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Model Networks

Characterization of Model Networks Containing Both Trifunctional and Tetrafunctional Junctions

J. P. Queslel and J. E. Mark

Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, Ohio 45221, USA

Summary

Expressions for the number density of junctions μ and the cycle rank ξ of model networks having a mixture of trifunctional and tetrafunctional junctions are obtained by simple topological arguments. The results are consistent with those derived by making use of an average junction functionality.

Introduction

Model networks, i.e. those prepared in such a way that the number and functionality of the cross-links are reliably known, have been extensively used to test the molecular theories of rubberlike elasticity (1-3). Recently, networks formed with a mixture of trifunctional and tetrafunctional junctions were investigated (4,5), and it is therefore now useful to predict the affine and phantom moduli of such networks.

Theory

As shown by Flory (6), the shear modulus exhibited by a phantom network is given by

$$f_{ph} = \xi RT \qquad (1)$$

where R is the gas constant, T the absolute temperature, and ξ the cycle rank density (which is the difference between the number density of effective chains ν and junctions μ) (6,7):

$$\xi = \nu - \mu + 1 \simeq \nu - \mu \qquad (2)$$

For model networks formed by cross-linking end-reactive chains of number-average molecular weight M_n with ϕ-functional agents, the molecular weight between cross-linking sites is $M_c = M_n$, and the functionality of the junctions is ϕ. Since the number 2ν of chain ends equals the number $\phi\mu$ of reactive groups on the end-linker molecules

$$\mu/\nu = 2/\phi \tag{3}$$

Therefore

$$f_{ph} = (1 - 2/\phi)\nu RT \tag{4}$$

For affine networks the shear modulus is

$$f_{aff} = \nu RT \tag{5}$$

where the number density of effective chains ν is given by

$$\nu = \rho/M_c \tag{6}$$

with ρ being the density.

A possible way to derive the expression for the number density of cross-linking points μ of a model network formed with a mixture of trifunctional and tetrafunctional junctions is to build a network in which, in a first stage, only the trifunctional junctions are present. To prepare this topology to receive tetrafunctional junctions, chains of molecular weight $2M_c$ are included in the network. These chains are then coupled two at a time at their centers by tetrafunctional bridges. The final network is characterized by its number density of trifunctional and tetrafunctional junctions, $\mu(\phi=3)$ and $\mu(\phi=4)$, respectively, and these can be expressed as mol fractions of the total number of junctions μ by

$$\mu(\phi=3) = x\mu \tag{7}$$

$$\mu(\phi=4) = (1 - x)\mu \tag{8}$$

Perfect trifunctional and tetrafunctional networks correspond to $x = 1$ and $x = 0$, respectively.

In the first-stage network defined above, there are $2\mu(\phi=4) = 2(1 - x)\mu$ chains of molecular weight $2M_c$. Since this network is trifunctional,

$$\mu(\phi=3) = x\mu = 2\nu_o/3 \tag{9}$$

when ν_o is the total number of chains of molecular weight M_c or $2M_c$. In unit volume, there are ρ/M_c segments of molecular weight M_c. Some chains are formed with one segment and others with two. The number of chains ν_o is obtained by subtracting unity from ρ/M_c for each chain composed of two segments. Therefore

$$\nu_o = \rho/M_c - 2(1 - x)\mu \tag{10}$$

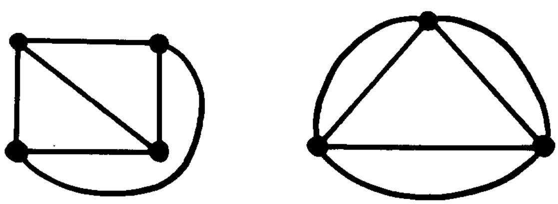
As a check, it will be seen that if $x = 1$, $\nu_o = \rho/M_c$ and if $x = 0$, $\nu_o = \rho/2M_c$ (since $\mu = \nu_o/2$). Introducing expression 10 in equation 9 leads (after rearrangement) to

$$\mu = \left[2/(4 - x)\right]\rho/M_c \tag{11}$$

$$\mu/\nu = 2/(4 - x) \tag{12}$$

where ν is the number density of chains in the final network, i.e., ρ/M_c. As expected, $\mu/\nu = 2/3$ and $1/2$, respectively, for purely trifunctional and tetrafunctional networks.

Another way to obtain this result is to construct a trifunctional network of molecular weight M_c between cross-links, and, for a specified number of times, let three tetrafunctional cross-links replace four trifunctional ones. This is shown schematically by the conversion 1→2 of Figure 1. For the first-stage trifunctional network



1 2

Figure 1. Simple six-segment networks consisting of (1) four trifunctional junctions or (2) three tetrafunctional junctions.

$$\mu = 2\rho/3M_c \tag{13}$$

where μ consists of $\mu(\phi=3)$ junctions (which will exist as such in the final network), and μ_o trifunctional junctions (which will be substituted to give $\mu(\phi=4)$ tetrafunctional cross-links). The quantity μ_o is easily seen to be

$$\mu_o = (4/3)\mu(\phi=4) \tag{14}$$

Therefore

$$\mu_1 = \mu(\phi=3) + (4/3)\mu(\phi=4) = 2\rho/3M_c \qquad (15)$$

Equation 11 is then obtained by making using of equations 7 and 8.

A number average functionality can be defined by

$$\phi_{av} = 3x + 4(1 - x) = 4 - x \qquad (16)$$

use of this expression in equation 12 gives

$$\mu/\nu = 2/\phi_{av} \qquad (17)$$

Therefore, the relationship between the number of network chains and the number of junctions (equation 3) remains valid for mixed junction networks so long as a number-average junction functionality is employed.

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