Solution Properties of Poly(di-*n*-hexylsilane): An Estimate of Its Unperturbed Dimensions

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ABSTRACT: A series of 10 samples of poly(di-*n*-hexylsilane) spanning a molecular weight range of 10^5–10^7 were characterized by low-angle light scattering and dilute solution viscosity measurements. The weight average molecular weight, M_w, the second virial coefficient, A_2, the intrinsic viscosity, $[\eta]$, and the Huggins constant, k_H, were determined for all samples using tetrahydrofuran, a marginal to good solvent for the polymer. Determination of $[\eta]$ in the marginal to poor mixed solvent of 41.3 wt % 2-propanol/hexane was also done for five of the samples. The results were correlated according to the method of Burchard, Fixman, and Stockmayer by plotting $[\eta]/M_w^{1/2}$ vs M_w and then extrapolating to zero molecular weight to obtain the product of the Flory viscosity constant, Φ, and $(\langle r^2\rangle_0/M)^{3/2}$. Here $\langle r^2\rangle_0$ is the mean square end-to-end distance of the polymer unperturbed by excluded volume interactions. Using a value of Φ determined from many experimental studies, these results lead to a characteristic ratio, C_∞, of 19 and a Kuhn statistical segment length, l_k, of 5.4 nm. The data in THF are also well represented by a Mark–Houwink–Sakarada equation of $[\eta] = 0.0170M_w^{0.672}$. Some potential limitations of the Burchard–Stockmayer–Fixman plot and similar methods for obtaining the unperturbed dimensions of a polymer chain are discussed.

Introduction

The group of high molecular weight polymers comprised of an all silicon backbone with two alkyl and/or aryl substituents on each silicon atom are known collectively as polysilanes or polysilylenes.[1,2] Although first synthesized in the 1920s, these materials have received increasing attention recently in industrial and academic laboratories with the successful synthesis of high molecular weight soluble polymers. Their unusual properties suggest potential applications as lithographic materials, precursors to silicon carbide, photoconductors, and as nonlinear optical materials.[3,4] The existence of the electronic absorption band at wavelengths above 300 nm, which is not usually observed for σ-bonded structures, has led to the characterization of these and similar materials such as the polygermanes as "σ-conjugated".[5,6] An area which has received significant attention is the thermochromism of the electronic absorption band observed in the solid state and in solution.[7–9] The expected delocalization of the electronic absorption along the backbone suggests that shifts in the electronic absorption spectrum may reflect conformational changes in the polymer. Wide-angle X-ray diffraction,[10] vibrational spectroscopy,[9,11,12] and ^{13}C and ^{29}Si NMR[13,14] have been used to investigate the structures associated with the electronic absorption bands in the solid state. In solution, the shift of the absorption band to longer wavelength at low temperatures is less understood. Light and neutron scattering methods to investigate molecular dimensions at these low temperatures have been complicated by aggregation of the polymer.[15,16] The solution behavior of the polysilanes is very similar to that reported for a group of poly(diacetylenes) which also display thermochromism, as well as solvatochromism.[17] Several theoretical studies of equilibrium configurations of polysilanes have also been done using conformational energy calculations.[18–20]

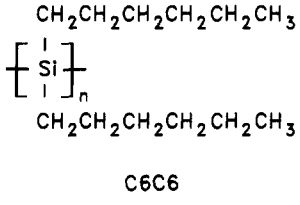

Figure 1. Repeat unit of poly(di-*n*-hexylsilane).

In the present study light scattering and dilute solution viscometry experiments at a temperature above the usual thermochromic transition were used to measure the molecular weight and dimensions of poly(di-*n*-hexylsilane) (PDNHS). The data so obtained were analyzed by the Burchard–Stockmayer–Fixman technique to determine the dimensions of the polymer unperturbed by excluded volume interactions.[21,22] The structure of the repeat unit is shown in Figure 1. PDNHS has been studied in more detail than other polysilanes, and in its equilibrium behavior is representative of many of the dialkyl derivatives. In earlier work reported by one of us,[23] a single sample of PDNHS was photochemically degraded to produce a series of molecular weights. The characteristic ratio, C_∞, was estimated to be approximately 20, and the Kuhn statistical segment length, l_k, to be approximately 6 nm. These estimates were obtained using substantial corrections for the effects of polydispersity and excluded volume. In this study, 10 samples of PDNHS with $10^5 < M_w < 10^7$ were studied, covering 2 decades in molecular weight. The hydrodynamic size of the polymer in solution was determined by viscometry. Although hydrodynamic techniques are an indirect measurement of the static molecular dimensions, they are frequently subject to less error than determining the radius of gyration by light scattering and are less affected by polydispersity.

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Table I
dn/dc of PDNHS in Various Solvents

solvent	n	dn/dc (mL/g) ±3%
hexane	1.375	0.177
THF	1.405	0.138
cyclohexane	1.427	0.123
toluene	1.496	0.044

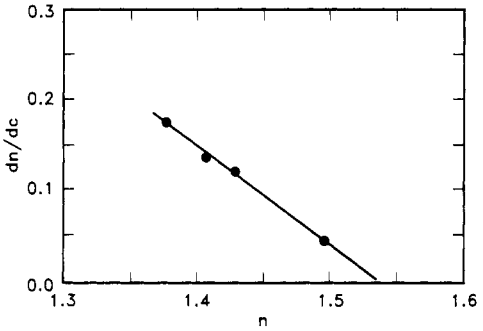

Figure 2. Dale–Gladstone relation (eq 2 in text) for PDNHS in four solvents.

Experimental Methods

Light Scattering. Light-scattering measurements were made using a Chromatix KMX-6 photometer (LDC Analytical). Solution concentrations in tetrahydrofuran (THF) varied from 0.06 to 8 mg/mL. The excess Rayleigh factor, (R_Θ), of five concentrations were measured for each sample. Solutions were introduced into the flow-through cell with the aid of a syringe pump equipped with a 0.5-μm Fluoropore filter (Millipore Corp.). The 6–7° annulus and 0.2-mm field stop were used, resulting in a scattering angle, Θ, of 4.6°, which may be assumed equivalent to the zero scattering angle for these samples. The weight average molecular weight, M_w, and second virial coefficient, A_2, were determined from a linear least-square regression fit to

$$\left[\frac{Kc}{R_0}\right]^{1/2} = \frac{1}{M_w^{1/2}} + A_2 M_w^{1/2} c \qquad (1)$$

where $K = 4\pi^2 n^2 (dn/dc)^2/\lambda^4 N_A$, with n the refractive index of the solvent, λ the wavelength of the incident light (632.8 nm), (dn/dc) the differential refractive index increment, and N_A Avogadro's number. This "square-root" expression has been suggested several times in the literature as a graphical aid to extend the range of c within which linearity of the concentration dependence is observed.[24,25]

dn/dc. The differential refractive index increment (dn/dc) was measured using a Chromatix KMX-16 (LDC Analytical) laser differential refractometer at 623.8 nm and 25 °C. Five concentrations, 2 mg/mL < c < 10 mg/mL, of PDNHS in hexane, THF, toluene and cyclohexane were measured. The results are listed in Table I. As previously noted,[16] the dn/dc reported earlier by one of us[23] for PDNHS in THF is incorrect. The dependence of dn/dc on the refractive index of the solvent, n, is given by the Dale–Gladstone relation:[26]

$$dn/dc = v(n_P - n) \qquad (2)$$

where v is the specific volume of the polymer in the solvent and n_P is the refractive index of the polymer. Figure 2 is a plot of dn/dc versus n of the solvents measured and yields v = 1.08 mL/g and n_P = 1.54. The specific volume of 1.08 mL/g is in good agreement with the film density of 0.924 g/mL.[27]

Size-Exclusion Chromatography. Size-exclusion chromatography was carried out using a Waters 150C, equipped with a set of four (PLGel, Polymer Laboratories) columns maintained at 40 °C, which were 30 cm in length, with the separation range specified as 10^6, 10^5, 10^4, and 10^3 Å (10-μm sample particle size). The mobile phase used was THF. A 150-μL sample of a 2.5 mg/mL solution was injected for each analysis. The flow rate was 1.0 mL/min. The columns were calibrated with a series of 15 narrow distribution polystyrene standards for calculation of molecular weight averages "relative to polystyrene", indicated as M_w^{PS}, M_n^{PS}, etc. The 15 calibration points were fit in a semilog plot of log M versus elution volume with a third-order polynomial expression. The signal from the refractometer were monitored by a PC-XT with SEC software from Nelson Analytical.

Viscometry. The viscosity of solutions of PDNHS were determined with Cannon–Ubbelohde viscometers thermostatted at 25 and 30 °C, respectively. Solutions were prepared in THF and in a mixed solvent of 41.4 wt % 2-propanol in hexane (iPrOH/hexane). The solution concentrations were prepared at about $^1/_2$ the overlap concentration and were then further diluted in five stages to about $^1/_{10}$ the overlap concentration. The data so obtained was analyzed with a least-square procedure using the two leading terms in the Huggins' and Kraemer's relations:[28,29]

$$\frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2 c + \ldots \qquad (3a)$$

and

$$\frac{\ln \eta_{rel}}{c} = [\eta] - (^1/_2 - k_H)[\eta]^2 c + \ldots \qquad (3b)$$

The limiting $[\eta]$ and k_H from the Huggins' and Kraemer's relations agreed within 1%, and the averages are reported in Tables II and III.

Dilute solutions of very high molecular weight polymers display non-Newtonian viscosities at moderately high shear rates.[30] This *shear thinning* has been attributed to hydrodynamic interaction, excluded volume, and internal viscosity.[31] Experimental data show that the shear-rate dependence is usually negligible below a dimensionless shear rate, β, of about 0.5, defined as

$$\beta = \tau\gamma \qquad (4)$$

with γ the shear rate, and τ the characteristic relaxation time, given by

$$\tau = \frac{[\eta]M\eta_s}{N_A k_B T} \qquad (5)$$

with η_s the solvent viscosity, and the other symbols have their usual meaning. Since capillary viscometers have moderately high shear rates of 300–1000 s^{-1}, the shear dependence is expected to be significant for the highest M samples 10 and 11. For these samples, a four-bulb viscometer was used which permits determination of the viscosity at four different shear rates. The values for $[\eta]$ for these samples were obtained by extrapolation of the data to zero shear rate, as shown in Figure 3 for sample 11 in iPrOH/hexane.

Results and Discussion

Light Scattering. The results from the light scattering, SEC, and viscometry in THF are listed in Table II. $[Kc/R_\Theta]^{1/2}$ versus c for Θ = 4° are shown in Figure 4 for samples 1–7, 9, and 10; measurements of sample 8 were reported previously.[23] A plot of A_2 versus M_w is shown in Figure 5, and a linear regression fit to this data yields

$$A_2 = 0.0019 M_w^{-0.19} \qquad (6)$$

The exponent of −0.19 is consistent with the values of approximately −0.2 obtained for other flexible chain polymers. Earlier measurement of A_2 for one sample in hexane indicated that hexane is a somewhat better solvent thermodynamically than THF.[23]

Viscometry. Figure 6 is a plot of $[\eta]$ in THF versus M_w, and the Mark–Houwink–Sakurada expression, $[\eta] = KM^a$ is

$$[\eta] = 0.0170 M_w^{0.672} \qquad (7)$$

for PDNHS in THF at 25 °C, with $[\eta]$ in milliliters/gram. The exponent of 0.672 is consistent with a flexible polymer expanded in a marginal to good solvent and may be substituted into $3\nu - 1$ to obtain ν = 0.56, for the exponent ν in $R_g \sim M^\nu$. No deviation from linearity of the $[\eta]M_w$ relation was observed at the very high molecular weights

Table II
Molecular Parameters of PDNHS in THF

sample	$M_{w,SEC}$ ±5%	M_w/M_n ±20%	$M_{w,LS}$ ±6%	10^4A_2 mL mol/g² ±10%	[η] mL/g ±5%	k_h ±10%	$\frac{A_2M_w}{[\eta]}$ ±15%
1	73 000	3.4	99 000	2.12	–	–	–
2	164 000	1.45	181 000	1.83	58	0.33	0.57
3	290 000	–	321 000	1.78	87	0.36	0.66
4	500 000	1.7	650 000	1.65	133	0.34	0.81
5	550 000	1.8	700 000	1.44	143	0.40	0.70
6	900 000	1.8	1 060 000	1.44	192	0.44	0.80
7	1 150 000	2.1	1 400 000	1.28	–	–	–
8	1 900 000	2.3	2 400 000	1.13	–	–	–
9	3 600 000	1.6	4 580 000	0.97	515	0.38	0.86
10	3 000 000	2.2	9 600 000	0.92	831	0.66	1.06
11	–	–	8 500 000	0.7	–	–	–

Table III
[η] of PDNHS in 41.4 wt % iPrOH/Hexane at 30 °C

sample	[η] ±8%, mL/g
2	54.7
3	80.5
4	128.8
7	194.5
11	610

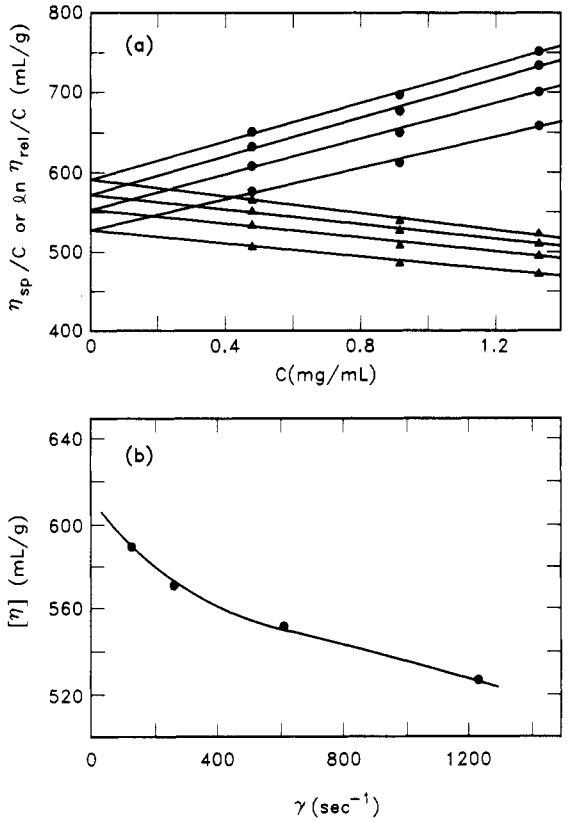

Figure 3. (a) η_{sp}/c (●) and $\ln \eta_{rel}/c$ (▲) versus c for sample 11 in 41.4 wt % iPrOH/hexane at four different shear rates. (b) [η] as a function of shear rate γ.

studied. The Huggins' coefficients, k_H, listed in Table II, are very close to the value of about $^1/_3$ usually observed for flexible polymers in good solvents. The parameter $A_2M_w/[\eta]$ has been used as an indication of excluded volume interactions.[25] This parameter is also listed in Table II and increases from about 0.6 at low M_w to about 1 at the highest M_w. This behavior is also consistent with flexible carbon backbone polymers and indicates that expansion of the chain due to excluded volume effects must be considered in determination of the chain dimensions.

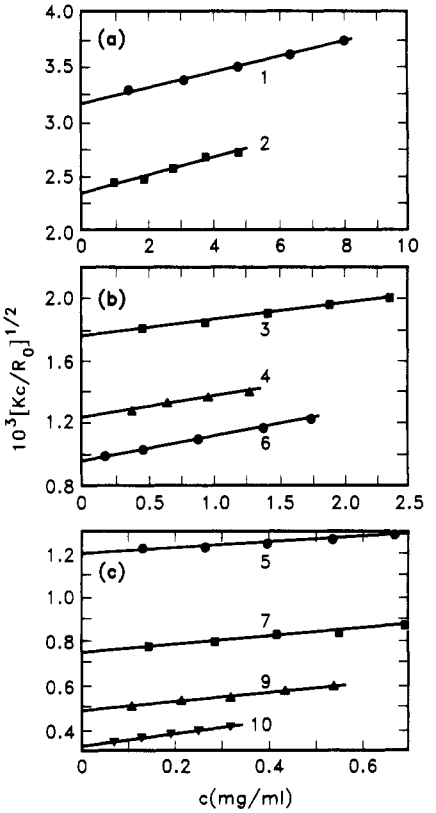

Figure 4. $[Kc/R_0]^{1/2}$ versus concentration c for nine samples of PDNHS in THF. (a) sample 1 (●) and sample 2 (■); (b) sample 6 (●), sample 4 (▲), and sample 3 (■); (c) sample 5 (●), sample 7 (■), sample 9 (▲), and sample 10 (▼).

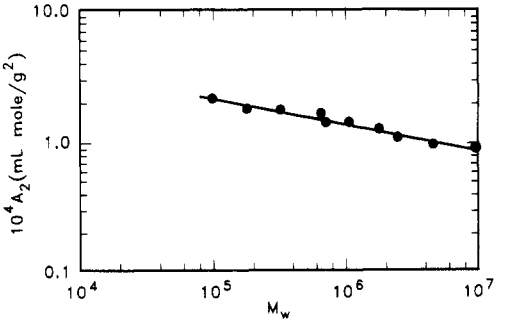

Figure 5. A_2 as a function of M_w for the 10 PDNHS samples in THF. The line is a linear log–log fit, eq 6 in the text.

Polydispersity. The ratios M_w/M_n and M_z/M_w determined from SEC are listed in Table II. The moments of the distributions were determined from the usual summation expressions, with M_i determined from the polystyrene calibration curve, and c_i from the differential

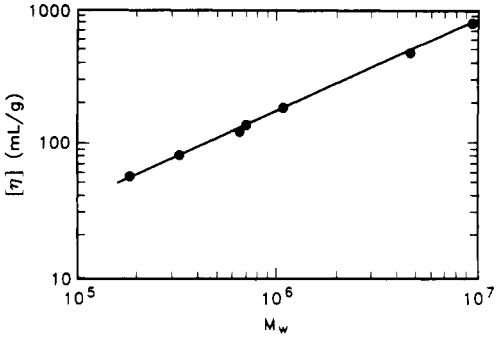

Figure 6. $[\eta]$ versus M_w for seven PDNHS samples in THF. The line is a linear log–log fit, eq 7 in the text.

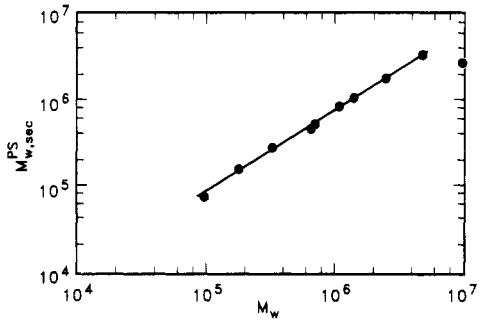

Figure 7. $M_{w,SEC}^{PS}$ determined by SEC with a PS calibration as a function of M_w determined by low-angle light scattering. The line is *not* a fit to the data, but rather is eq 9 in the text, calculated from the K and a values for PS and PDNHS in THF.

refractive index of the solution eluting at volume i. The distributions are all monomodal and similar to a most probable or Zimm–Schulz distribution with $M_w/M_n = 2$, $M_z/M_w = 1.5$, etc. Figure 7 is a plot of the weight-averaged molecular weight determined by SEC using the PS calibration curve, $M_{w,SEC}^{PS}$, as a function of the M_w determined by light scattering. A linear relation is obtained, except for the highest molecular weight, 10^7; at this molecular weight, the exclusion limit of the SEC columns is reached and $M_{w,SEC}$ is very unreliable. For most flexible polymers in good solvents, separation in SEC is determined by hydrodynamic size, which can be expressed as the product $[\eta]M$, using the Fox–Flory relation:[32]

$$[\eta] = \Phi_0 \frac{\langle r^2 \rangle^{3/2}}{M} \tag{8}$$

with Φ_0 the viscosity constant, with the subscript 0 indicating the limit of infinite hydrodynamic interaction. The molecular weight of PDNHS at an elution volume i, $M_{i,PDNHS}$, may then be expressed in terms of the molecular weight of the PS which elutes at i, $M_{i,PS}$:

$$M_{i,PDNHS} = 0.857 M_{i,PS}^{1.025} \tag{9}$$

where the Mark–Houwink–Sakurada K and a values for PDNHS in THF and PS in THF were obtained from eq 7 above and the work of Appelt and Meyerhoff,[33] respectively. Figure 7 shows that eq 9 is a good fit to the experimental points measured, so that the separation is occurring according to the hydrodynamic volume. The SEC measurements were obtained at 40 °C, and the values of $[\eta]$ for both PDNHS and PS were obtained at 25 °C. Since THF is a marginal to good solvent for PDNHS and a good solvent for PS, it is assumed that the PDNHS intrinsic viscosity depends only negligibly on temperature in the range 25–40 °C. Equation 9 may be used to estimate molecular weights of PDNHS when only SEC data obtained using a polystyrene calibration are available. In general, molecular weight averages obtained from SEC with a PS calibration will be lower than the actual PDNHS molecular weight averages, by factors of 10–30%. The Mark–Houwink–Sakurada relation for PDNHS in THF, eq 7, is obtained using M_w from light scattering and the measured $[\eta]$ of these unfractionated samples. The values for K and a are not identical to those which would be expected for narrow distribution fractions. A viscosity average molecular weight, M_η, may be defined as the average molecular weight which would yield the same K and a as for narrow distribution samples when used with the measured $[\eta]$. Flory has shown that[24]

$$\frac{M_w}{M_\eta} = \frac{2}{[(1+a)\Gamma(1+a)]^{1/a}} \tag{10}$$

for polymers with a most probable distribution. Since this ratio is independent of M, using M_η rather than M_w will only affect K in eq 7. Substituting $a = 0.672$ from eq 7 above into eq 10, we obtain $M_w/M_\eta = 1.082$, so that

$$[\eta] = 0.0179 M_\eta^{0.672} \tag{11}$$

and eq 9 then becomes

$$M_{i,PDNHS} = 0.733 M_{i,PS}^{1.025} \tag{12}$$

Unperturbed Dimensions. The identification of a Θ solvent, where $A_2 = 0$ and excluded volume effects are absent, is often difficult for a new polymer. The root-mean-square radius of gyration measured by light scattering is a z-averaged quantity and is thus strongly affected by the molecular weight distribution. With conventional light sources, measurement of $R_g < 20$ nm is impractical, and thus measurements are often confined to the higher molecular weights where the contribution of the excluded volume interaction is most significant. For these reasons, viscosity measurements in marginal to good solvents are often used to determine unperturbed dimensions.[25] In these plots, the extrapolation to $M = 0$ is assumed to remove the excluded volume interaction, a long-range effect which becomes negligible at sufficiently low M. The most well-known is the Burchard–Stockmayer–Fixman plot of $[\eta]/M^{1/2}$ versus $M^{1/2}$:[21,22]

$$[\eta]/M^{1/2} = K_\Theta + 0.51 \Phi_0 B M^{1/2} \tag{13}$$

with K_Θ the MHS K for a Θ solvent, and B the interaction parameter, related to A_2. The unperturbed dimensions, $\langle r^2 \rangle_0/M$, is then obtained from the Fox–Flory equation. The use of the Burchard–Stockmayer–Fixman (BSF) plots and other similar plots to estimate unperturbed dimensions of polymers in good solvents has been frequently challenged in the literature. Yamakawa has discussed the limitations for flexible carbon backbone polymers[25] and suggested a modification to eq 13:

$$[\eta]/M^{1/2} = 1.05 K_\Theta + 0.287 \Phi_0 B M^{1/2} \tag{14}$$

valid for $[\eta]/[\eta]_0 < 2.5$, where $[\eta]_0$ is the intrinsic viscosity in a Θ solvent. Figure 8 shows a plot of $[\eta]/M^{1/2}$ versus $M^{1/2}$ for the PDNHS samples measured in THF and iPrOH/hexane. The horizontal line indicates the upper limit for application of eq 14. A linear regression fit to the five points below this limit yields $K_\Theta = 0.100 \pm 0.007$, with eq 14. An alternative plot of $([\eta]/M^{1/2})^{5/3}$ versus $M^{1/2}$ has recently been suggested by Tanaka.[34] This latter plot has been shown to be linear for a larger range of molecular weights than the BSF plot. Since the highest molecular weights used in this study fall outside the linear range of the Tanaka plot as well, we have used the BSF plot. Both

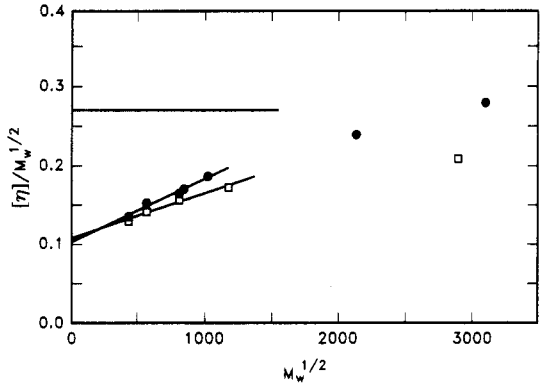

Figure 8. The BSF plot of $[\eta]/M_w^{1/2}$ versus $M_w^{1/2}$ used to estimate unperturbed dimensions from measurements obtained in marginal to good solvents: THF (●) and iPrOH/hexane (□). The lines through the data are linear fits for each solvent for M < 1 million. The horizontal line indicates the limit of applicability of eq 14 in the text.

plots yield the same value of K_Θ. Using $\Phi_0 = 2.5 \times 10^{23}$ estimated from many experimental studies, $\langle r^2\rangle_0/M = 5.43 \times 10^{-3}$ nm^2. Substituting the mass per repeat unit, $m_0 = 198$ and Si–Si bond length, $l = 0.235$ nm into

$$C_\infty = \frac{\langle r^2\rangle_0}{M}\frac{m_0}{l^2} \tag{15}$$

yields a characteristic ratio, C_∞, of 19.

Flory suggested early[35] that the viscosity plots could yield erroneous values for unperturbed dimensions due to the contributions of chain stiffness at low M. If the polymer is sufficiently inflexible so that the MHS exponent a is larger than $^1/_2$ even in a Θ solvent, then the BSF plot overestimates the excluded volume effect and the intercept will give an estimate for C_∞ which is too small. In an extreme case, the intercept may even be negative.[36] While this has not been a problem for flexible carbon backbone polymers, the PDNHS polymers are more extended, and chain stiffness may be a factor. Unfortunately, the linearity of the plot is no indication of its validity. Stockmayer[37] has also suggested caution in the use of the BSF plot and indicates that values for the exponent a greater than 0.8 are certain to yield an incorrect K_Θ, while values less than 0.7 (such as the 0.672 observed here) would probably not lead to great error. If the BSF plot is inappropriate, then the value of B obtained from the slope (eq 14, above) will be larger than expected from the measured A_2. Equation 14 yields $10^{27}B = 1.09$ from Figure 8, and the interaction parameter z may be defined as

$$z = \left(\frac{3}{2\pi}\right)^{3/2}\left(\frac{B}{A^3}\right)M^{1/2} \tag{16}$$

where $A^2 = \langle r^2\rangle_0/M$. For the lowest molecular weight sample 1, eq 16 yields $z = 0.28$ in THF with A and B from Figure 8. The second virial coefficient A_2 may be expressed as

$$A_2 = (N_A B/2)h(z) \tag{17}$$

where N_A is Avogadro's number and $h(z)$ is a function which reflects the molecular weight dependence of A_2 due to the polymer chain flexibility. The function $h(z)$ decreases from unity at $z = 0$ and may be estimated at low M from several theories for $h_0(z)$ where the subscript 0 indicates neglect of intramolecular interactions.[25] For sample 1, with $z = 0.28$, these estimates yield $h_0(z) = 0.55 \pm 0.05$, and substituting into eq 17 above, we obtain $10^4A_2 = 1.80 \pm 0.18$, in good agreement with the experimental value of $10^4A_2 = 2.1 \pm 0.2$. It appears that the PDNHS polymer is sufficiently flexible for the BSF plot to be valid.

Another possibility is that the more expanded PDNHS chains cannot be treated with the assumption of infinite hydrodynamic interaction. Both early theories[38-40] and more recent studies[41,42] predict *draining* effects in more expanded polymer chains. In this case, the Φ_0 valid for infinite hydrodynamic interaction would be too large and C_∞ would be underestimated. While a complete assessment of this effect requires comparison of dimensions obtained by hydrodynamic (e.g., $[\eta]$) and scattering techniques spanning a large range of M, we can obtain an approximate measure of the effect using the R_g reported earlier for sample 8.[23] The weight averaged radius of gyration, $R_{g,w}$, is calculated from the measured $R_{g,z}$ from light scattering with

$$R_{g,w}^2 = R_{g,z}^2\frac{(1+u)}{(1+2u)} \tag{18}$$

where $u = (M_w/M_n) - 1$.[43] Substituting into eq 8 above, and assuming $\langle r^2\rangle = 6R_g^2$, we obtain a calculated $[\eta]$ of 314 mL/g, in reasonable agreement with the value of 330 mL/g obtained from eq 7, the MHS relation. Since these measurements were obtained in marginal to good solvents at high molecular weights, it is unlikely that there is any large error in the use of Φ_0 to calculate C_∞.

A third possibility of error in the value of K_Θ obtained from the BSF plot is the contribution of a concentration-dependent χ parameter. This contribution is independent of molecular weight and cannot be eliminated by extrapolation to low M, as pointed out by Pouchly and Patterson.[44] Additional reassurance about the validity of the K_Θ intercept may be obtained by comparing values obtained in another solvent. Solvents which are thermodynamically poor for the polymer will have a smaller extrapolation error. A solvent mixture of 41.4 wt % 2-propanol in hexane is a marginal to poor solvent for PDNHS,[45] and values of $[\eta]$ at 30 °C for five samples in this solvent are listed in Table III. These data are also included in the BSF plot (Figure 8) and yield the same intercept. The C_∞ of 19 is similar to the estimate reported earlier and is also quite similar to values of 12–15 calculated by Welsh and co-workers for a dimethyl-substituted silane.[19] The increased steric hindrance to rotation which might be expected for the hexyl groups relative to methyl groups may account for the value of 19.

An alternative measure of chain flexibility is the Kuhn length, l_k, or persistence length, l_{pers}, from the Kratky–Porod wormlike chain model.[46,47] The K–P wormlike chain encompasses the two limiting cases of a random coil (or infinite molecular weight) and rigid rod. The *global* dimensions of macromolecules may generally be described as random coils if the molecular weight is sufficiently high and will show contributions of the finite flexibility at low M. While carbon backbone polymers may be described as random coils even at moderately high molecular weights, many polymers, particularly those which contain aromatic groups in the chain backbone, or can form helices, do not attain random coil behavior in the molecular weight range accessible and are characterized as *stiff*. Comparison among these polymers with such varied structures is more useful in terms of l_k or l_{pers}, which do not contain a bond length term. In the coil or high M limit, $l_k = 2l_{pers}$, and l_k may be regarded as the effective "bond" length which produces the correct unperturbed mean-square end-to-end distance for a given number of Kuhn segments, n_k:

$$\langle r^2 \rangle_0 = n_k l_k^2 \quad (19)$$

with the contour length or maximum stretched-out length of the chain, L, given by

$$L = n_k l_k \quad (20)$$

The contour length can also be defined as nl, with n and l the actual number and length of bonds, or nl_{eff} where l_{eff} is the projection of the bond onto the chain backbone, $l_{eff} = l \sin(\theta/2)$ with θ the bond angle. Using this latter definition, with a Si–Si bond angle of 116° and the $\langle r^2 \rangle_0/M$ ratio calculated above, we estimate l_k of 5.4 nm.

Summary

PDNHS has been shown to be a flexible coil in dilute solution, with a C_∞ of 19. While this C_∞ is significantly larger than the values of 8–10 observed for carbon backbone polymers,[46] the solution properties may still be treated in terms of flexible chain theories. In THF, $A_2 > 0$, and the polymer dimensions are expanded from the unperturbed state by the excluded volume interactions.

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References and Notes

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Registry No. PDNHS, 94904-85-5; $Cl_2Si((CH_2)_5CH_3)_2$ (homopolymer), 97036-67-4.