Stress–strain relations and molecular orientation in highly crosslinked *cis*-polyisoprene networks

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Results of equilibrium stress–strain experiments and Fourier transform infra-red measurements of segmental orientation, previously reported for moderately crosslinked *cis*-polyisoprene networks by Amram *et al.* (*Polymer* 1986, **27**, 877), are extended to networks with high degrees of crosslinking. The samples were stretched to the limit of maximum chain extensibility. The absence of strain-induced crystallization during experiments was inferred from infra-red measurements, according to which the 844 cm^{-1} absorption band specific to crystalline regions did not exhibit any systematic shift in one direction. The reduced force *versus* inverse extension ratio showed strong upturns while the reduced orientation curves did not exhibit any upturns. Likewise, the analogue of the stress optical coefficient, defined as the ratio of molecular orientation to true stress, exhibited a strong decrease with extension, in contrast to Gaussian networks in which it is approximately independent of the degree of deformation.

(Keywords: stress–strain; molecular orientation; polyisoprene networks)

Introduction

The relation between stress and strain in rubbers is conventionally given in terms of the Mooney–Rivlin plot[1], where the reduced stress $[f^*]$ is presented as a function of inverse extension ratio. The extension ratio α is defined as the ratio of the final length to the initial length of the sample. The reduced stress is defined for dry rubbers as:

$$[f^*]=\frac{f}{A_0(\alpha-\alpha^{-2})} \tag{1}$$

where A_0 is the cross-sectional area of the specimen in the undeformed state and f is the applied force for a given α. The $\alpha=1$ intercept of the Mooney–Rivlin plot equates to the small deformation shear modulus of the rubber. Values of $[f^*]$ typically exhibit a drop with increasing elongation, followed by an upturn at high deformations. The drop is usually ascribed to the softening of intermolecular effects by stretching. The upturn may be due to either strain-induced crystallization or to finite chain extensibility[1]. The latter is observed around the maximum extension ratio, $\alpha_{\max}$, defined as:

$$\alpha_{\max}=\frac{r_{\max}}{\langle r^2\rangle_0^{1/2}}=\frac{n^{1/2}\cos(\theta/2)}{C_n^{1/2}} \tag{2}$$

where $r_{\max}$ is the maximum end-to-end distance corresponding to the fully extended all-*trans* configuration of the chain, $\langle r^2\rangle_0$ is the mean-square end-to-end distance for the unperturbed chains, n is the number of repeat units, π-θ is the angle between the backbone bonds, and C_n is the characteristic ratio of a chain of n backbone bonds.

In parallel with the reduced force, the reduced orientation, $[S]$, is defined for dry networks formed in the bulk state as:

$$[S]=\frac{S}{(1-2/\phi)(\alpha^2-\alpha^{-1})} \tag{3}$$

where ϕ is the average functionality of the network junctions, S is the molecular orientation expressed as the second Legendre polynomial averaged over all vectors whose orientation is recorded with a suitable experimental technique. A convenient method for measuring orientation is Fourier transform infra-red spectroscopy (*FT*i.r.), according to which the molecular orientation is obtained as[2,3]:

$$S=\langle P_2(\cos\vartheta)\rangle\equiv\tfrac{1}{2}(3\langle\cos\vartheta\rangle-1)=\frac{R-1}{R+2}\frac{R_0+2}{R_0-1} \tag{4}$$

Here, the angle brackets denote the averaging over all configurations of the network chain, ϑ is the angle between the local chain axis and the direction of stretch, R is the dichroic ratio ($R=A_\perp/A_\parallel$, with $A_\parallel$ and $A_\perp$ being the absorbances measured with radiation polarized parallel and perpendicular, respectively, to the direction of stretch), $R_0=2\cot^2\beta$, where β is the angle between the transition moment vector of the measured vibrational mode and the local chain axis.

Following the practice for birefringence data, one may also define the stress optical coefficient, C, as[1,4]:

$$C=\frac{S}{\tau} \tag{5}$$

where τ is the true stress, defined as the force per unit deformed cross-sectional area.

In the present communication, the reduced force, reduced orientation and stress optical coefficient for a network with a high degree of crosslinking are presented. In terms of these data, it is shown that the effects of finite

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extensibility in amorphous networks are exhibited differently in stress–strain and orientation–strain relations.

Experimental

Several networks of *cis*-polyisoprene with high degrees of crosslinking were prepared by the usual crosslinking procedure with dicumyl peroxide. Data from only one representative sample are reported in the present communication. The crosslinking procedure reported by Amram *et al.*[3] was followed. Dicumyl peroxide (2%) at 140°C for 40 min was used to prepare the sample. The average molecular weight of chains between crosslinks was determined as 4500 g mol^{-1} from stress–strain measurements and from swelling. This relatively low value corresponds to about 260 C–C bonds along the chains and leads to $\alpha_{max} = 6$ from equation (2) with $\theta = 68°$ and $C_n = 4.9$. In previous work[3], networks with relatively lower values of crosslink densities were studied, and extension ratios of the order of 9 were reached.

Simple tension experiments were performed by applying a dead weight to the lower clamp of a sample with dimensions *c.* $0.2 \times 5 \times 20$ mm^3, and measuring the distance between two fiducial marks after allowing sufficient time for equilibration. The time between the application of a load and measurement of length was at least 1 h. Length measurements were made with an accuracy of 0.002 mm with a cathetometer (Gaertner, 7023-P). The infra-red spectra were recorded with an *FT*i.r. spectrometer (Perkin–Elmer model 1600), with a resolution of 2 cm^{-1} and an accumulation of 16 scans. The infra-red beam was polarized by a rotatable Specas (Kent, UK) polarizer (0.2 μm wide gold polarizer on a KRS-5 substrate) which was set between the sample and the detector. Measurements on stretched samples were made while the samples were held under the applied weight. This ensured that orientation measurements, like stress–strain measurements, were made in equilibrium. The i.r. data were evaluated according to the method of Amram *et al.*[3], who showed that the three vibrational modes at 837, 1376 and 1663 cm^{-1} may be used to determine the orientation function. Accordingly, these bands were analysed in the present study. It should be noted that the least scatter in experimental data occurred for the 1663 cm^{-1} band, which was therefore selected as a measure for determining segmental orientation in polyisoprene networks. Further details of data analysis may be found in Figure 7 of reference 3 and the related discussion.

Results and discussion

The relation between stress (force per unit undeformed cross-sectional area) and extension ratio for the representative sample is shown in *Figure 1*. The points represent equilibrium experimental data. The curve through the points is the least-squares fit obtained as a third-order polynomial:

$$f/A_0 = -1.4833 + 2.0199\alpha - 0.6383\alpha^2 + 0.0829\alpha^3 \ (\mathrm{N\,mm^{-2}}) \qquad (6)$$

The reduced stress is given in *Figure 2* as a function of inverse extension ratio. The points are obtained from the experimental data shown in *Figure 1* and the curve through the points is a least-squares fit. Calculations of the reduced stress based on equation (6) gave somewhat smaller values at small deformations. This is due to the high sensitivity of the reduced force in this region, resulting from the term $\alpha^2 - 1/\alpha$ in the denominator, as given in equation (1). A very sharp upturn is observed at high extension ratios, which is attributed to the effect of finite chain extensibility and not to the more common strain-induced crystallization. This conclusion follows from the fact that the i.r. 844 cm^{-1} absorption band specific to crystalline regions does not exhibit any systematic shift during stretching. The maximum extension ratio for which a reading was taken before rupture is around 5.25, which is rather close to $\alpha_{max} = 6$, obtained from equation (2).

The dependence of the average molecular orientation on deformation is displayed in *Figure 3*. The experimental data are fitted with a third-order polynomial of the form:

$$S = -0.3815 + 0.5321\alpha - 0.1705\alpha^2 + 1.8589\alpha^3 \qquad (7)$$

The typical sigmoidal character of the orientation–deformation curve of *Figure 3* is observed in all other samples with relatively high crosslink densities. The corresponding reduced orientation curve is presented in *Figure 4*. The points represent experimental data. The

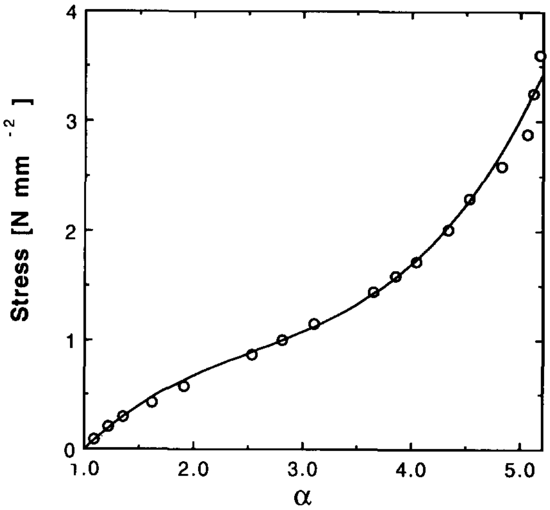

Figure 1 The relationship between stress (force per unit undeformed cross-sectional area) and extension ratio. Points represent equilibrium experimental data. The curve through the points is obtained by a least-squares fit

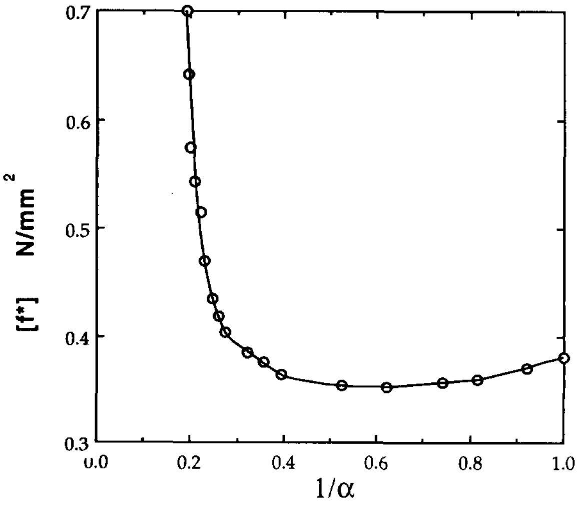

Figure 2 Reduced stress as a function of inverse extension ratio. Points are obtained from experimental data of *Figure 1* and the curve through the points is a least-squares fit

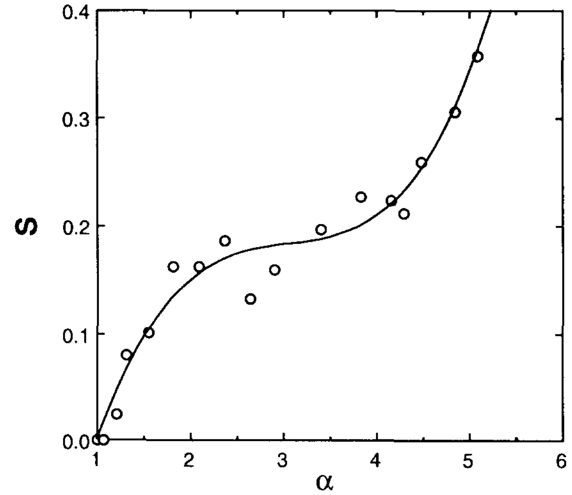

Figure 3 Dependence of average molecular orientation on deformation. Points represent equilibrium experimental data. The curve through the points is obtained by a least-squares fit

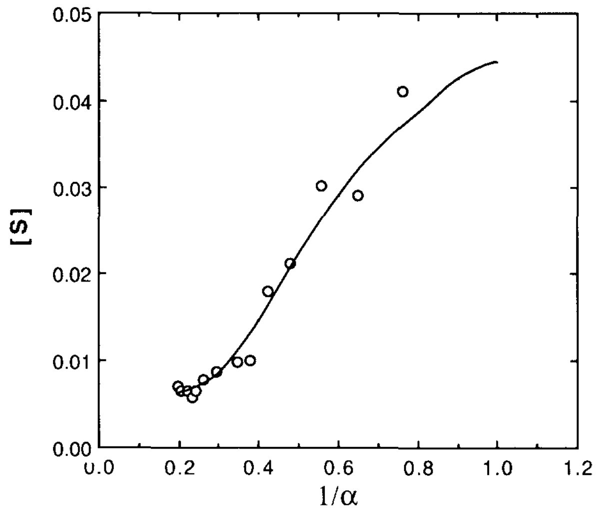

Figure 4 Reduced orientation as a function of inverse extension ratio. Points represent experimental data. The solid curve is a least-squares fit to guide the eye

solid curve is a least-squares fit to guide the eye. As in the case of reduced stress, calculations of the reduced orientation based on equation (7) gave somewhat lower values at small deformations, due to sensitivity of the data in this region. In contrast to the stress–strain behaviour, the reduced orientation does not exhibit an upturn at high elongations. This is an intuitively plausible phenomenon, since in the absence of crystallization one should not expect further orientation in chains that have reached their ultimate extensibilities, while the stress may continue to increase until the rupture of the chains in the system. In contrast to the present results, $[S]$ *versus* α^{-1} plots obtained by *FT*i.r. measurements on natural rubber and polybutadiene networks[3] exhibited sharp upturns resulting from strain-induced crystallization.

The differences in the dependence of stress and orientation on deformation are better understood from the plot of the ratio S/τ *versus* α, given in *Figure 5*. This ratio, denoted by C in equation (5), is analogous to the stress optical coefficient used in interpreting birefringence data, and is expected to be independent of α provided that the stress and the orientation exhibit the same response to deformation. In fact, previous birefringence measurements for Gaussian chain networks were found[4] to lead to constant values of the stress optical coefficient over a wide deformation range. The present experiments, however, yield a continuously decreasing curve with increasing extension, indicating the stronger dependence of τ on α, compared to that of S. Although both quantities exhibit a change in the same direction with increasing α, as shown in *Figures 1* and *3*, their relative dependences differ from each other, as may be best illustrated in *Figure 5*.

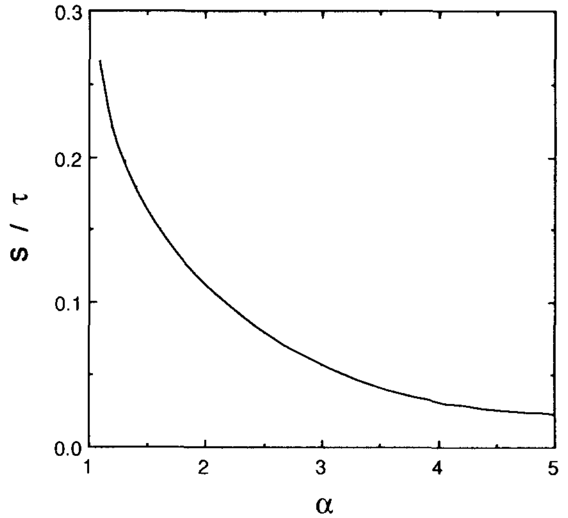

Figure 5 Ratio of orientation to true stress presented as a function of deformation

Finally, it should be noted that the relation of $[f^*]$ to $1/\alpha$ obtained in the present experiments is in qualitative agreement with previous theoretical predictions[5–9] for networks with non-Gaussian chains. On the other hand, to our knowledge there are no well-established arguments in the literature on the dependence of molecular orientation on deformation for non-Gaussian networks. Recent theoretical calculations based on the rotational isomeric state model[10,11] show definite upturns at high deformations in short polyethylene and polyoxyethylene chains. Calculations for short polyisoprene chains are in progress.

Acknowledgement

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