previously derived non-Gaussian distribution model of PEPPAS and LUCHT (1979) is given in equation (3).

$$\frac{1}{\overline{M}_c} = \frac{2}{\overline{M}_n} - \frac{(\bar{v}/V_1)[\ln(1-v_{2,s}) + v_{2,s} + \chi\, v_{2,s}^2][1-\frac{1}{N}v_{2,s}^{2/3}]^3}{[v_{2,s}^{1/3} - \frac{1}{2}v_{2,s}][1 + \frac{1}{N}v_{2,s}^{1/3}]^2} \qquad (3)$$

where N is defined as

$$N = \frac{\lambda\, \overline{M}_c}{\overline{M}_r} \qquad (4)$$

Here $\overline{M}_r$ is the molecular weight of the repeating unit, λ is the number of links per repeating unit, and the other parameters are as defined before.

A similar expression has also been developed (PEPPAS *et al.*, 1983) for the case of crosslinking in solution and it is given by equation (5).

$$\frac{1}{\overline{M}_c} = \frac{2}{\overline{M}_n} - \frac{(\bar{v}/V_1)[\ln(1-v_{2,s}) + v_{2,s} + \chi\, v_{2,s}^2][1-\frac{1}{N}v_{2,s}^{2/3}]^3}{v_{2,r}[(\frac{v_{2,s}}{v_{2,r}})^{1/3} - \frac{1}{2}(\frac{v_{2,s}}{v_{2,r}})][1 + \frac{1}{N}(\frac{v_{2,s}}{v_{2,r}})^{1/3}]^2} \qquad (5)$$

Effect of Junction Functionality

In the derivations of equations (1) and (3) there was an underlying assumption that the networks, whether Gaussian or non-Gaussian, could be characterized by junction-functionalities of four. There are, however, many polymers or macromolecular networks crosslinked with multifunctional crosslinking agents. These polymers or macromolecular networks exhibit junction functionalities greater than four and therefore functionality may become an important parameter in the determination of the number average molecular weight between crosslinks using the equilibrium swelling technique.

Inclusion of the functionality parameters into equation (3) yields equation (6).

$$\frac{1}{\overline{M}_c} = \frac{2}{\overline{M}_n} - \frac{(\bar{v}/V_1)[\ln(1-v_{2,s}) + v_{2,s} + \chi\, v_{2,s}^2][1 - \frac{1}{N}\, v_{2,s}^{2/3}]^3}{A_\phi[v_{2,s}^{1/3} - \omega\, v_{2,s}][1 + \frac{1}{N}\, v_{2,s}^{1/3}]^2} \qquad (6)$$

where ω is defined as

$$\omega = \frac{2}{\phi} \qquad (7)$$

Here ϕ is defined as the average functionality. The structural factor, A_ϕ, depends on how much the swelling deformation deviates from the affine limit. The extent of the deviation depends on the magnitude of the crosslink fluctuations. Theoretically and in the limit of phantom networks, A_ϕ is defined as

$$A_\phi = 1 - \frac{2}{\phi} \qquad (8)$$

For an affine network, a network where the displacement of the crosslinks due to stress is a simple linear function of the macroscopic strain applied on the network, FLORY (1979) shows that A_ϕ approaches one. In general, A_ϕ varies between

$$1 > A_\phi > 1 - \frac{2}{\phi} \tag{9}$$

and can be determined either theoretically (FLORY, 1976; FLORY, 1977; ERMAN and FLORY, 1978) or experimentally from data of model networks (MARK, 1979; MARK, 1982; LLORENTE and MARK, 1979). For coal networks and other polymeric networks which swell moderately, A_ϕ should be close to one.

Predictions of Model

Equation (6) yields information on the importance of the junction functionality parameter as shown in Figure 1. In this analysis, the thermodynamic interaction parameter, χ, was assumed to be 0.30, the polymer volume fraction at equilibrium, $v_{2,s}$ was 0.50, the molecular weight of the repeating unit, M_r, was 170, and the functionality was allowed to vary from 2 to 20. The graph shows that near the functionality of four, the molecular weight between crosslinks undergoes the greatest variation. As the functionality continues to increase the molecular weight between crosslinks levels off.

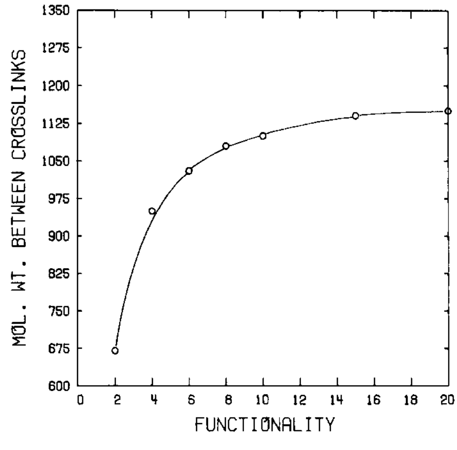

Figure 1. Molecular Weight Between Crosslinks as a Function of the Functionality Parameter for $\chi = 0.30$, $v_{2,s} = 0.50$, and $M_r = 170$.

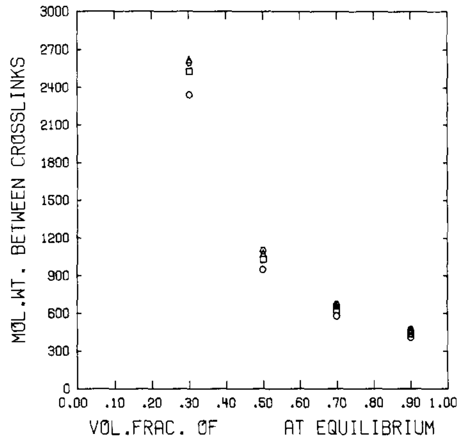

Figure 2. Molecular Weight Between Crosslinks as a Function of the Volume Fraction of the Polymer at Equilibrium, $v_{2,s}$, for Functionalities of $\phi = 4.0$ (o), $\phi = 6.0$ (□), $\phi = 8.0$ (∇), and $\phi = 10.0$ (⬡).

Figure 2 shows that for volume fraction of polymer at equilibrium of 0.3 there exists the largest dependence of molecular weight between crosslinks on functionality. This range of the volume fraction of polymer at equilibrium is typical of those values obtained experimentally for highly crosslinked systems. These results indicate the importance of the functionality parameter in the determination of the molecular weight between crosslinks.

Acknowledgements

This work was supported by a grant from the Department of Energy, No. DE-PG22-83PC-60792.

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Accepted January 23, 1985