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Effects of dimethylsiloxane diluents on the optical properties of poly(dimethylsilmethylene) networks

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Summary

Low molecular weight cyclic and linear molecules of highly flexible dimethylsiloxane (DMS) units [$-Si(CH_3)_2O-$] were used to swell elastomeric networks of poly(dimethylsilmethylene) [$-Si(CH_3)_2CH_2-$]. Strain birefringence measurements in elongation at 10°C showed the birefringence to decrease regularly with increase in degree of polymerization of the DMS diluent, with three of the four diluents having the unusual effect of increasing the birefringence. Therefore, if correlative effects are the origin of the increase, they do not seem to require high geometric asymmetry in the diluent molecules.

Introduction

The stress-optical properties of an elastomer can give much useful information on the configurational characteristics of the polymer chains making up the elastomeric network structure (1,2). An unusually interesting polymer (3,4) that has been studied in this way (5) is poly(dimethylsilmethylene) (PDMSM) [$-Si(CH_3)_2CH_2-$], which can be viewed as either a hydrocarbon analogue of poly(dimethylsiloxane) [$-Si(CH_3)_2O-$] or a silicon analogue of polyisobutylene [$-C(CH_3)_2CH_2-$]. One unusual property of PDMSM networks concerns the effects of diluents on its birefringence Δn and related optical properties (5). In general, most diluents decrease the correlations between polymer chains and thus decrease Δn. The values of Δn intrinsic to the chains themselves, and thus the ones most pertinent to rotational isomeric state interpretation (1), are therefore thought to be the minimum values exhibited. Such values are generally obtained in the case of highly symmetric, optically anisotropic diluents (6,7).

In the case of the PDMSM networks, swelling with a dimethylsiloxane (DMS) cyclic pentamer was found to have the unusual effect of increasing Δn (5). Correlative interactions between chain segments and diluent molecules are the origin of such increases and can be due to both the optical anisotropy of the diluent molecules and their geometric asymmetry (7).

The present study delves further into this issue through measurements of the strain birefringence of PDMSM networks swollen with

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one of several DMS oligomers, three cyclic and one linear. Of particular interest is the dependence of the optical properties on the degree of polymerization of the diluent molecules and whether they're cyclic or linear.

Experimental Details

The PDMSM elastomer was generously provided by Dr. C.-L. Lee and M. E. Cifuentes of the Dow Corning Corporation, and had been prepared by peroxide cure of a polymer having a number-average molecular weight M_n of 21.4 x 10^3 g mol^{-1}. The sample sheet, which had a thickness of approximately 1 mm, was extracted in toluene for six days in order to remove any uncross-linked material. The soluble fraction thus removed was found to amount to approximately 6 wt %.

Two cyclic DMS diluents having degrees of polymerization x of four and five were obtained from the Petrach Company, and a linear diluent having x = 11 was obtained from the Dow Corning Corporation. A cyclic DMS sample having x = 18 was kindly supplied by Professor J. A. Semlyen of the University of York, England. Gas-liquid chromatography indicated that all the diluents were of very high purity.

Strips having dimensions of approximately 1 mm x 8 mm x 30 mm were cut from the crosslinked sheets. The thickness of the unswollen specimens were determined by weighing them after their lateral dimension had been measured with a cathetometer; a density of 0.924 g cm^{-3} for PDMSM at 25°C (3) was used for the conversion. The product of the three dimensions then gave the unswollen, unstretched cross-sectional area A^*.

The swollen samples were prepared by immersing the strips in the chosen diluent until swelling equilibrium was reached. The degree of swelling was determined by comparing the linear dimensions of the sample in the swollen and unswollen states.

The instrumentation used for the stress-optical measurments was based on a well-known design (8). A 4-mW He-Ne (632.8 nm) laser that served as light source provided a highly polarized and well-defined incident beam (obviating focusing lenses). The polarizer and analyzer were Glan-Thomson prisms and the retardation R was measured with a Babinet compensator. The sensor was a silicon-diode photomultiplier connected to an analog meter (both from the Karl-Lambrecht Co.). The sample chamber was thermostatted to ±0.1°C, and its windows were found to show only negligible birefringence.

The equilibrium tensile force f was measured by using a strain-gauge (Statham Co.) run by a constant direct current voltage power supply. A Hewlett-Packard recorder was used to monitor and record the output of the strain-gauge. Extensions of the sample were determined by measuring the distance between fiducial marks, ca. 1.0 cm apart, with a cathetometer (Gaertner Co.) having a precision of ±0.001 cm. All stress-optical measurements were carried out at 10°C.

Refractive indices of the swollen samples were estimated by assuming the specific refractivities to be additive in the volume fractions of the two components. The refractive index of PDMSM was taken to follow the expression (5)

$$n_D(t) = 1.5078 - 3.793 \times 10^{-3}t \qquad (1)$$

where t is the temperature in °C. All refractive indices were measured by means of an Abbe refractometer (Na lamp). Their values and the parameters characterizing their temperature dependence are given in Table I.

Table I

Refractive Index Information on the DMS Diluents

x	$n_D(20°C)$	a[a]	10^4b[a]
4 (cyclic)	1.3922	1.4014	4.611
5 (cyclic)	1.3923	1.4010	4.582
11 (linear)	1.3928	1.4021	3.640
18 (cyclic)	1.3997	1.4037	2.331

[a] a and b are the coefficients in the relationship $n_D = a - bt$, where t is the temperature in °C.

Theory

The first relationship of interest is the dependence of the birefringence on the true stress $\tau = f/A$, where A is the cross-sectional area under the conditions at which t was measured. This dependence is represented by the stress optical coefficient defined by

$$C \equiv \Delta n/\tau \qquad (2)$$

and is thus simply the slope of the straight line obtained by plotting Δn vs. τ.

The optical anisotropy tensors $\hat{\alpha}_i$ enter into C via Γ_2, which is a molecular optical anisotropy parameter and is defined by (1,9)

$$\Gamma_2 = (9/10) \sum_i \langle r^T \hat{\alpha}_i r\rangle_o / \langle r^2 \rangle_o \qquad (3)$$

where $\hat{\alpha}_i$ is the anisotropic part of the polarizability tensor contributed by the structural unit or group indexed by i; the angle brackets and subscript zero denote the average over all configurations of the unperturbed chain. The stress-optical coefficient C is related to Γ_2 through the equation (1)

$$\Gamma_2 = (27nkTC)/[2\pi(n^2 + 2)^2] \tag{4}$$

where k is the Boltzmann constant, T the absolute temperature and n the retractive index. Even though the tensors $\hat{\alpha}_i$ are formally attributed to the chain units, they generally include contributions from neighboring molecules and segments correlated with them. Such contributions have been reported in a number of studies, some of which are cited below.

Stein and Hong (9) suggest that adsorbed anisotropic diluent molecules are oriented along with the network chains and add to their anisotropy, thus affecting the value of the coefficient C. Similarly, Gent (6,10) concludes that packing effects in a molecularly asymmetric medium are responsible for the observed changes in the optical properties. Frisman et al. (11,12) and Nagai (13-15) also conclude that such interactions between network chains and diluent molecules can affect the magnitude of the stress-optical coefficient.

More recently, Erman and Flory (7) emphasized that correlative effects may involve units of neighboring chains in the network structure as well as molecules of the diluent. These effects are believed to depend on the optical anisotropy of the neighboring molecules or chain segments, as expressed by the tensor $\hat{\alpha}_i$, and on any asymmetry in the shape of this molecule.

Assuming that these correlations with a given unit should be expressed in a linear fashion, Erman and Flory write for the anisotropy parameter

$$\Gamma_2 = \Gamma_2^{o} + a_1(1 - v_2) + a_2v_2 \tag{5}$$

where Γ_2^{o} represents the intrinsic contributions of the units of the network chain, $a_1(1 - v_2)$ represents the contribution from correlations with diluent molecules, and a_2v_2 represents the contributions from correlations with units of neighboring chains. The quantities a_1 and a_2 thus express the intensities of these two contributions. Therefore, values of C obtained at volume fractions v_2 of polymer of 1.00 (unswollen) and at v_{2m} (equilibrium degree of swelling) can be extrapolated to give values of C at $v_2 \rightarrow 0$. Equation (5) then permits the direct calculation of $\Gamma_2^{o} + a_1$, the intrinsic anisotropy parameter as modified by correlations with the diluent molecules.

Results and Discussion

The values of v_{2m} employed are given in the second column of Table II. The results of the stress-optical measurements on the unswollen sample are shown in Figure 1, and for two of the swollen samples in Figure 2. The slopes of these and the other two curves, obtained by

Table II

Stress-Optical Results

Diluent x	v_{2m}^{a}	10^3C ($N^{-1}mm^2$)	$\Gamma_2^o + a_1$ ($Å^3$)
None	1.000	1.40	--
4 (cyclic)	0.500	3.12	4.53
5 (cyclic)	0.488	2.18	3.16
11 (linear)	0.896	1.88	2.65
18 (cyclic)	0.910	0.29	0.41

[a] Volume fraction of polymer present at swelling equilibrium and during the stress-optical measurments.

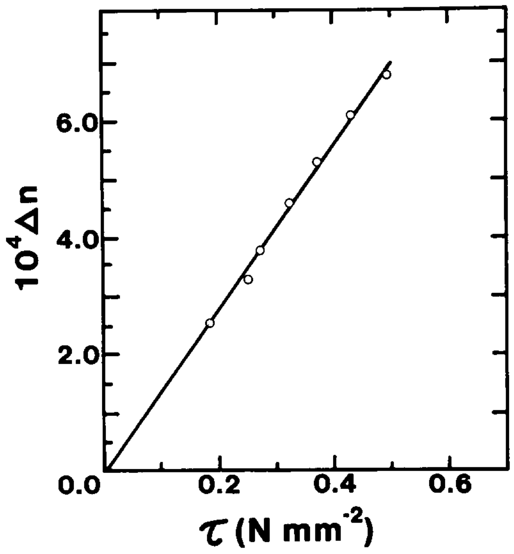

Figure 1. Dependence of the birefringence on the true stress for the unswollen PDMSM network at 10°C.

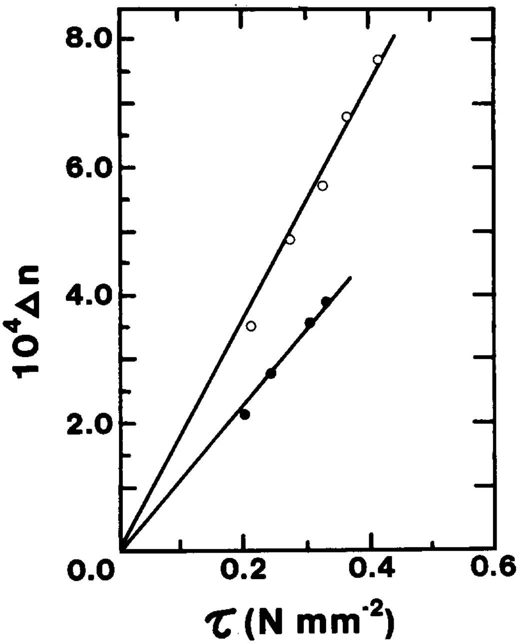

Figure 2. Birefringence-true stress results for the networks swollen with the cyclic tetramer (unfilled circles) and the cyclic pentamer (filled circles).

least-squares analysis are the desired values of C, and are given in the third column of Table II. As can be seen, three of the four diluents have the unusual effect of increasing the birefringence and thus the stress-optical coefficient.

Values of C for $v_2 \rightarrow 0$, obtained by extrapolations based on Equation (5), were used to calculate the values of $\Gamma_2{}^o + a_1$ given in the last column of Table II. The values gotten from the data at $v_{2m} = 0.896$ and 0.910 have a relatively high degree of uncertainty, of course, because of the long extrapolations involved. In any case, all of the values of $\Gamma_2{}^o + a_1$ obtained are shown as a function of the degree of polymerization x of the diluent in Figure 3. As can be seen from the least-squares line included in the figure, the anisotropy decreases approximately linearly with increase in x. Also, the result for the linear diluent lies, within experimental error, along the same line as that determined by the cyclic diluents. Although all chain molecules are thought to have significant asymmetry at small x (16-19), this effect should be minimized in the case of the DMS diluents because of their high flexibility (1). Thus, in the PDMSM - DSM system, the optical anisotropy of the diluent may be of unusually great importance.

Acknowledgement

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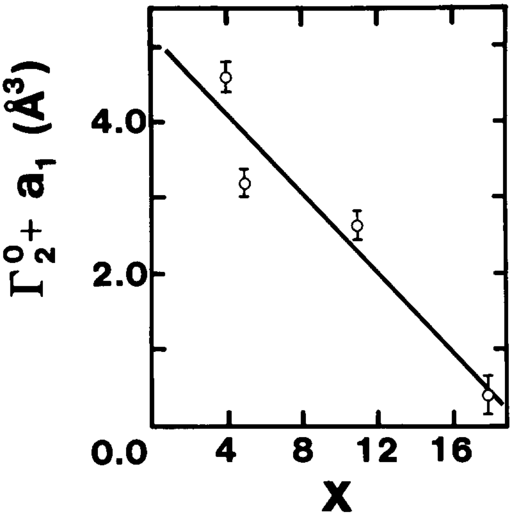

Figure 3. The effect of the degree of polymerization of the diluents on the intrinsic anisotropy parameter as modified by correlations with the diluent molecules.

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