

The constant  $\gamma$  has a nature of modulus, and determines the deviation of the Gaylord-Douglas model from the phantom model. For  $\gamma \rightarrow 0$ , Equation 10 reduces to the phantom model. Moreover,  $\gamma$  can vary with swelling ratio and also the synthesizing conditions under which the dry network has been formed.

Regardless of what models are employed to physically explain the macroscopic properties of a polymer network, the only parameters that directly relate the macroscopic deformation of a network to its structural characteristics are the density of elastically active chains,  $\nu/V_o$ , and the density of crosslinking points,  $N_c/V_o$ . These two terms are both connected to each other by:

$$N_c/V_o = (2/f)\nu/V_o \quad 11$$

with  $f$  representing the functionality of the crosslinking units. Hence, for an ideal network, the defining structural parameters are the nature of the crosslinking points—reflected by  $f$ —and the degree of crosslinking—determined as either  $\nu/V_o$  or  $N_c/V_o$ . Other parameters that appear in these models, such as  $\kappa$ ,  $\zeta$  or  $\gamma$  remain mostly empirical, since independent information on actual status of the crosslinking points and constraints is hard to directly obtain in the molecular state. In terms of network stiffness, the elastic constant  $k_B T \nu/V_o$  is equivalent to the shear modulus of the dry network,  $G_o$ . By defining  $M_c$  as the number average of molecular weight of the chains between two adjacent crosslinking points, the shear modulus of a dry network can be determined from  $M_c$  and the dry network density,  $\rho$ , at any given temperature,  $T$ :

$$G_o = \rho RT/M_c \quad 12$$

where  $R$  is the universal gas constant. In Equation 12,  $M_c$  is the only network parameter and can be controlled through the crosslinking process. As the degree of crosslinking increases, the molecular weight between two adjacent crosslink points decreases resulting in an increase in  $\rho/M_c$  and increase in network modulus.

## Swelling of Polymer Networks

In the previous section, various expressions in which macroscopic deformations are related to the applied stresses have been presented. The source of dimensional deformation in all those theories is assumed to be the external stresses; with linear extension ratios are based on the dimension of the dry network. However, a crosslinked network can also undergo a dimensional deformation in the presence of a swelling agent while there is no external force is applied (swelling). The driving force for this dimension change is the interaction between solvent molecules and the long polymer chains of the network. As the network swells, the configurational entropy of the network decreases while the configurational entropy of the mixture increases. Eventually, equilibrium is reached at which the network is equilibrated in the swelling agent and its degree of swelling remains unchanged. Thermodynamically, this hypotheses has been expressed by Frenkel, Flory and Rehner as the contribution of two additive free energy terms to the overall free energy of the system: (1) the elastic free energy,  $\Delta F_{el}$ , and (2) the mixing free energy,  $\Delta F_{mix}$ :

$$\Delta F = \Delta F_{el} + \Delta F_{mix} \quad 13$$