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Thermodynamic and Hydrodynamic Size of a Dialkyl-Substituted Polysilane in a Mixed Θ-Solvent

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ABSTRACT: Previous studies of solution properties of dialkyl-substituted polysilanes have been measured in good solvents where long-range excluded volume interactions are present. Comparison of the experimental data on the polymer dimensions with theoretical predictions requires dimensions unperturbed by these long-range interactions. The mixed solvent of 2-propanol and hexane (41.3 wt % iPrOH) is shown to be a macroscopic Θ-solvent for poly(di-*n*-hexylsilane) at room temperature. Both the root-mean-square radius of gyration and the Stokes radius have been measured for a series of five molecular weights. The intrinsic viscosity in this mixed Θ-solvent has also been determined for seven molecular weights. These direct measurements of unperturbed dimensions are compared with previous estimates obtained by extrapolation to low *M* where long-range excluded volume interactions are minimized. The ratio of the thermodynamic and hydrodynamic dimensions is compared with those reported for more flexible polymers.

Introduction

We have previously reported estimations of the unperturbed dimensions of dialkyl- and arylalkyl-substituted organosilane polymers.[1,2] These have been based exclusively on measurements of these polymers in relatively good solvents in which long-range excluded volume interactions are present. Estimation of the dimensions under "Θ-conditions" was done by extrapolation to low molecular weight where long-range interactions are negligible. In this study, we report light scattering and viscometry measurements on poly(di-*n*-hexylsilane) (PDNHS) in a mixed solvent of 2-propanol and hexane (iPrOH/hexane). This mixed solvent (with 41.3 wt % iPrOH) is a Θ-solvent for PDNHS at room temperature; that is, the second virial coefficient, A_2, measured by light scattering is zero. The results of these direct measurements of the unperturbed dimensions are compared with the previous estimates from data obtained in marginal to good solvents such as tetrahydrofuran, hexane, and toluene.

The global size of the polymer coils in dilute solution was measured using three techniques: (1) intensity (static or classical) light scattering, in which the intramolecular interference of the scattered light provides a measure of the root-mean-square radius of gyration, R_g; (2) dynamic light scattering (quasielastic light scattering, photon correlation spectroscopy), in which the time correlation of the fluctuations in scattered light yields a diffusion coeffcicent (D_0); and (3) viscometry to obtain the intrinsic viscosity, $[\eta]$. These three size parameters are compared with previous estimates and also with predictions of current theories.

Experimental Methods

Synthesis. The di-*n*-hexyl polysilane polymers are, with one exception, the same materials used in ref 1 and were a gift from Dr. Robert Miller. They were synthesized as described previously.[3]

Viscometry. Dilute solution viscometry was performed with Ubbelohde semimicro dilution capillary viscometers (size 50, Cannon Instrument Co.). Viscometers were held in a constant-temperature bath, and dilutions were made in the viscometer. Flow times were measured using an optical assembly with an automatic timer and were >150 s in all cases. Solutions were introduced into the viscometer using a syringe equipped with a 0.2-μm Fluoropore filter (Millipore Corp.). Three to four concentrations were measured for each molecular weight, with concentrations selected so that $1.2 < \eta_{rel} < 1.6$; $\eta_{rel} \equiv \eta/\eta_0$, with η and η_0 the solution and solvent viscosities, respectively. Determination of the intrinsic viscosity, $[\eta]$, was made by extrapolation of the reduced and specific viscosities using the Huggins and Kraemer relations as is usual; the intercepts from these two extrapolations were the same within experimental uncertainty.[1] Results are listed in Table 1. Results for samples 2-4, 7, and 11 were reported previously.[1] As noted previously, for very high *M* samples such as sample 11, extrapolation to zero shear rate was required to obtain the limiting $[\eta]$.

Light Scattering. Measurement of the intensity of light scattered from dilute solutions of five of the samples was done using both a KMX-6 low-angle light scattering photometer (LDC Analytical) and a Brookhaven 200 SM goniometer. Generally, five or six concentrations $0.05c^* < c < 0.2c^*$, where c^* is the

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Table 1. Molecular Parameters of PDNHS in 41.3 wt % iPrOH/Hexane

sample	M_w	$[\eta]$ (mL/g)	$R_{g,\eta}$ (nm)	$R_{g,z}$ (nm)	$R_{g,w}$ (nm)	$10^3\langle r^2\rangle_0/M$ (nm^2)	10^7D_0 (cm^2/s)	R_h (nm)	$-k_D{}^c$ (mL/g)	$-k_D{}^\phi$	$\rho \equiv R_{g,w}/R_h$
PDNHS-1A	20 000	12.3	4								
PDNHS-2	181 000	54.7	14								
PDNHS-3	318 000	80.5	19	22	18	6	3.1	14			1.28
PDNHS-4	640 000	129	28	33.7	28	7.4	2.14	20.4	48	1.43	1.37
PDNHS-7	1 620 000	195	44	52.8	43	6.8	1.32	33.1	84	1.49	1.30
PDNHS-8A	3 760 000	360	72	82	68	7.4	0.78	56			1.21
PDNHS-11	8 750 000	610	113	125	102	7.1	0.51	80	213	1.44	1.27

overlap concentration (taken as $[\eta]^{-1}$) were prepared. Solutions were filtered through a 0.5-μm Fluoropore filter (Millipore Corp.) directly into the KMX-6 cell and collected in 14-mm-diameter culture tubes for subsequent measurements in the Brookhaven instrument. The culture tubes were cleaned before use by inverting them over refluxing 2-propanol for 2–3 h.

The weight-average molecular weight M_w, second virial coefficient A_2, and z-average root-mean-square radius of gyration $R_{g,z}$ were calculated from the concentration and wave vector dependence of the reciprocal scattering in the usual manner:

$$\frac{Kc}{R_\theta} = \frac{1}{M_wP(\theta)} + 2A_2c + ... \tag{1}$$

where R_θ is the measured excess Rayleigh factor for a solution of concentration c at a scattering angle θ,

$$K = \frac{4\pi^2n^2(\mathrm{d}n/\mathrm{d}c)^2}{\lambda^4N_A} \tag{2}$$

and

$$P(q)^{-1} = 1 + q^2R_{g,z}{}^2/3 + ... \tag{3}$$

where the scattering vector $q = (4\pi n/\lambda)\sin(\theta/2)$, with n denoting the refractive index, and λ the vacuum wavelength of light. The refractive indices of hexane and 2-propanol are very similar, 1.375 and 1.377, respectively, so that dn/dc in the mixed solvents is the same as that measured in hexane, 0.177 mL/g.[1] Measurements in the Brookhaven instrument were made at 11 scattering angles, $15 < \theta < 150°$. Concentrations were sufficiently dilute that the angular dependence was independent of concentration. Values for R_g were calculated from eq 3 and averaged over all concentrations. Although values of R_g were quite large for the highest molecular weights, a linear dependence of the reciprocal scattering intensity on q^2 was observed for all samples. This is due to the compensating effect of the polydispersity on the expected curvature of the Debye scattering function for a random coil.[4] For measurements in the mixed Θ-solvents of 41.3 wt % iPrOH/hexane, the concentration dependence was negligible, and M_w was obtained from the average of both R_θ at $\theta = 4°$ from the low-angle KMX-6 instrument and R_0 extrapolated from the series of angles measured with the Brookhaven photogoniometer. Although the molecular weights are quite high, there was no discernible difference between $R_{4°}$ and R_0. A Zimm plot showing both the linear q^2 dependence and the negligible concentration dependence for the highest molecular weight sample in the mixed Θ-solvent of 41.3 wt % iPrOH/hexane is shown in Figure 1.

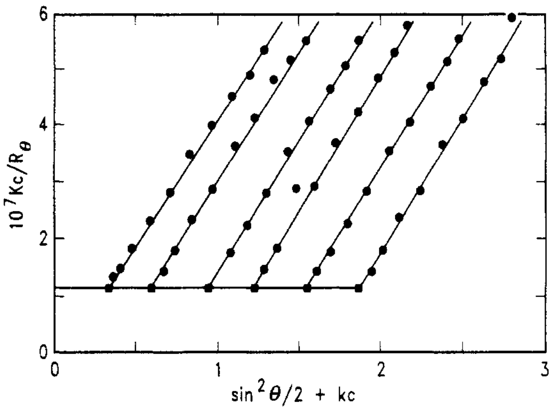

Figure 1. Zimm plot of light scattering data for PDNHS-11 in the mixed Θ-solvent iPrOH/hexane.

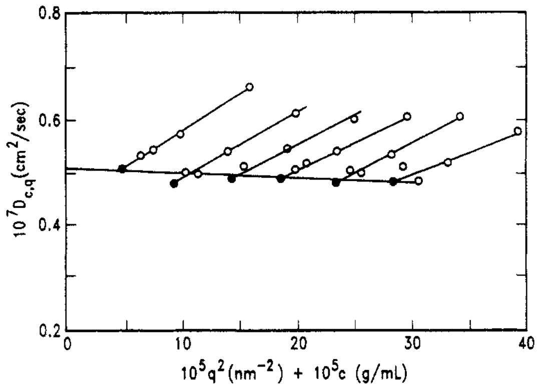

Figure 2. Dynamic light scattering "Zimm plot" for PDNHS-11 in the mixed Θ-solvent iPrOH/hexane.

Dynamic Light Scattering. The time correlation function ($C(t)$) of the light scattered from the same solutions was measured using a Brookhaven correlator. The $C(t)$ were analyzed by the method of cumulants:

$$\ln\left(\frac{C(t)}{B} - 1\right)^{1/2} = \ln b^{1/2} - \Gamma t + \frac{\mu_2t^2}{2} \tag{4}$$

neglecting higher order terms. The baseline B was taken as the average of four delay times 1028 times the last delay time in the measured $C(t)$. For these samples, this "measured" baseline was within 0.1% of the calculated baseline for all runs. In eq 4, b is an optical constant, equal to ~0.4 for this optical arrangement. The mutual diffusion coefficient $D_{c,q}$ at concentration c and scattering vector q was then calculated from the first cumulant, Γ:

$$D_{c,q} = \Gamma_{c,q}/q^2 \tag{5}$$

The normalized second cumulant, μ_2/Γ^2, which for these samples can be taken as an indication of the sample polydispersity, was equal to 0.3 ± 0.1. Measurements were made at 15, 20, 30, and 45° scattering angle. Figure 2 shows the concentration and q^2 dependence observed for the highest molecular weight sample. In general, in the limit $c \rightarrow 0$, the q^2 dependence may be expressed as

$$D_q = D_0[1 + Cq^2R_{g,z} + ...] \tag{6}$$

with C around 0.2 for polydisperse linear chains.[5] The data shown in Figure 2 yield $C = 0.18$. For lower molecular weights, as $R_{g,z}$ becomes smaller and D_0 becomes larger, the q^2 dependence becomes experimentally insignificant in this range of q. The limiting diffusion coefficient D_0 obtained by extrapolating $D_{c,q}$ to $q = 0$ and $c = 0$ was used to calculate the Stokes radius R_h from

$$D_0 = \frac{k_bT}{6\pi\eta_0R_h} \tag{7}$$

The solvent viscosity, η_0, for 41.3 wt % iPrOH/hexane was measured by a capillary viscometer to be 0.496 cP at 25 °C.

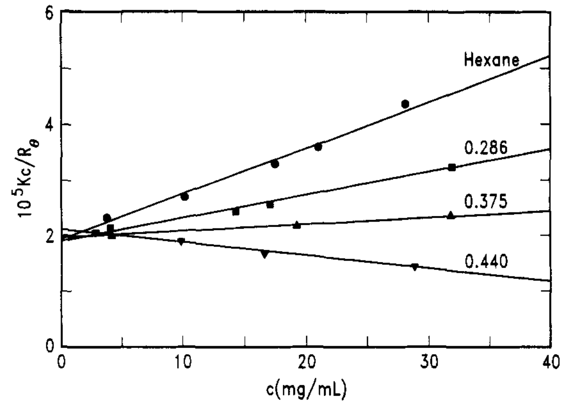

Figure 3. Low-angle light scattering ($\Theta = 4°$) as a function of concentration for a low-M sample of PDNHS ($M_w = 50\,000$) in hexane and three mixtures of iPrOH/hexane. The volume fraction of hexane is indicated on each curve.

Determination of Θ-Solvent. Since hexane was previously shown to be a good solvent for PDNHS and 2-propanol (iPrOH) is known to be a nonsolvent, it could be surmised that an A_2 of 0 would be found at a certain volume fraction of iPrOH in the absence of specific cosolvent effects. The combination of hexane and 2-propanol was chosen because of the nearly identical refractive index of these two solvents, which simplifies the interpretation of the light scattering data from a three-component system. To obtain a reasonably precise estimate of the volume fraction of iPrOH at which $A_2 \rightarrow 0$, low-angle light scattering measurements of a low molecular weight sample of PDNHS ($M_w = 28\,000$) extending to $c^*/2$ were carried out in hexane and three different volume fractions of iPrOH/hexane, as shown in Figure 3. The solvent mixture of 41.3 wt % iPrOH in hexane resulted in an A_2 of 0, and this solvent was used for all subsequent measurements. For all other samples, A_2 was zero within experimental uncertainty (see Figure 1).

Results and Discussion

Polydispersity. Table 1 summarizes the molecular parameters obtained for all the PDNHS samples measured in the mixed Θ-solvent. As discussed in ref 1, these polymers are polydisperse in M, with $M_w/M_n = 2 \pm 0.4$ and $M_z/M_w = 1.5 \pm 0.1$, so that the molecular weight distribution may be approximated by the Flory–Schulz, or most-probable distribution. The quantities measured experimentally by viscometry and light scattering are averaged over the distribution. In the case of R_g measured by intensity light scattering, the z-averaged mean-square radius, $R_{g,z}{}^2$ is obtained. For Gaussian coils in a Θ-solvent

$$R_{g,z}{}^2 = kM_z \tag{8}$$

where k is independent of M, so that calculation of $R_{g,w}$ for comparison with M_w is straightforward. Equation 8 is valid for Gaussian coils independent of the shape of the molecular weight distribution. The averages obtained for the Stokes radius, R_h, from dynamic light scattering and for $[\eta]$ are more complicated and are not simply related to any of the standard molecular weight averages.[6] However, for distributions similar to the most probable, both $[\eta]$ and R_h are most closely related to M_w (within 6%), and further correction is within the uncertainty in the data.

Radius of Gyration and Stokes Radius. Figure 4 is a log–log plot of $R_{g,w}$ and R_h *versus* M_w for the five molecular weights measured by static and dynamic light scattering. The molecular weight dependence is given by

$$R_{g,w} = 0.0264M_w{}^{0.52} \tag{9}$$

for the weight-average root-mean-square radius of gyration, and

$$R_h = 0.016M_w{}^{0.54} \tag{10}$$

for the Stokes radius, respectively. The exponents for both R_g and R_h are somewhat larger than the values of 0.5 expected for Gaussian coils in a Θ-solvent.

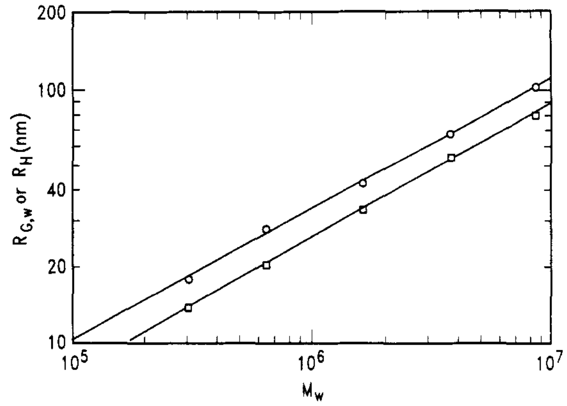

Figure 4. $R_{g,w}$ (○) and R_h (□) as a function of M_w for the five samples of PDNHS measured by static and dynamic light scattering.

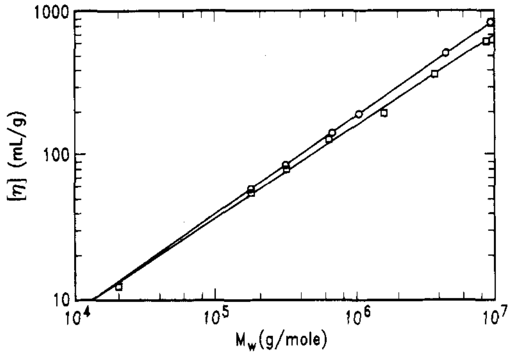

Figure 5. $[\eta]$ as a function of M_w for PDNHS samples in THF (○)[1] and in the mixed Θ-solvent iPrOH/hexane (□).

The $R_{g,w}$ values are larger than the R_h values by a factor ρ which is independent of M, as has been observed for many polymers.[7] This factor ρ is also listed in Table 1 and the average value is 1.29 ± 0.06, quite consistent with literature values for well-studied polymers such as polystyrene and poly(methyl methacrylate) in Θ-solvents.[8-10]

The concentration dependence of $D_{c,q}$ in the limit $q \rightarrow 0$ was determined for three samples which were available in sufficient quantity. Values of $k_D{}^\phi$, in which concentration is expressed in terms of the volume fraction ϕ, are listed in Table 1 and were calculated from $D_{c,0}$:

$$D_{c,0} = D_0(1 + k_D{}^c c) \tag{11}$$

and

$$k_D{}^\phi = \frac{k_D{}^c M}{N_A V_h} \tag{12}$$

with $V_h = {}^4/_3(\pi R_h{}^3)$. As has been observed experimentally for several flexible polymers in Θ-solvents,[11,13] values of $k_D{}^\phi$ listed in Table 1 are negative and independent of M.

Intrinsic Viscosity. Figure 5 is a log–log plot of $[\eta]$ *versus* M_w for PDNHS both in the mixed Θ-solvent and in the marginal solvent tetrahydrofuran (THF) reported previously.[1] The Mark–Houwink–Sakurada expression obtained by a linear regression fit to the data in iPrOH/

hexane is

$$[\eta] = 0.024 M_w^{0.63} \qquad (13)$$

The exponent $a = 0.63$, while smaller than the value of 0.67 obtained in THF (a better solvent[1]), is also significantly larger than the value of 0.5 expected for a Gaussian coil in a Θ-solvent, as was noted above with R_g and R_h. The root-mean-square radius of gyration may be calculated from $[\eta]$ using the Fox–Flory expression:[14]

$$[\eta] = \Phi \frac{(6R_{g,w}^2)^{3/2}}{M} \qquad (14)$$

Using $\Phi = 2.5 \times 10^{23}$ established from many experimental studies, we obtain the values listed in Table 1. For the polymers of sufficiently high M to permit measurement of $R_{g,z}$ by light scattering, the values obtained from $[\eta]$ and those from light scattering (corrected to $R_{g,w}$) are in good agreement.

Selective Solvation. Although the macroscopic second virial coefficient, A_2, is zero, the mixed Θ-solvent presents the possibility that individual polymer coils may be selectively solvated by the good solvent hexane and thus exhibit some departure from their true unperturbed dimensions. In the case where the two solvents have different refractive indices, the degree of selective solvation may be determined by measuring dn/dc at constant solvent composition and at constant chemical potential.[15] The dn/dc at constant chemical potential is required to obtain the true M_w from light scattering in a mixed solvent when the solvents have different refractive indices.[16] In the simpler case where the two components of the mixed solvent have the same refractive index (as here), determination of M_w and A_2 is greatly simplified, but no information about selective solvation may be obtained. If the PDNHS is selectively solvated by the better solvent hexane, the dimensions measured may not be equivalent to Θ-solvent dimensions. Measurements in a single Θ-solvent would be helpful.

Unperturbed Dimensions. With the global dimensions of a series of PDNHS polymers established by a variety of hydrodynamic and scattering measurements under macroscopic Θ conditions, the unperturbed dimensions may be estimated. The ratios $\langle r^2 \rangle_0/M$ for all but the lowest M sample are listed in Table 1 and are essentially independent of M, giving an average value of $(6.9 \pm 0.5) \times 10^{-3}$ nm^2. This is significantly larger than the value of 5.4×10^{-3} nm^2 which was obtained from $[\eta]$ measurements in the marginal solvent THF extrapolated to $M = 0$ to eliminate long-range interactions.[1] In contrast, we reported a more recent study of PDNHS using size exclusion chromatography with a multiangle light scattering detector which yielded an even higher value of $\langle r^2 \rangle_0/M$ than that obtained here: 9.0×10^{-3} nm^2.[2] In that study, measurements of R_g of PDNHS fractions eluting from a chromatographic column in THF were corrected for long-range excluded volume interactions by extrapolation to low M as was done for the $[\eta]$ measurements.

While the complications of excluded volume interactions, polydispersity, selective solvation, and uncertain hydrodynamics may make an exact determination of the unperturbed dimensions of PDNHS elusive, the consistency of both the scattering and hydrodynamic measurements and the approximation of Θ-conditions increases our confidence in the value reported here.

Effect of Equilibrium Stiffness. As discussed above, all three measurements of the global dimensions of the PDNHS polymer as a function of M displayed larger values of the exponents than the 0.5 expected for Gaussian coils in a Θ-solvent. Figure 6 shows the $[\eta]$ data in iPrOH/hexane along with the calculated $[\eta]$ using the analytical expressions for the Kratky–Porod wormlike chain developed by Yamakawa and Fujii.[17,18] For this calculation, a statistical segment length (or Kuhn length, l_k) of 7 nm was used, based on the experimental value of $\langle r^2 \rangle_0/M$. The diameter d of the equivalent cylinder was estimated as 0.75 nm:

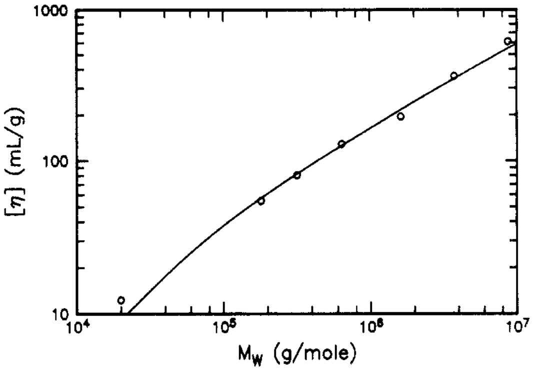

Figure 6. $[\eta]$ in the mixed Θ-solvent iPrOH/hexane as a function of M_w along with the calculated curve from the Yamakawa–Fujii theory for a wormlike chain[17] with $M_L = 995$ nm^{-1}, $l_k = 7$ nm, and $d = 0.75$ nm.

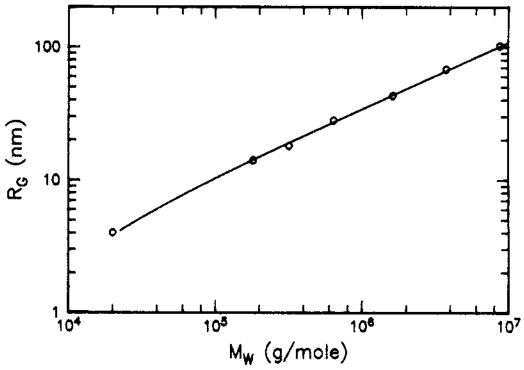

Figure 7. $R_{g,w}$ as a function of M_w along with the calculated curve for the wormlike chain[19] with $M_L = 995$ nm^{-1} and $l_k = 7$ nm.

$$v_{sp} = \frac{\pi d^2 N_A}{M_L} \qquad (15)$$

using a specific volume of 1.1 mL/g[1] and mass per unit length M_L of 995 nm^{-1}. This M_L was estimated as m_0/l_{eff}, where m_0 is the molecular weight of the repeat unit of PDNHS (198) and l_{eff} is the projection of the Si–Si bond onto the vector of the fully extended chain. The calculated $[\eta]$ are insensitive to small changes in d. The theoretical curve in Figure 6 clearly shows a steeper slope at lower M, reflecting the chain stiffness. The experimental data are insufficient to confirm this behavior for PDNHS. However, the portion of the theoretical curve for $10^5 < M_w < 10^7$ is nearly linear and in good agreement with the data. In this region, d ln $[\eta]$/d ln M = 0.6, indicating that the experimental exponent of 0.63 can be explained even in the absence of long-range interactions due to the extended conformations of the PDNHS polymer. For polymers with d/l_k of ~0.1, an exponent of 0.5 for d ln $[\eta]$/d ln M is not attained until $L > 1000 l_k$.[18,19]

Figure 7 shows the experimental values for $R_{g,w}$ as a function of M along with the theoretical curve calculated from the Benoit–Doty expression for R_g of a Kratky–Porod wormlike chain:[20]

$$R_g{}^2 = \left(\frac{l_k L}{6}\right) - \frac{l_k{}^2}{4} + \left(\frac{u_k{}^3}{4L}\right)\left[1 - \left(\frac{l_k}{2L}\right)(1 - e^{-2L/l_k})\right] \quad (16)$$

The $R_{g,w}$ values for the two lowest molecular weight samples are those estimated from $[\eta]$. The slight curvature in the theoretical curve would not be detectable in experimental data, and a linear fit of the theoretical values yields an exponent of 0.52, in good agreement with the experimental data.

The consistency of the experimental results with the theoretical predictions for the wormlike chain model suggests that even for polymers with only moderately large characteristic ratios, such as PDNHS, adherence to the Gaussian exponents of 0.5 may not be reached until extremely high M. This is particularly true for the intrinsic viscosity.

Comparison with Theoretical C_∞. A number of workers have reported calculated characteristic ratios, C_∞, of some polysilane polymers, notably, poly(dimethylsilane),[21] poly(phenylmethylsilane),[22,23] and poly(silastyrene),[23,24] the silicon analog of polystyrene.

$$C_\infty \equiv \frac{\langle r^2 \rangle_0}{n l^2} \quad (17)$$

with n and l the number and length of backbone bonds. Although conformational calculations have been reported for PDNHS,[25,26] they have not been extended to obtain values for C_∞. The limiting C_∞ reported by Welsh and co-workers for the dimethyl-substituted polysilane is 15. The average unperturbed dimensions $\langle r^2 \rangle_0/M$ of $(6.9 \pm 0.5) \times 10^{-3}$ nm^2 reported above may be used to estimate an experimental C_∞ of 26 ± 5 for PDNHS, using m_0 per repeat unit of 198 and the Si–Si bond length l of 0.235 nm. The larger C_∞ for PDNHS relative to the dimethyl-substituted analog is quite reasonable, since the larger hexyl substituents may be expected to further inhibit rotational freedom.

Summary

Global chain dimensions of PDNHS in a mixed Θ-solvent of iPrOH/hexane have been determined by independent techniques of static and dynamic light scattering and viscometry. All molecular size parameters are consistent with a C_∞ of 26 ± 5 or, equivalently, a statistical segment length l_k of 7 nm, about 35 bonds. The experimental parameters are consistent with a wormlike chain model and yield exponents in the molecular weight dependence which are larger than the 0.5 expected for Gaussian coils in a Θ-solvent.

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