The above analysis, although tentative,[31] does provide a consistent interpretation of both the equilibrium elastomeric behavior and the viscoelastic properties of solution cross-linked networks of PDMS.

Acknowledgments. It is a pleasure to acknowledge the financial support provided by the National Science Foundation (to R.E.C. and to J.E.M.) and by the Petroleum Research Fund, administered by the American Chemical Society (to R.E.C.).

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(27) It is obviously essential to include the factor $v_{2,C}^{2/3}$ in interpreting the mechanical properties of any network prepared in solution since, under these conditions, it may be considerably less than unity. Values of the reduced stress or storage modulus uncorrected for this effect should therefore not be used as a measure of effective cross-link density in comparisons[11,15] between samples prepared at different values of $v_{2,S}$. In simple, physical terms, the polymer chains are cross-linked at a volume V_0 characterizing the polymer solution. Subsequent removal of the solvent collapses the chains into a type of compressed or "super-contracted" state in which their configurational distribution is obviously very different from that associated with the state in which the cross-links were introduced. Under these conditions, the chains, and the entire polymer network, are much easier to deform than would be the case had the same number of cross-links been introduced in the undiluted state. The factor $v_{2,C}^{2/3} < 1$ must therefore be introduced to take account of the fact that the reference state for an unswollen network prepared in solution is not identical to the state of zero imposed stress in any subsequent study of its mechanical properties.

(28) As can be seen from Figure 2 and Table I, cross-linking in solution provides a convenient way of changing the viscoelastic loss of a polymer network independently of its modulus. For example, a network having a very small value of tan δ can be prepared by cross-linking it to a relatively large value of the cross-link density $\nu/2V$. If the cross-links are introduced in the presence of relatively large amounts of solvent, however, the large value of $\nu/2V$ would not give a large value of the modulus or reduced stress because it would be largely offset by the factor $v_{2,C}^{2/3} \ll 1$ appearing in eq 3.

(29) Langley and co-workers,[11] in a study of the dynamic mechanical properties of natural rubber, have reached the opposite conclusion, namely that cross-linking in solution does decrease the viscoelastic loss, and have attributed this decrease to a decrease in the number of inter-chain entanglements. They, however, compared solution and bulk cross-linked samples essentially at equal values of G' uncorrected by the important factor $v_{2,C}^{2/3}$ discussed above. We would therefore attribute the smaller values of tan δ which they report for the solution cross-linked samples (at constant G') simply to an increase in degree of cross-linking, unrecognized because of its being offset by decrease in the factor $v_{2,C}^{2/3}$.

(30) The expectation that cross-linking in solution would reduce the number of inter-chain entanglements implicitly assumes that such entanglements are rather numerous in a typical, bulk cross-linked network [see, for example, N. R. Langley and K. E. Polmanteer, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1023 (1974)]. The present experimental results and recent theoretical arguments,[24] however, suggest that such entanglements may be less numerous or less important than is widely thought to be the case.

(31) If one arbitrarily abandons the idea put forward here, that the observed viscoelastic losses are due to permanent entanglements, it may be possible to rationalize the present results in terms of network chain ends or untrapped entanglements (W. W. Graessley and N. R. Langley, private communications). At the present time, however, this interpretation would seem to be less plausible than the analysis presented here.

Temperature Dependence of Orientation Correlations in *n*-Alkane Liquids

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ABSTRACT: The depolarized Rayleigh intensities of *n*-hexadecane and *n*-docosane are measured as a function of temperature above the melting point. A parameter directly proportional to the magnitude of the orientation correlations is determined from the intensities. The results are then analyzed in terms of the general theory of orientation correlations in isotropic fluids developed by deGennes. We conclude that near their melting point the *n*-alkanes are far above a hypothetical rotational ordering transition comparable to an isotropic–nematic phase transition.

It is known[1,2] that the depolarized Rayleigh scattering intensities of *n*-alkane liquids indicate that there are orientation correlations between the chains for the higher alkanes. It has also been reported[3–6] that the intensities decrease with increasing temperature near the melting point. It has recently been suggested[7] that such effects are due to a near second-order transition comparable to the isotropic–nematic transition in liqud crystals which would occur below the melting point of the *n*-alkanes. This transition was predicted[7] to occur at 270 K for *n*-hexadecane. In the present work, new measurements of the depolarized Rayleigh ratio R_{HV} are reported as a function of temperature for *n*-hexadecane and *n*-docosane. The various contributions to R_{HV} are discussed in detail and evaluated either theoretically or experimentally. The results are discussed in terms of the general theory of orientation correlations in fluids developed by deGennes.[8]

Theory

Depolarized Rayleigh scattering in liquids is due to fluctuations in the mean-squared optical anisotropy of the elements of the fluid.[9-11] To each unit of the medium we assign an effective polarizability tensor, α_i. The effective anisotropy tensor is then given by

$$\hat{\alpha}_i = \alpha - \overline{\alpha}\mathbf{E}_3 \qquad (1)$$

where $\overline{\alpha} = (1/3)Tr\alpha$ is the scalar mean effective polarizability and $\mathbf{E}_3$ is the unit tensor. The depolarized Rayleigh ratio R_{HV} is

$$R_{\mathrm{HV}} = \frac{16\pi^4}{15\lambda^4}\frac{3}{2V}\sum_{i,j}^{N}\langle\hat{\alpha}_i^{\mathrm{R}}\cdot\hat{\alpha}_j^{\mathrm{C}}\exp(i\mathbf{k}\cdot\mathbf{r}_{ij})\rangle \qquad (2)$$

where λ is the incident wavelength in a vacuum, $\hat{\alpha}_i^{\mathrm{R}}$ is the row form of the effective anisotropy tensor for unit i, $\hat{\alpha}_j^{\mathrm{C}}$ is the corresponding column form, $\mathbf{k}$ is the scattering vector with magnitude $(4\pi\tilde{n}/\lambda)\sin\theta/2$, where θ is the scattering angle in the scattering plane and $\tilde{n}$ is the refractive index, $\mathbf{r}_{ij}$ is the vector from unit i and j, and the sum is over all pairs of units in volume V.

The effective anisotropy tensor in a dense medium differs from the inherent equilibrium anisotropy tensor of an isolated unit in the gas phase. In a dense medium, the unit is polarized by a socalled effective field. The effective field in the medium differs in a complicated way from the incident field outside the fluid. Since an exact solution to this problem is not available, we introduce a phenomenological effective anisotropy. Also, at any particular time, the actual effective anisotropy will differ from the mean effective anisotropy due to local distortions of the unit itself[12] and to the anisotropic motions of neighboring units.[13] The existence of transient local anisotropy leads to depolarized Rayleigh scattering in all fluids.

The depolarized Rayleigh scattering due to transient anisotropy may be separated from that due to the inherent equilibrium anisotropy by examining the spectrum of the scattered light. In general the transient anisotropy fluctuations relax much faster than the inherent anisotropy fluctuations. This leads to a spectrum with a broad line due to the transient anisotropy and a narrower line due to the equilibrium anisotropy.

If the scattered intensity due to transient anisotropy is subtracted, the inherent depolarized Rayleigh ratio is given by

$$\Delta R_{\mathrm{HV}} = \frac{16\pi^4}{\lambda^4}\frac{\rho}{15}\langle\gamma^2\rangle_0 g_2 \qquad (3)$$

where ρ is the number density of units, $\langle\gamma^2\rangle_0$ is the effective inherent mean-squared optical anisotropy of an isolated unit, and

$$g_2 = \frac{3/2\sum_{ij}^{N}\langle\hat{\alpha}_i^{\mathrm{R}}\cdot\hat{\alpha}_j^{\mathrm{C}}\rangle}{N\langle\gamma^2\rangle_0} \qquad (4)$$

The quantity g_2 is a direct measure of the orientation correlations between units in the fluid. In the case of n-alkanes we will choose the unit to be the whole molecule.

It has been shown by deGennes[8] that for liquids in the isotropic phase the quantity g_2 can be represented as

$$g_2 = T/(T - T_0) \qquad (5)$$

where T_0 is a hypothetical second-order transition temperature. Even if a first-order transition occurs above T_0, the fluid will still obey eq 5 above the transition temperature. If g_2 or a quantity directly proportional to it can be measured as a function of temperature, then T_0 can be determined by plotting $1/g_2$ vs. $1/T$.

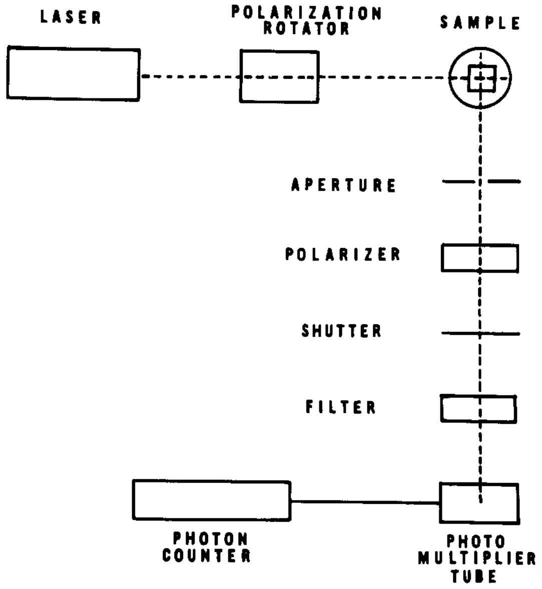

Figure 1. Diagram of the light-scattering photometer.

There will be at least three reasons why ΔR_{HV} decreases with increasing temperature for the n-alkanes: (1) the number density ρ is a decreasing function of temperature, (2) the quantity $\langle\gamma^2\rangle_0$ will decrease with temperature for the n-alkanes, and (3) the orientation correlations should decrease with increasing temperature.

Although *absolute* values of $\langle\gamma^2\rangle_0$ cannot be reliably calculated at this time, a dimensionless quantity

$$C_\gamma = \langle\gamma^2\rangle_0/n\Gamma^2 \qquad (6)$$

where n is the number of carbon–carbon bonds and Γ^2 is the effective mean-squared optical anisotropy per main chain bond can be obtained as a function of temperature. A parameter proportional to g_2 can then be calculated according to

$$g_2' = \Delta R_{\mathrm{HV}}/\rho C_\gamma \qquad (7)$$

Experimental Section

Materials. *N*-Hexadecane (99%) and *n*-Docosane (97%) were obtained from the Chemical Samples Co. They were filtered through 0.2 μm membrane filters directly into square quartz scattering cells.

Apparatus. A diagram of the depolarized Rayleigh scattering photometer is shown in Figure 1. The light source is a Spectra-Physics Model 162 argon ion laser operated at 4880 Å. The typical incident power level is 15 mW. The incident polarization can be adjusted with a double Fresnel rhomb polarization rotator. The sample cell is held in a temperature controlled aluminum block with holes drilled at right angles to allow the incident beam to pass through and to observe the scattered light at 90°. The scattered light is collimated with a cylindrical aperture followed by a Glan-Thompson polarizer with extinction of 10^5:1. The Rayleigh scattering is isolated with a narrow bandpass filter (35 Å half-width) at 4880 Å. The scattered light is detected with a cooled RCA 8850 photomultiplier and an SSR Model 1108 photon counter. The number of photocounts in a fixed time interval is displayed digitally. The typical counting period was 10 s. The incident intensity is stabilized to better than 1%. The dark count fluctuations and stray light were typically less than 0.1% of the total depolarized signal and were subtracted from the observed intensity. The inherent photon counting statistics yield a fluctuation of $\pm N^{1/2}$. Typical values of N were 10^4 to 10^6 counts/s. Thus, the scattered intensities were known with a precision of 1% in all cases.

Data Analysis

The determination of absolute Rayleigh ratios requires that some standard be known to a high absolute accuracy. Unfortunately, there is no universally accepted standard for Ray-

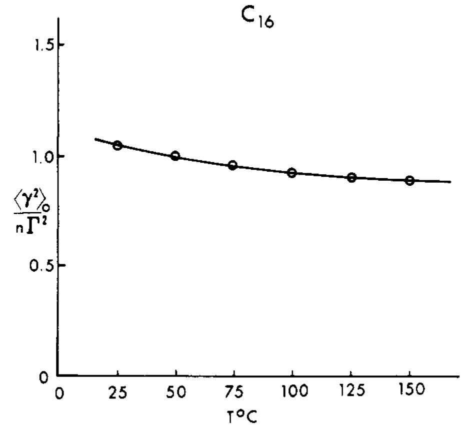

Figure 2. Dimensionless optical anisotropy parameter C_γ vs. temperature for n-hexadecane.

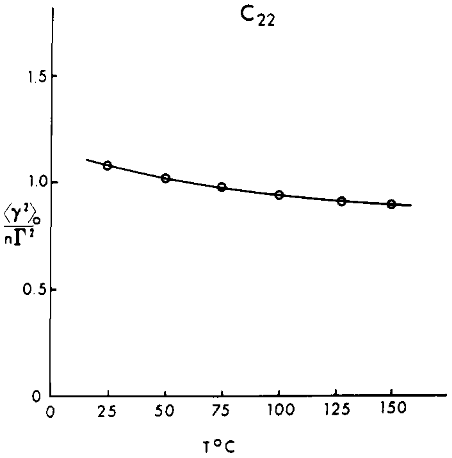

Figure 3. Dimensionless optical anisotropy parameter C_γ vs. temperature for n-docosane.

leigh scattering. One of the most widely used standards is benzene. In this work we adopt the values of R_{90} for benzene reported by Coumou,[14] interpolated to 4880 Å. This value also agrees with that determined by Finnigan and Jacobs[15] directly at 4880 Å.

The raw depolarized intensities are corrected for differences in scattering volume and converted to absolute Rayleigh ratios according to

$$R_{\mathrm{HV}}(2) = \frac{I_{\mathrm{HV}}(2)}{I_{\mathrm{HV}}(1)}\left(\frac{\tilde{n}(2)}{\tilde{n}(1)}\right)^2 \cdot R_{\mathrm{HV}}(1) \qquad (8)$$

where $\tilde{n}$ is the refractive index, 2 denotes the sample, and 1 denotes the standard. The initial standard was benzene (as noted above), but for the temperature-dependent studies, the standard was chosen to be R_{HV} for the pure n-alkane at a fixed temperature.

The total depolarized Rayleigh ratio R_{HV} was corrected for scattering due to transient anisotropy as described previously.[1,4] The value of R_{HV} for carbon tetrachloride was subtracted from the total to give ΔR_{HV}. This approximation is undoubtedly crude, but it was found to be acceptable in the determination of the mean-squared optical anisotropies $\langle\gamma^2\rangle_0$ of n-alkanes in solution. Also, for the longer pure liquid n-alkanes near the melting point the scattered intensity due to transient anisotropy is less than 20% of the total. If the correction is made consistently the relative excess intensities should be reasonably accurate for each n-alkane as a function of temperature.

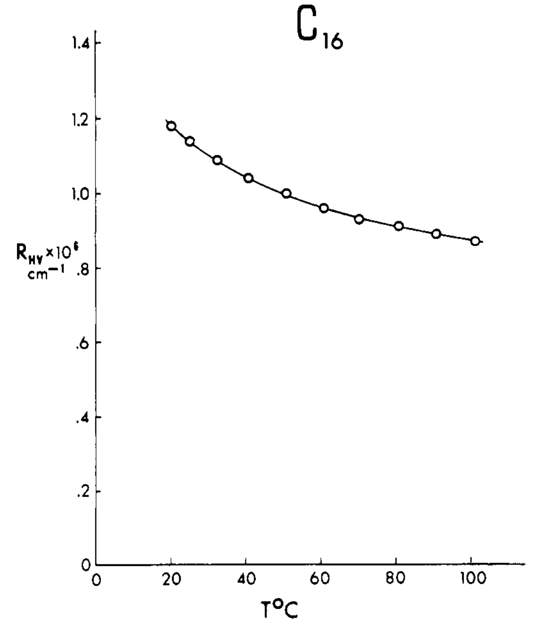

Figure 4. Depolarized Rayleigh ratio R_{HV} vs. temperature for n-hexadecane.

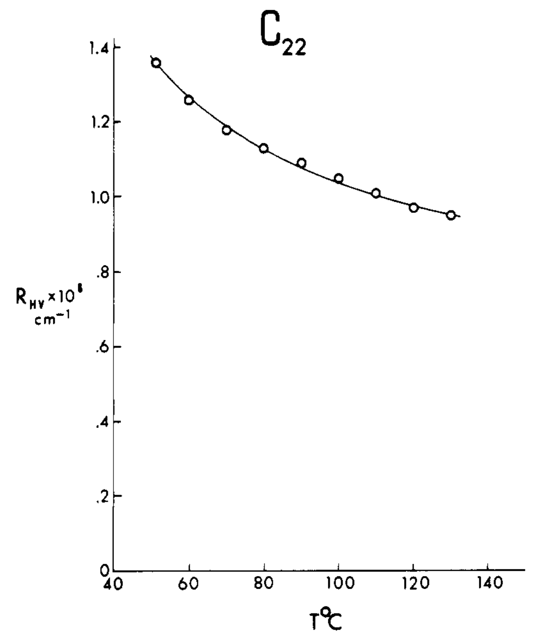

Figure 5. Depolarized Rayleigh ratio R_{HV} vs. temperature for n-docosane.

The densities of n-hexadecane and n-docosane as a function of temperature were obtained from the work of Orwoll and Flory.[16] The refractive indices were calculated from the known densities and molecular polarizabilities according to the Clausius–Mosotti relation

$$\frac{n^2-1}{n^2+2} = \frac{4\pi}{3}\rho\bar{\alpha} \qquad (9)$$

The mean-squared optical anisotropies of isolated n-alkane molecules were calculated according to the rotational isomeric state theory outlined previously.[1,4] Values of the dimensionless parameter $\langle\gamma^2\rangle_0/n\Gamma^2$ were computed as a function of temperature for tetrahedral model chains. The statistical weights were those used previously in the analysis of n-alkane chains.[1,4,17] The trans-gauche energy difference was taken to

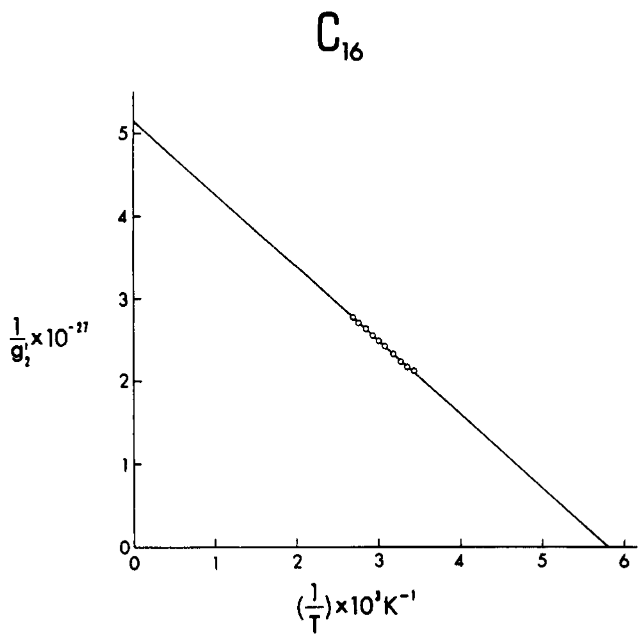

Figure 6. Angular correlation parameter $1/g_2'$ vs. $1/T$ for *n*-hexadecane.

be 500 cal/mol, and the excess energy due to steric overlap in $g^{\pm}g^{\mp}$ conformations was set equal to 2000 cal/mol. The results are shown in Figures 2 and 3.

Results and Discussion

The values of R_{HV} for *n*-hexadecane and *n*-docosane are plotted vs. temperature in Figures 4 and 5. The usual decrease in R_{HV} with temperature is observed. The quantity $1/g_2'$ is plotted vs. $1/T$ for *n*-hexadecane and *n*-docosane in Figures 6 and 7. The values of T_0 obtained from the graphs are 172 ± 10 K for *n*-hexadecane and 216 ± 10 K for *n*-docosane.

The melting point of *n*-hexadecane is 291 K and for *n*-docosane T_m = 317 K. Thus, near their melting points, both *n*-alkanes appear to be far above a hypothetical second-order transition temperature. The extrapolations necessary to obtain T_0 are quite long, but the present results should rule out the range of T_0 suggested by Bendler.[7]

Further evidence that the *n*-alkanes are not near an isotropic–nematic transition at their melting points is provided by examining the depolarized Rayleigh spectra.[18,19] The line width is proportional to $1/g_2$. The spectra are much too wide at T_m to be near a rotational ordering transition. This is also confirmed by the observation of the central shear dip[20] in the depolarized Rayleigh spectrum of the *n*-alkanes. A detailed analysis of the depolarized spectra of the *n*-alkanes is in preparation.[21]

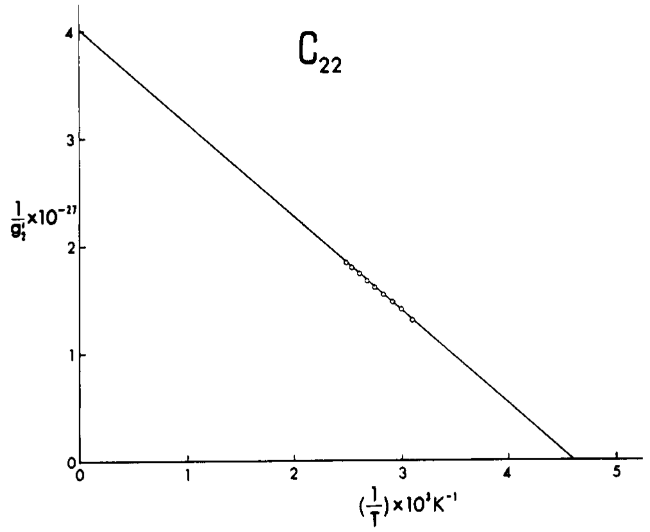

Figure 7. Angular correlation parameter $1/g_2'$ vs. $1/T$ for *n*-docosane.

Although the present results cast doubt on the existence of an isotropic–nematic transition in the *n*-alkanes near the melting point, they do suggest that such a transition is possible at much lower temperatures. If such a concept proves to be valid, it should have important consequences for the understanding of the nature of the amorphous regions in semicrystalline polyethylene at temperatures well below T_m.

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