Structure and Properties of Highly Cross-Linked Polymers

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Tetrafunctional cross-linked polymers can generally be divided into three types, as shown in Figure 1, assuming that $\bar{n}_c$ is the chain length of a crosslinkage, and $\bar{n}_m$ is that between two cross-linkages. Figure 1a is considered to be the most general case for tetrafunctional cross-linked polymers. Z is the index showing the functionality of the cross-linking agent; $Z=2$ in this case.

$Z=3$ in the case of $\bar{n}_m \approx \bar{n}_c$, as shown in Figure 1b and Z will approach unity as $\bar{n}_m < \bar{n}_c$, *i.e.,* as the cross-linked polymer becomes more tight, as shown in Figure 1c.

It is well known that eq 1 is applicable for the rubbery region of ideally Affine deformed network polymers.[1]

$$G=\frac{f}{\alpha-\alpha^{-2}}=\nu(0)RT \qquad (1)$$

Here, G is the shear modulus, f the stress at relative length, and $\nu(0)$ the initial number of effective network chains per cubic centimeter.

R and T are, respectively, the gas constant and the absolute temperature.

For tightly cross-linked polymers and their special structures,[2] eq 1 should be modified to eq 2.

$$f=\frac{\overline{r^2}}{\overline{r_0^2}}\nu(0)RT(\alpha-\alpha^{-2}) \qquad (2)$$

Here, $\overline{r^2}$ is the mean-square end-to-end separation of a chain in the isotropic network, and $\overline{r_0^2}$ is the mean-square end-to-end separation of a chain in the absence of network constraint.

Equation 3 was recently suggested by Smith for such tightly cross-linked polymers.[3]

$$\frac{\nu(0)RT}{G}=\frac{1}{\Phi}-\frac{6\bar{C}_n}{5q^2 n} \qquad (3)$$

Here Φ is the front factor, $\Phi=\overline{r^2}/\overline{r_0^2}$. $\bar{C}_n$ and q are values which will be shown by the following relations.

For a free chain having n backbone bonds of length l, eq 4 and 5 can be employed:
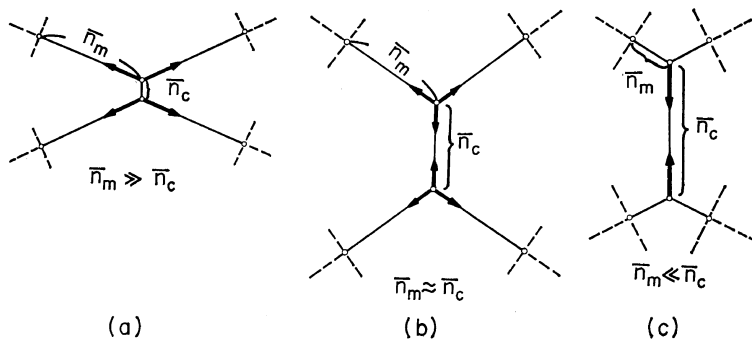

Figure 1. (a) Cross-linking mechanism for $\bar{n}_m > \bar{n}_c$; (b) cross-linking mechanism for $\bar{n}_m \approx \bar{n}_c$; (c) cross-linking mechanism for $\bar{n}_m < \bar{n}_c$.

$$\overline{r_0{}^2} = C_n n l^2 \qquad (4)$$

$$r_m = q n l \qquad (5)$$

where the characteristic ratio[4] C_n is a function of n when n is small. For example, C_n for poly(oxyethylene) essentially equals its asymptotic value C_∞ when $n=50$, but C_n decreases rapidly with a decrease of n when n is less than about 25.

For ethyl acrylate—dimethacrylate networks, C_n is closely represented by eq 6.

$$C_n = n^{0.57} \qquad \text{for} \quad 1 \leqslant n \leqslant 20 \qquad (6)$$

q is, in general, a dimensionless factor determined by bond angles and lengths.

As it is very clear that eq 1 is not applicable for such tightly cross-linked polymers, the value of $\nu(0)$ obtained by eq 1 is now designated as $\nu_M(0)$, which means the apparent value for these polymers. Therefore, from eq 1 and 3, eq 7 is derived.

$$\frac{\nu_{\text{real}}(0)}{\nu_M(0)} = \frac{1}{\varPhi} - \frac{6\bar{C}_n}{5q^2 n} \qquad (7)$$

Where, $\nu_{\text{real}}(0)$ is the real cross-linking density of such tightly cross-linked polymers.

For a chain-containing only carbon—carbon single bonds, q equals 0.83. Substituting this value of q and eq 6 into eq 7, eq 8 is obtained.

$$\frac{\nu_{\text{real}}(0)}{\nu_M(0)} = \frac{1}{\varPhi} - \frac{6}{5(0.83)^2 n^{0.43}} \qquad (8)$$

Here, $\varPhi = 0.5$ is used in eq 8 for those tightly cross-linked polymers whose polymerization degree, between two cross-linkages, is $n = 10$—20.[3]

For measuring the cross-linking density of amorphous polymers, there are in general two kind of methods. One is based upon eq 1, which is not applicable for tightly cross-linked polymers, and the other uses the swelling method derived by Flory and Rehner.[5] The cross-linking density obtained by the latter is signified as $\nu_S(0)$.

The relation between $\nu_M(0)$ and $\nu_S(0)$ for vulcanized natural rubber, is depicted in Figure 2. From this figure, it will be observed that $\nu_M(0)$ is larger than $\nu_S(0)$ below a certain point (for example, $\nu_M(0) \approx 4.2 \times 10^{-4}$ mol/cc for natural rubber vulcanizates), and once over that point, $\nu_M(0)$ is smaller than $\nu_S(0)$, independent of the
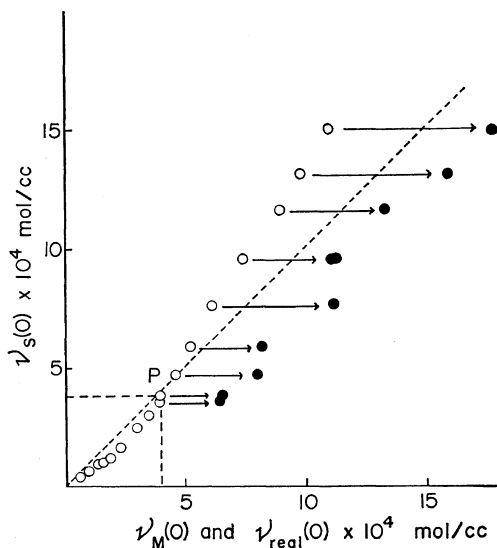

Figure 2. The relation of $\nu_M(0)$ vs. $\nu_S(0)$ and $\nu_{\text{real}}(0)$ vs. $\nu_S(0)$ for natural rubber vulcanizates: ○, $\nu_M(0)$ vs. $\nu_S(0)$; ●, $\nu_{\text{real}}(0)$ vs. $\nu_S(0)$.

kind of polymers and solvents used for the swelling measurement.

Hereafter the cross point between the curve and the straight line of slope=1 is called P.

The fact that $\nu_M(0)$ is larger than $\nu_S(0)$ in the range where the cross-linking density $\nu(0)$ is lower than P as seen in Figure 2 is considered to be due to $\nu_M(0)$, which usually involves a number of entanglements which are surrounded with the real cross-linkages and then regarded as the primary bonds[6] and strong dipole groups[7] of the apparent primary bonds. Some of these semiprimary bonds will probably not contribute to $\nu_S(0)$.

The reason why it will be $\nu_S(0) > \nu_M(0)$ in the range of $\nu(0) > P$, however, remained unsolved in our previous report.[6] By using the value of $\nu_{\text{real}}(0)$ from eq 8 instead of $\nu_M(0)$ for tightly cross-linked polymers $(\nu(0) > P)$, the relation between $\nu_{\text{real}}(0)$ and $\nu_S(0)$ for natural rubber vulcanizates was depicted as shown in Figure 2. As is clearly seen from this result, the tendency of $\nu_M(0) > \nu_S(0)$ was observed even in the range of $\nu(0) > P$: the reason was satisfactorily explained in the case of $\nu(0) < P$ described above.

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