An infra-red dichroism investigation of segmental orientation in dry and swollen poly(dimethylsiloxane) networks

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(Received 21 May 1992)

The effects of polymer concentration during network formation and deformation are investigated by infra-red dichroism measurements of segmental orientation in uniaxially strained samples. Experiments are performed on end-linked poly(dimethylsiloxane) networks. The results, consistent with the predictions of the theory of segmental orientation, show that the orientation results predominantly from intramolecular effects in response to network deformation. The contributions to orientation from trapped entanglements and from local intermolecular effects are found to be negligibly small.

(Keywords: poly(dimethylsiloxane); networks; segmental orientation; Fourier transform infra-red measurements; swollen networks)

INTRODUCTION

Measurements of molecular orientation in stretched polymeric networks are of particular importance for the understanding of rubber elasticity. Recent developments in spectroscopic techniques allow accurate measurement of orientation of specific vector directions within chain segments. Fluorescence polarization, ^{2}H nuclear magnetic resonance (n.m.r.) and infra-red (i.r.) dichroism are the most widely used techniques.

One application of these methods is to test the validity of molecular theories on segmental orientation. Correct interpretation requires crosslinked polymers in which the structural parameters, such as the average molecular weight of chains between crosslinks and the functionality, are well defined. For this reason, we have used networks formed by end-linking difunctional poly(dimethylsiloxane) (PDMS) precursor chains of known lengths. This kind of model network presents a negligible number of defects such as loops and dangling chains.

In this paper, infra-red dichroism is used to investigate the influence of polymer concentration during network formation as well as the effect of swelling on the observed orientation.

THEORETICAL BACKGROUND

The volume fractions v_{2c} and v_2 characterizing the system during network formation and during elongation/infra-red measurements are respectively defined as[1]:

$$v_{2c} = V_d/V_0$$

$$v_2 = V_d/V_i \tag{1}$$

where V_d is the volume of the dry network, V_0 is the reference volume representing the total volume of polymer and solvent during crosslinking, and V_i is the volume of the network during infra-red measurements.

The orientation function S for a phantom network is given by the expression:

$$S = D_0(1 - 2/\phi)[\lambda_x^2 - (\lambda_y^2 + \lambda_z^2)/2] \tag{2}$$

where D_0 is the configurational factor and ϕ is the junction functionality. The three deformation ratios λ_x, λ_y and λ_z are related by:

$$\lambda_x \lambda_y \lambda_z = V_f/V_0 \tag{3}$$

For an elongation along the x axis:

$$\lambda_x = (v_{2c}/v_2)^{1/3}\alpha$$

$$\lambda_y = \lambda_z = (v_{2c}/v_2)^{1/3}\alpha^{-1/2} \tag{4}$$

The deformation ratio α is defined as the ratio of the final length of the sample along the direction of stretch to its initial length before deformation. In the case of samples swollen prior to deformation, the initial length is that of the swollen sample. Substitution of equations (4) into equation (2) yields:

$$S = D_0(1 - 2/\phi)(v_{2c}/v_2)^{2/3}(\alpha^2 - 1/\alpha) \tag{5}$$

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0032-3861/93/061179-04

EXPERIMENTAL

Samples

The study was carried out on networks obtained by reacting stoichiometric mixtures of precursor chains of α,ω-di(hydrogeno)-PDMS of average molecular weight $M_n = 12\,000$ with 1,3,5,7-tetravinyltetramethylcyclotetrasiloxane used as a tetrafunctional crosslinking agent. The syntheses were performed in the presence of chloroplatinic acid used as a catalyst.

The analysis of the influence of solvent present during network formation was performed on samples prepared in toluene at various concentrations (v_{2c} varying between 0.6 and 1). The film obtained by casting the reaction mixture onto a Teflon plate was extensively dried under vacuum to remove the solvent before infra-red measurements.

The effect of swelling on the orientational behaviour was carried out on networks prepared in the bulk, then swollen, prior to the elasticity measurements, with n-hexadecane at various polymer fractions (v_2 varying between 0.56 and 1).

Infra-red dichroism method

In a previous paper[2] devoted to the analysis of the properties of model networks of PDMS as a function of molecular weight between crosslinks, infra-red dichroism has been successfully applied to segmental orientation under uniaxial tension. The infra-red dichroism technique is based on the measurement of the orientation of a specific transition moment vector associated with a vibrational mode. The anisotropy consecutive to the applied deformation is characterized by the dichroic ratio R of the selected absorption band. This ratio is defined as $R = A_{\parallel}/A_{\perp}$, $A_{\parallel}$ and $A_{\perp}$ being the absorbances measured with radiation polarized parallel and perpendicular to the stretching direction, respectively.

For a network under simple tension, the segmental orientation detected by infra-red spectroscopy is expressed in terms of the dichroic ratio R as:

$$S = \frac{(R-1)}{(R+2)} \frac{2}{(3\cos^2 \alpha - 1)} \tag{6}$$

where α is the angle between the transition moment vector of the vibrational mode considered and a directional vector characteristic of a given chain segment.

Deformation and infra-red measurements

Network elongation was performed as described earlier[3]. Infra-red spectra were obtained with a Fourier-transform infra-red (*FT*i.r.) Nicolet 7199 spectrometer, using a resolution of 2 cm^{-1} and a number of scans of 100. For a given extension ratio, four or five dichroic ratios were determined and averaged. The dichroic behaviour of the band at 2500 cm^{-1} has been examined. This band is ascribed to the overtone of the symmetrical bending vibration located at 1260 cm^{-1}. Its transition moment lies along the Si–C bond direction and the angle α is equal to 90°.

RESULTS AND DISCUSSION

According to the above description, segmental orientation depends on the conformational characteristics of the individual chains as embodied in the factor D_0 and on network structural features given by ϕ and v_{2c}. Additional contributions to segmental orientation can arise from local intermolecular interactions or from the presence of trapped entanglements. These contributions, which would enhance the orientation, may be accounted for by the front factor D, which is defined as:

$$D = D_0 + D_1 v_{2c} + D_2 v_2 \tag{7}$$

Here, the terms $D_1 v_{2c}$ and $D_2 v_2$ refer to the effects of entanglements and intermolecular contributions, respectively. D_1 and D_2 are constant coefficients. The importance of these two additional sources of orientation can be evidenced through the analysis of the dependence of segmental orientation on the state of swelling both during network formation and prior to infra-red measurements.

Influence of polymer concentration upon crosslinking

We have studied the influence of v_{2c} on the orientational behaviour of networks prepared with the same precursor polymer ($M_n = 12\,000$) in the concentration range between 0.6 and 1.

Values of the segmental orientation S are plotted against $(\alpha^2 - 1/\alpha)$ in *Figure 1*. For a given elongation, S is found to decrease with a decrease in the volume fraction v_{2c} of polymer present during network formation.

A similar result has already been observed by Dubault *et al.*[4] in deuterium n.m.r. studies of PDMS networks either having deuterated chain segments or swollen with a deuterated solvent. This decrease in orientation with decreasing v_{2c} was attributed to chain entanglements trapped inside the gel during the crosslinking reaction. More recently, Erman and Mark[5] pointed out that it is not necessary to invoke trapped entanglements to explain the observed results. They showed that the dependence of S on v_{2c} can simply be explained by taking into account the term $(v_{2c}/v_2)^{2/3}$ appearing in equation (5). The reduced orientation defined as:

$$[S] = S/[(\alpha^2 - 1/\alpha)(v_{2c}/v_2)^{2/3}] \tag{8}$$

reduces to

$$[S] = S/[(\alpha^2 - 1/\alpha)(v_{2c})^{2/3}] = D/2$$

since $v_2 = 1$ in these experiments. A plot of the reduced orientation against v_{2c} is shown in *Figure 2*. The approximate constancy of the front factor indicates that the contribution from D_1 to the configurational factor D is not significant. So our results tend to support Erman

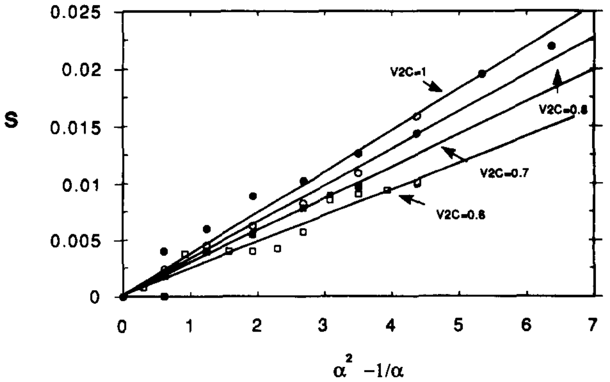

Figure 1 Influence of polymer concentration during network formation on segmental orientation S. Experimental data obtained at different polymer fractions: $v_{2c} = 1$ (●), $v_{2c} = 0.8$ (○), $v_{2c} = 0.7$ (■), $v_{2c} = 0.6$ (□). Best-fitting straight lines through the data are shown

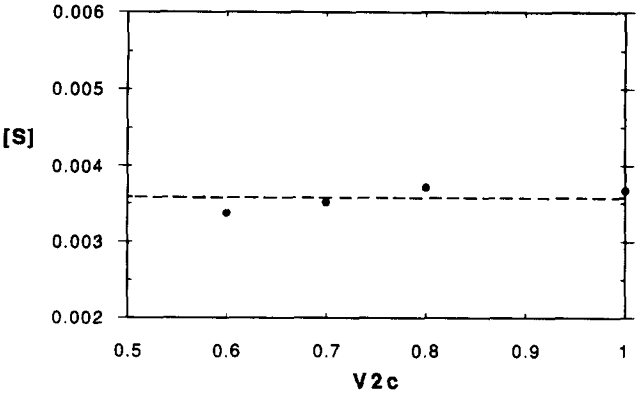

Figure 2 Reduced orientation $[S]$ as a function of v_{2c}

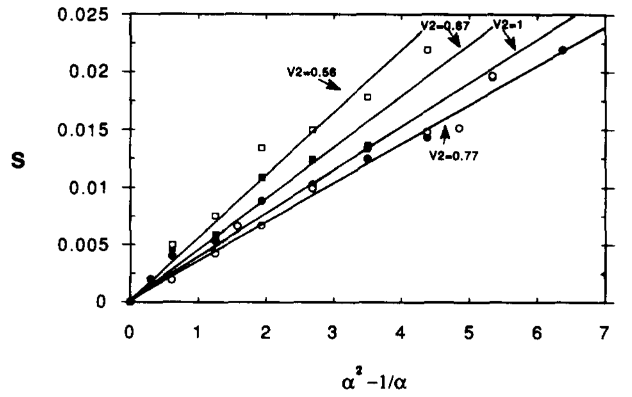

Figure 3 Effect of swelling on segmental orientation S. Experimental data obtained at different volume fractions v_2 during deformation: $v_2=1$ (●), $v_2=0.77$ (○), $v_2=0.67$ (■), $v_2=0.56$ (□). Best-fitting straight lines through the data are shown

and Mark's previous theoretical arguments[5] that the variation of S is only ascribed to a change in the reference state of the network (reflected through $(v_{2c}/v_2)^{2/3}$) and the interpretation including chain entanglements has not to be considered here.

Influence of swelling

The interest of swelling measurements is to demonstrate the existence of short-range correlations taking place among neighbouring chain segments.

Deuterium magnetic resonance studies by Deloche *et al.*[6] indicate that free chains of deuterium-labelled PDMS dissolved in a PDMS network under uniaxial stress exhibit the same segmental orientation as that of the network chains. This effect is attributed to local intermolecular orientational correlations in the deformed network, which induce an orientational order at the segmental level of the free chain. These intermolecular orientational correlations should lead to larger values of S, on account of the contribution of the term D_2v_2 to the front factor D (ref. 7), as given by equation (7). Swelling of networks should lead to rapid elimination of intermolecular correlations and consequently to a decrease of segmental orientation. Our results are not consistent with this prediction. In fact, the data reported in *Figure 3* show that S increases with decreasing v_2. The results are better visualized in *Figure 4*, representing S against v_2 at a fixed α ($\alpha=1.8$ for example). The orientation is observed to increase in general with decreasing v_2, in contrast to the implications of intermolecular effects. These results are nevertheless consistent with the predictions of equation (5). In fact, using $v_{2c}=1$, corresponding to the present set of data, a plot of the reduced orientation $[S]$ against v_2, in *Figure 5*, leads to a value of the configurational factor that can be considered constant within experimental error. So the infra-red dichroic measurements lead us to believe that short-range correlations are not significant in PDMS networks.

Another way of confirming the absence of contributions from D_1 and D_2 terms to the reduced orientation is to perform a set of experiments by keeping the v_{2c}/v_2 ratio constant and equal to 1. The results shown in *Figure 6* prove that the segmental orientation conforms with the (v_{2c}/v_2) factor as predicted by equation (5).

A detailed analysis and a more theoretical discussion will be proposed in a future paper[8] devoted to an intepretation of the orientation in the PDMS networks in terms of the constrained junction model.

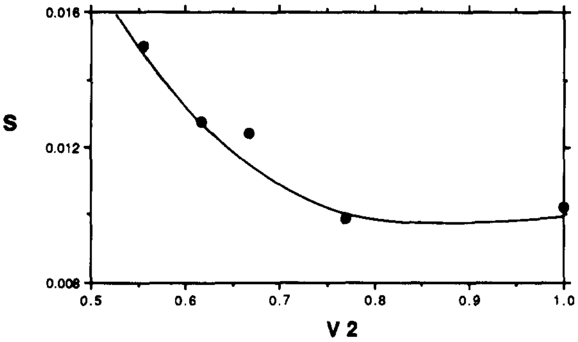

Figure 4 Orientation S as a function of v_2 for $\alpha=1.8$. A curve of best fit is drawn through the data points

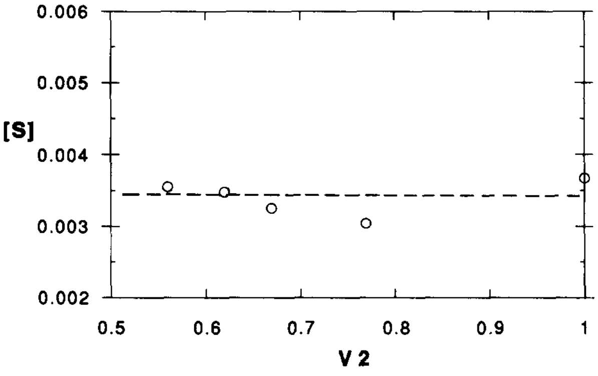

Figure 5 Reduced orientation $[S]$ as a function of v_2

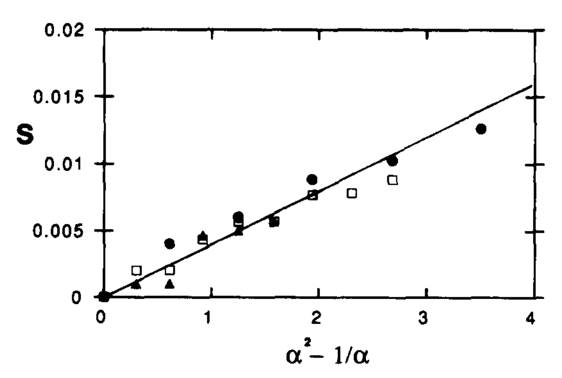

Figure 6 Orientation S as a function of α^2-1/α when v_{2c}/v_2 is constant and equal to 1. Experimental data are obtained for $v_{2c}=v_2=1$ (●), 0.8 (□), 0.6 (▲)

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