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# Rheological and Rheooptical Studies of Poly(alkylsilanes)

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ABSTRACT: Rheological and rheooptical properties of poly(di-$n$-hexylsilane) were investigated in oscillatory and steady-shearing experiments. The samples consisted of concentrated solutions up to 6 wt % of a very high molecular weight polymer ($M_w = 4.6 \times 10^6$) dissolved in decalin. Experiments showed that the flow-induced shear and normal stresses were linearly related to the birefringence and that the constant of proportionality—the stress-optical coefficient—was larger than that of typical polymers. The enhanced stress-optical coefficient is a result of both the intrinsic rigidity of the polysilane chain and the higher polarizability of the $\sigma$-conjugated electrons. This result is similar to that found recently for a $\pi$-conjugated polymer. Additional results on the concentration dependence of various rheological properties are reported.

## Introduction

Polysilanes are a new class of materials with a range of applications that continues to increase. They are now being used as precursors for silicon carbide, as photoinitiators for polymerization, as UV-active resists in microlithography, as photoconductors having a very high hole mobility, and as active materials in nonlinear optical devices.[1] A more detailed understanding of the polymer's flow behavior and its optical properties would help advance all of these applications. To obtain this information, a study of the rheological and rheooptical properties of poly(di-$n$-hexylsilane) (PDNHS) was undertaken. Interpreting the results required additional information on the molecular structure of PDNHS, which we obtained by extending previous studies.[2]

## Experimental Section

**Synthesis and Fractionation of Materials.** The polymer used in this study was synthesized by a Wurtz coupling of dichlorodi-$n$-hexylsilane. The reaction mixture consisted of 35 g of monomer in a solvent consisting of 140 mL of toluene and 16 mL of diglyme. A sodium dispersion (0.28 mol) was added to initiate polymerization at room temperature. Additional details can be found in a previous publication.[3]

The polymer was isolated from the reaction bath by terminating with 2-propanol and then precipitating in a large excess of 2-propanol. For the sample used in this study, it was necessary to remove low molecular weight material by redissolving the polymer in toluene and adding the nonsolvent 2-propanol until the cloud point was reached. The solution was allowed to stand for 24 h, and then the supernatant was decanted away.

Samples of different molecular weight were prepared in a similar way or by degrading high molecular weight polymer. They were used to determine the molecular weight dependence of the intrinsic viscosity from which the characteristic ratio, $C_\infty$, was estimated.[2]

**Molecular Characterization.** The molecular characteristics of the samples were determined by a combination of light scattering, size-exclusion chromatography, and dilute solution viscometry. Experimental techniques that are briefly described here can be found in more detail in a previous publication.[3] Integrated light-scattering measurements were performed with a Brookhaven BI-200 SM photogoniometer equipped with a He-Ne laser. Both toluene and tetrahydrofuran (THF) were used as solvents. Size-exclusion chromatography was performed with THF as the solvent. The intrinsic viscosity values, $[\eta]$, were determined by measuring the specific viscosity with a Cannon Ubbelohde viscometer for a number of concentrations less than $1/[\eta]$. These values were divided by concentration and then extrapolated to zero concentration to obtain $[\eta]$. Measurements in decalin, toluene, and THF are reported. Various results from the three types of experiments are given in Table I.

**Solution Preparation.** All materials used for rheological and rheooptical measurements were solutions in decalin that had been previously dried by sparging nitrogen through it. Decalin is a good solvent for PDNHS, and it has a low enough vapor pressure at room temperature to prevent any significant evaporation during the course of our experiments, which frequently lasted several days. Although it is known that PDNHS shows liquid-crystalline order in the solid state,[4] we were able to make up solutions with concentrations as high as 6% ($c[\eta] \cong 27$) that remained isotropic. All of the concentrations were sufficiently high ($c[\eta] > 6$) so that form birefringence[5] effects should be negligible.

**Rheometry.** Rheological measurements were performed with a Rheometrics RMS 800 mechanical spectrometer. A cone and plate flow geometry was used with 50-mm-diameter fixtures. The rheometer was equipped with a force rebalance transducer, which uses a feedback control loop to maintain a constant vertical gap between the cone and plate. The bandgap of the controller is such that during transient experiments it takes approximately 0.1 s to reposition the cone to its correct position. The transient behavior of the sample during constant shear rate and oscillatory shearing experiments was determined. Because the latter experiments were conducted under linear viscoelastic conditions, there was no need to control the gap. The range of steady-shear rates explored was $10^{-2}$–$10^3$ s$^{-1}$, and the circular frequencies for the oscillatory experiments were between $10^{-2}$ and $10^2$ rad/s.

**Rheooptical Measurements.** The flow birefringence apparatus, which is very similar to that developed by Frattini and Fuller,[6] has been described in our previous papers.[7,8] Samples were loaded into the Couette cell, and then the birefringence ($\Delta n$) and the average orientation angle of the sample ($\chi$) were measured at constant shear rate under both transient and steady-state conditions. Shear rates in the range of $10^{-2}$–$10^3$ s$^{-1}$ were used for these experiments. They are the same as those used in the rheology experiments described above.

**Degradation by Light.** It is well-known that polysilanes degrade when exposed to visible light.[1] In fact, a number of the applications described in the Introduction are derived from this property. However, in our work, we carefully avoided degradation by working in the dark or with only low-energy radiation (a He-Ne laser or light from a yellow incandescent bulb). Nevertheless, Figure 1 contains data obtained from a 3 wt % solution of sample 1 that was purposely exposed to fluorescent light for 8 h. The figure shows the complex viscosity, $\eta^*(\omega)$, before and after exposure. Although the amount and uniformity of the exposure

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**Table I**
**Molecular Characterization of Poly(di-*n*-hexylsilane)**

| $M_w$ | $R_{g,z}$, nm | [η], dL/g |  |  |
|---|---|---|---|---|
|  |  | decalin | THF | toluene |
| $4.6 \times 10^6$ | 152 | 5.41 | 5.15 | 6.8 |

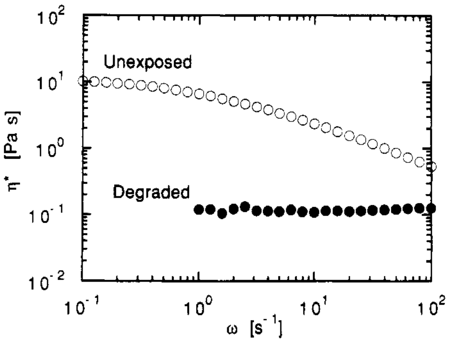

**Figure 1.** Steady-shear viscosities of a 3 wt % solution of PDNHS in decalin. Unexposed solution, ○; solution exposed to fluorescent light for 8 h, ●.

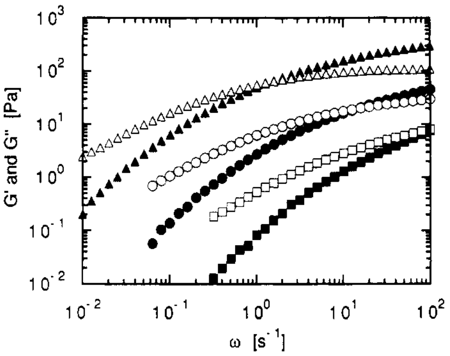

**Figure 2.** Dynamic moduli of PDNHS solutions, $G'$ (filled symbols) and $G''$ (open); 1.5 wt %, □; 3 wt %, ○; and 6 wt %, △.

in these experiments was not quantitatively determined, they nevertheless demonstrate the degrading effect of light. The drop in viscosity is substantial (100 times), providing ample proof that precautions similar to those described above are necessary when handling samples of PDNHS.

## Results and Discussion

Three semidilute solutions of PDNHS were prepared in decalin at weight fractions of 0.014, 0.028, and 0.056 (nominally referred to as 1.5, 3, and 6 wt %). At these concentrations, the solutions were well past the overlap concentration as indicated by products of the concentration, $c$, and $[\eta]$, which were 6.7, 13.5, and 27.1.

Values of the dynamic moduli, $G'(\omega)$ and $G''(\omega)$, determined for all three samples are shown in Figure 2. In each case, it was possible to make measurements at low enough frequency so that the zero shear rate viscosity, $\eta_0$, could be obtained from the limit of $G''(\omega)/\omega$ as $\omega$ goes to zero. This quantity is shown in Figure 3 as a function of concentration (see also Table II). The smallness of the in-phase forces generated at low frequencies prevented us from obtaining an accurate value of the steady-state compliance, $J_e^0$, from the limit of $G'(\omega)/[G'(\omega) + G''(\omega)]^2$ as $\omega$ goes to zero. In a similar fashion, the lack of data at frequencies above 100 rad/s prohibited a reasonable estimate of the plateau modulus, $G_N$. Nevertheless, it was possible to characterize the elastic properties by noting the magnitude of the moduli when $G'$ equals $G''$. This value, $G_{\mathrm{cross}}$, is plotted in Figure 3. The frequency of this crossing point, $\omega_{\mathrm{cross}}$, and its reciprocal, $\tau_{\mathrm{cross}}$, were also noted (see Figure 3 and Table II). This last quantity provided an estimate of the relaxation time of the material and hence the region where nonlinear effects should begin (i.e., where $\dot{\gamma}\tau_{\mathrm{cross}} > 1$).

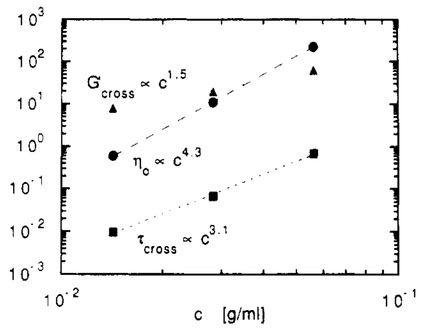

**Figure 3.** Scaling of rheological parameters with the concentration of PDNHS solutions; $G'_{\mathrm{cross}}$ [Pa], ▲; $\eta_0$ [Pa·s], ■; and $\tau_{\mathrm{cross}}$ [s], ●.

**Table II**
**Rheological Characterization of Poly(di-*n*-hexylsilane)**

| c, wt % | $\eta_0$, Pa·s | $\tau_c$, s | $G_c$, Pa | $C_s$, $10^{-8}$ Pa$^{-1}$ | $C_{N_1}$, $10^{-8}$ Pa$^{-1}$ |
|---|---|---|---|---|---|
| 1.5 | 0.60 | 0.0096 | 8.0 | 5.6 | 5.2 |
| 3.0 | 11.0 | 0.068 | 19 | 5.1 | 5.4 |
| 6.0 | 225 | 0.69 | 63 | 5.5 | 5.1 |

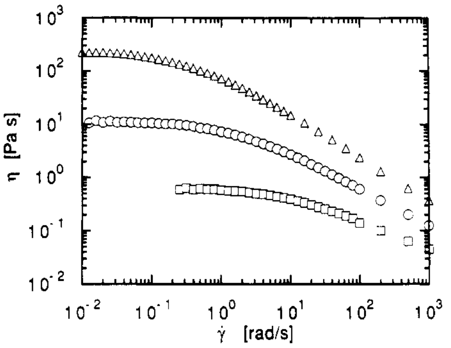

**Figure 4.** Steady-shear viscosities of PDNHS solutions; 1.5 wt %, □; 3 wt %, ○; and 6 wt %, △.

The behavior following the inception of a constant shear rate was determined in both rheological and rheooptical experiments. Figure 4 shows the steady-state viscosity as a function of shear rate for the three solutions. The viscosity at low shear rates becomes constant at a value equal to that found in the dynamic oscillatory experiments. At the shear rate where $\dot{\gamma}\tau_{\mathrm{cross}} = 1$, the viscosity is far into the non-Newtonian region and has dropped approximately 20% for each of the samples.

For concentrated polymer liquids, it is usually found that the major contribution to the stress comes from the orientation of the polymer molecules.[5] Under these conditions, a stress-optical relationship exists such that the deviatoric parts of the stress tensor and the refractive index tensor are colinear and proportional to each other. For a shear flow in which $\Delta n$ is the difference in the principal values of the refractive index in the plane perpendicular to the shear plane and $\chi$ is the smallest angle between one of the principal axes and the direction of shear, the stress-optical relationship becomes[9]

$$\sigma = (\Delta n/2C) \sin 2\chi \tag{1}$$

and

$$N_1 = (\Delta n/C) \cos 2\chi \tag{2}$$

where $\sigma$ and $N_1$ are the shear stress and first normal stress difference and $C$ is the stress-optical coefficient.

In steady-shearing experiments using cone and plate geometry in the rheometer and a Couette cell in the flow

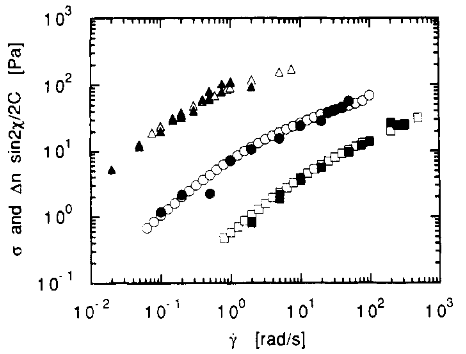

**Figure 5.** Comparison of shear stress data for PDNHS solutions obtained mechanically and rheooptically, $\sigma$ (open) and $\Delta n$ sin $2\chi/2C$ (filled); 1.5 wt %, □; 3 wt %, ○; and 6 wt %, △. The stress-optical coefficient is taken uniformly as $5.3 \times 10^{-8}$ Pa$^{-1}$.

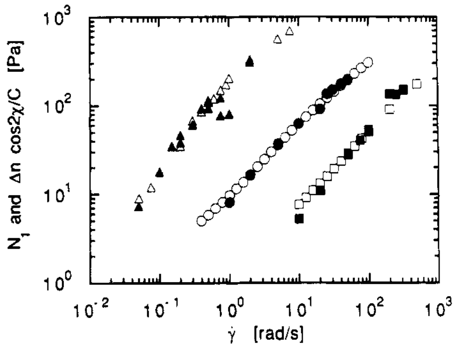

**Figure 6.** Comparison of normal stress data for PDNHS solutions obtained mechanically and rheooptically, $N_1$ (open) and $\Delta n$ cos $2\chi/C$ (filled); 1.5 wt %, □; 3 wt %, ○; and 6 wt %, △. The stress-optical coefficient is taken uniformly as $5.3 \times 10^{-8}$ Pa$^{-1}$.

birefringence instrument, we were able to measure all of the quantities in eqs 1 and 2 except for $C$. Figure 5 is a double-logarithmic plot of $\sigma$ and $\Delta n$ sin $2\chi/2$ as a function of shear rate. Figure 6 shows the quantities $N_1$ and $\Delta n$ cos $2\chi$. The constant $C$ was obtained by determining the factor required to superimpose the optical and mechanical data. This was determined for each solution (see Table II). The values so obtained are in remarkably good agreement with each other ($5.1 \leq C{\cdot}10^8$ Pa $\leq 5.6$) and independent of the concentration used. The magnitude of $C$ so obtained is approximately 10 times larger than that of typical flexible, saturated polymers and 10 times smaller than that of the stiff, conjugated polydiacetylene chain reported recently.[7]

In principle, $C$ can be calculated directly by using the rotational isomeric state theory[9] together with bond rotation potentials and bond polarizabilities for the various substituents of the monomer. However, neither the bond rotational potentials nor the Si–Si bond polarizability are known well enough to accurately do this. Furthermore, there is evidence of $\sigma$-bond delocalization of the electrons in polysilane,[10] which adds a further uncertainty to the valence optical method for calculating $C$.[9]

Instead we have used the data to obtain further information on the optical properties of the di-*n*-hexylsilane monomer. According to the theory of Kuhn,[11] the constant $C$ can be related to the molecular properties of the polymer by

$$C = (2\pi/45kT)[(n^2 + 2)^2/n]\Delta\alpha \qquad (3)$$

where $n$ is the refractive index of the solution, $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$ is the difference in polarizability of a hypothetical freely rotating segment (Kuhn step) parallel and perpendicular to the chain axis. The quantity $\Delta\alpha$ can be related to the difference in polarizability per monomer unit, $\Delta a = a_{\parallel} - a_{\perp}$, by dividing by the characteristic ratio for the polymer chain, $\langle r^2\rangle/Nl^2$, where $\langle r^2\rangle$ is the mean square end-to-end distance of a chain containing $N$ monomers of length $l$. A characteristic ratio of 20 was obtained from our most recent solution studies on this polymer.[2] This value along with information on the solution refractive index ($n = 1.484$) and the Si–Si bond length ($l = 2.35$ Å) leads to a value of $\Delta a$ equal to 6.2 Å$^3$.

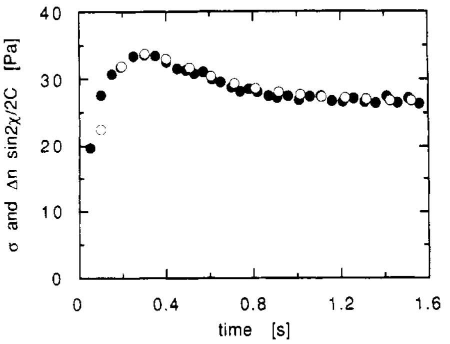

**Figure 7.** Comparison of shear stress data for a 3 wt % PDNHS solution obtained mechanically and rheooptically at the start-up of steady shear, $\dot{\gamma} = 10$ rad/s; $\sigma$ (open) and $\Delta n$ sin $2\chi/2C$ (filled) with $C = 4.7 \times 10^{-8}$ Pa$^{-1}$.

A logical way to proceed further in this analysis would be to obtain a reasonable estimate of the minimum energy configuration of the monomer and then use the valence optical method[8] together with the Si–Si, Si–C, C–C, and C–H bond polarizabilities to estimate the optical anisotropy of the monomer. If the value of $\Delta a$ so obtained was less than that determined experimentally, it would provide evidence for $\sigma$-bond delocalization. Experimental measurements of the UV absorption as well as calculations already suggest that this occurs.[10,12] The advantage of the method described here is that it provides information on the direction in which the polarizability is enhanced (see ref 7). However, before this can be done, additional information is needed on the Si–Si bond polarizability.[13]

In addition to the steady-shearing results, we obtained information on the growth of stress and birefringence during the transient period following the inception of shear. For many rheometers, the flow during this period is not unidirectional because the increasing normal stresses cause axial movement of the force transducer. This added flow prevents accurate measurements of the normal stresses.[14] However, in our rheometer, the transducer is equipped with a force rebalance system that can keep the cone at its correct position. As long as the shear rate is not too high ($\dot{\gamma} < 10$ s$^{-1}$), the control system is fast enough to properly measure the normal stresses. To prove this point, we have compared our rheometer data to flow birefringence data that are not be affected by transducer compliance. Figures 7 and 8 show that the shear stresses and normal stresses measured with both techniques are in good agreement. This suggests that, under the conditions used in our experiments, the force rebalance transducer accurately measures transient normal stresses.

## Conclusions

Rheological and rheooptical properties of poly(di-*n*-hexylsilane) solutions in decalin were measured under a variety of conditions. The results indicate the stress and birefringence are directly proportional even under nonlinear and transient conditions. The stress-optical coefficient obtained from these experiments is larger than that of

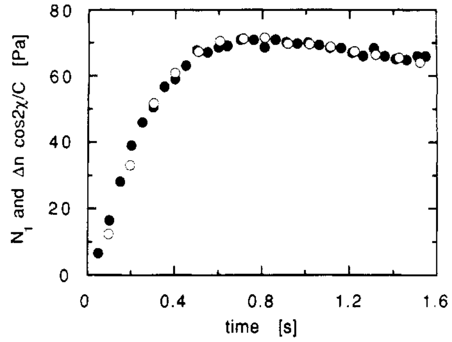

**Figure 8.** Comparison of normal stress data for a 3 wt % PD-NHS solution obtained mechanically and rheooptically at the start-up of steady shear, $\dot{\gamma}$ = 10 rad/s; $N_1$ (open) and $\Delta n \cos 2\chi/C$ (filled) with $C = 5.1 \times 10^{-8}$ Pa$^{-1}$.

typical polymers presumably due to the rigid nature of the chain and the highly polarizable electron system in polysilanes. Further information about the extent of $\sigma$-bond delocalization could be obtained if additional information on the polarizability of the Si bonds and on the average configuration of the hexyl silane monomer were available.

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**Registry No.** Dichlorodi-*n*-hexylsilane (homopolymer), 97036-67-4; poly(dihexylsilylene) (SRU), 94904-85-5.