The Effect of Cross-Link Mobility and Chain Interdependence on the Photoelastic Behavior of A Simple Polymeric Network Model

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There have been several recent investigations[2-4] into the effect of cross-link mobility and the interdependence of network chains on the elastic properties of polymeric networks. These studies start with a common model for a simple network system consisting of f chains of equal contour length, emanating from a central junction point, which is assumed to be mobile while the other end of each chain is constrained to deform affinely. The results indicate that the number of "elastically effective chains" is $(f - 1)$, in agreement with the analysis of the viscoelastic behavior of a monodisperse four-chain system.[5] In this paper, we will recalculate the elasticity of the above system for the case of monodisperse non-Gaussian chains, using a different approach from previous calculations, and will then extend the method to the birefringence calculation for the same system. We will find that in both the elastic and photoelastic behavior, the mobility of an internal cross-link reduces the number of "effective chains" by one and that the number of links in these "effective chains" is different for the elasticity and birefringence calculations.

Theory

We consider a simple network consisting of f chains emanating from a central junction point having coordinates (x_0, y_0, z_0), with the other end of the ith chain having coordinates (x_i, y_i, z_i). Using the leading correction terms to the Gaussian approximation, the probability density function for the ith chain is[6]

$$W(\mathbf{r}_{0i}) = \left[\frac{\beta_i^2}{\pi}\right]^{3/2} e^{-\beta_i^2 r_{0i}^2} \times \left\{1 - \frac{3}{4N} + \frac{\beta_i^2 r_{0i}^2}{N} - \frac{\beta_i^4}{5N} r_{0i}^4\right\} \quad (1)$$

where $\mathbf{r}_{0i} = \mathbf{r}_0 - \mathbf{r}_i$, $\beta_i^2 = 3/(2Nb^2)$. The joint probability density of the system can be written as the product of the individual densities,

$$\Omega = \prod_{i=1}^{f} W(\mathbf{r}_{0i})$$

While it is possible to perform the following calculation for a system of polydisperse chains in the Gaussian approximation,[7] the mathematics become prohibitive for the non-Gaussian case and so we will only consider a system of non-Gaussian chains of equal contour length here. The entropy of this system is given by the Boltzmann relation $S = k \ln \Omega$. We now average the entropy of the system in the deformed state subject to the condition that the central junction is completely mobile while the remaining cross-links deform affinely. Thus we can write

$$\frac{\langle S\rangle}{k} = -\beta^2 \left\langle \sum_{i=1}^{f} r_{0i}^2 \right\rangle + \frac{\beta^2}{N} \left\langle \sum_{i=1}^{f} r_{0i}^2 \right\rangle - \frac{\beta^4}{5N} \left\langle \sum_{i=1}^{f} r_{0i}^4 \right\rangle - const. \quad (2)$$

where $r_{0i}^2 = x_{0i}^2 + y_{0i}^2 + z_{0i}^2$, $x_{0i}^2 = (x_0 - \lambda_x x_i)^2$, λ_x is the deformation ratio in the x direction and

$$\left\langle \sum_{i=1}^{f} x_{0i}^2 \right\rangle = \int \sum_{i=1}^{f} x_{0i}^2 \Omega \, d\mathbf{r}_0 \, d\mathbf{r}_1 \ldots d\mathbf{r}_f \quad (3)$$

Averaging over $\mathbf{r}_0$ yields an expression which can be written in terms of x_{ij}, etc. We then transform the variables of integration from $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_f$ to $\mathbf{r}_1, \mathbf{r}_{12}, \ldots, \mathbf{r}_{1f}$. The Jacobian of this transformation is unity.

Completing the integration, we obtain

$$\left\langle \sum_{i=1}^{f} x_{0i}^2 \right\rangle = \frac{1}{2\beta^2} + \frac{\lambda_x^2 (f-1)}{2\beta^2} \quad (4a)$$

Evaluating other terms in eq 2 yields

$$\left\langle \sum_{i=1}^{f} x_{0i}^2 y_{0i}^2 \right\rangle = \frac{(\lambda_x^2 + \lambda_y^2)(f-1)}{4f\beta^4} + \frac{1}{4f\beta^4} + \frac{(f-1)^2}{4f\beta^4} (\lambda_x^2 \lambda_y^2) \quad (4b)$$

$$\left\langle \sum_{1=i}^{f} x_{0i}^4 \right\rangle = \frac{3}{4f\beta^4} + \frac{3(f-1)}{2f\beta^4} \lambda_x^2 + \frac{3(f-1)^2}{4f\beta^4} \lambda_x^4$$

with analogous expressions for the other terms in eq 2. Substituting back into eq 2 then yields

$$\frac{\langle S\rangle}{k} = \frac{-(f-1)}{2} [\lambda_x^2 + \lambda_y^2 + \lambda_z^2] + \frac{(f-1)}{N'} [\tfrac{1}{2}(\lambda_x^2 + \lambda_y^2 + \lambda_z^2) - \tfrac{3}{20}(\lambda_x^4 + \lambda_y^4 + \lambda_z^4) - \tfrac{1}{10}(\lambda_x^2\lambda_y^2 + \lambda_x^2\lambda_z^2 + \lambda_y^2\lambda_z^2)] \quad (5)$$

where $N' = Nf/(f-1)$. Equation 5 demonstrates that, elastically, the total number of links, Nf, is divided up among the number of "elastically effective chains", $(f-1)$. This is in agreement with a previous calculation.[3]

We can apply the preceding calculation directly to the calculation of the birefringence of the simple network system.

The polarizability difference of the ith chain in the network along the z and x axes can be expressed in our notation as[8]

$$\Delta\gamma_{0i} = \frac{2\beta_i^2(\zeta_1 - \zeta_2)}{5} \left\{\left[1 - \frac{2}{5N}\right][z_{0i}^2 - x_{0i}^2] + \frac{8\beta_i^2}{35N}[z_{0i}^4 - x_{0i}^4 + z_{0i}^2 y_{0i}^2 - x_{0i}^2 y_{0i}^2]\right\}$$

where ζ_1 and ζ_2 are the parallel and transverse link polarizabilities, respectively. The total average polarizability difference of the system is therefore

$$\langle\Delta\gamma\rangle = \frac{2\beta^2(\zeta_1 - \zeta_2)}{5} \left\{\left[1 - \frac{2}{5N}\right]\left[\left\langle \sum_{i=1}^{f} z_{0i}^2 \right\rangle - \left\langle \sum_{i=1}^{f} x_{0i}^2 \right\rangle\right] + \frac{8\beta^2}{35N}\left[\left\langle \sum_{i=1}^{f} z_{0i}^4 \right\rangle - \left\langle \sum_{i=1}^{f} x_{0i}^4 \right\rangle + \left\langle \sum_{i=1}^{f} z_{0i}^2 y_{0i}^2 \right\rangle - \left\langle \sum_{i=1}^{f} x_{0i}^2 y_{0i}^2 \right\rangle\right]\right\} \quad (6)$$

The result can immediately be written by comparison with eq 4 in the preceding calculation as

$$\langle\Delta\gamma\rangle = \frac{(f-1)(\zeta_1 - \zeta_2)}{5} [\lambda_z^2 - \lambda_x^2] + \frac{(f-1)(\zeta_1 - \zeta_2)}{5N'} \left[\frac{12}{35}(\lambda_z^4 - \lambda_x^4) + \frac{4}{35}(\lambda_y^2\lambda_z^2 - \lambda_x^2\lambda_y^2) - \frac{2}{5}\frac{(f-2)}{(f-1)}(\lambda_z^2 - \lambda_x^2)\right] \quad (7)$$

where $N' = Nf/(f-1)$.

Thus, while the number of chains which are "photoelastically or elastically effective" is $(f-1)$ in each case, the number of links in the "photoelastically effective chain" does not have the simple relationship found for the "elastically effective chain". This is indicated by the $(f-2)/(f-1)$ term in eq 7.

Conclusion

We can conclude that the effect of chain interdependence and cross-link mobility in this simple non-Gaussian network system is to reduce the number of "elastically and photoelastically effective chains" but the number of links in these "effective chains" differs for each case. Previous extrapolations to more realistic network models[3-5] do not appear to be well founded and hence we have not attempted it herein. A new approach is needed which incorporates the main features of this simple calculation: cross-link mobility and chain interdependence.

References and Notes

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Communications to the Editor

^{13}C Nuclear Magnetic Resonance Observation of the Oxidation of Polyethylene

The oxidation of polyolefins is a problem of considerable technological importance and scientific interest. The literature is voluminous (see ref 1–3 for reviews) and the general outlines of the thermal reaction are now generally felt to be quite well understood. Lingering doubts persist, however, as to the details of the mechanism, particularly from the quantitative standpoint, and the exact nature of the oxidation products is by no means completely clear.[4-7] This is in large part due to heavy reliance on ir spectroscopy in studies reported to date. Informative as it is, ir spectroscopy suffers from the difficulty of band overlap, particularly in the important carbonyl stretch region near 1725 cm^{-1}, and from the troublesome necessity of establishing reliable extinction coefficients.

Because of the wide range of ^{13}C chemical shifts, over 200 ppm for the resonances of interest, peak overlap does not present a problem. In addition, because of the sensitivity of ^{13}C chemical shifts to local structure, much more positive and detailed identification of oxygen-containing groups is possible. A third major advantage of FT ^{13}C NMR is that with due attention to spin–lattice relaxation, i.e., by selecting pulse intervals equal to at least $3T_1$, quantitative estimation of the oxidation products can be carried out directly from peak intensity measurements.[8]

We wish to report in a preliminary fashion our utilization of FT ^{13}C NMR for the observation and measurement of the oxidation products of low density (i.e., branched) polyethylene. The polymers employed were commercial materials from Union Carbide having the properties shown in Table I. The branch contents were determined by ^{13}C NMR as described by Dorman et al.[10] and by Bovey et al.[11] Spectra were observed at 25 MHz at a temperature of 110°.[12] The polymers were exposed to 1 atm of oxygen in the form of 5-in. diameter circular films of 5-mil thickness (ca. 1.4 g) placed in flat-bottomed conical oxidation cells held in a 140° oil bath and connected to mercury manometers. After the desired volume of oxygen was absorbed, the oxidized polymer was dissolved as 30% (w/v) solutions in a 4:1 (by volume) mixture of 1,2,4-trichlorobenzene and deuteriobenzene. The solutions were placed in 12-mm NMR tubes which were then flushed with argon and stoppered.

Figure 1 shows the ^{13}C spectrum of polymer B (Table I) before (a) and after (b and c) thermal oxidation. The principal peak at 30 ppm (vs. TMS) is that of the methylene

Table I

	Polymer A	Polymer B
Melt index	0.3	21.9
$\bar{M}_w$	3.50×10^5	1.43×10^5
Density, g cm^{-3}	0.9175	0.9245
Branch content[a]		
Methyl	0	0
Ethyl	2.6	1.9
n-Butyl	11.4	9.7
n-Amyl	4.4	2.1
"Long"	4.1	3.4
Total branch points	22.5	17.1

[a] Branch points per 1000 CH_2.

carbons which are four or more carbons removed from any branch, chain ends, or oxidized groups. The resonances associated with branches are known[10,11] and are indicated on spectrum (a). In spectra (b) and (c) the new peaks resulting from oxidation are shaded. Most of these have been unequivocally assigned. This was done by comparison with appropriate long-chain model compounds[14] which were individually observed as 20% (w/v) solutions under identical conditions. In order to simulate the polymer solutions still more closely, mixed solutions of model compounds were also observed. Deviations from the chemical shifts of the pure compounds were less than 0.1 ppm in the alkyl region and ca. 1 ppm in the carbonyl region. (Smaller deviations are to be expected for the actual polymer solutions, in which functional group concentrations were smaller.)

As Figure 1 (b and c) shows, the groups believed to be unequivocally assigned were: long-chain ketones, long-chain carboxylic acids, long-chain secondary alcohols, long-chain secondary hydroperoxides, esters of long-chain carboxylic acids with long-chain secondary alcohols, and long-chain γ-lactones. *Not* observed at our present level of detection (ca. 0.3%) were the following groups: aldehydes, conjugated ketones, olefins, peresters, primary and tertiary hydroperoxides, and primary and tertiary alcohols and their esters. The presence of all of these has been proposed or reported by various authors.[1,4,5,7]

In other respects, our data agree in a general way with ir findings,[5] but provide considerably more detailed structural information as well as a sounder quantitative basis for mechanistic conclusions. In Figure 2, the distribution of established oxidation products is depicted as a function of time and extent of oxidation. The highest extent of oxida-