Stiffness of Polysilylenes Depending Remarkably on a Subtle Difference in Chiral Side Chain Structure: Poly{*n*-hexyl-[(*S*)-2-methylbutyl]silylene)} and Poly{*n*-hexyl-[(*S*)-3-methylpentyl]silylene}

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ABSTRACT: Light scattering and vicosity measurements were made on fractionated samples of poly{*n*-hexyl-{(*S*)-2-methylbutyl]silylene)} (PH2MBS, **1**) and poly{*n*-hexyl-[(*S*)-3-methylpentyl]silylene} (PH3MPS, **2**) in isooctane to determine their stiffness, which are expressed in terms of the persistence length *q* of Kraty and Porod. The *q* of polymer **1** is as large as 85 nm and depends only slightly on temperature, indicating that its conformation is almost rodlike, whereas the *q* of polymer **2** is 6.2 nm, its global conformation being close to a random coil. It is concluded that the global conformation of polysilylene is determined by its side chain; polysilylene with a *β*-branch is much stiffer compared to those without it.

Introduction

Polysilylenes are unique for their main chain consisting of silicon−silicon single bonds, which, unlike carbon−carbon single bonds, are easily deformed with concomitant changes in electronic structure. Indeed, it has been found that their UV spectra, optical activities, etc. change sensitively with the side chain structure and solvent conditions, which in turn determine the backbone conformation.[1−3] Recently, Fujiki[4−14] synthesized a variety of chiral polysilylenes exhibiting interesting chiro-optical properties and showed[7] that their properties are closely correlated with their global conformations using the Mark−Houwink−Sakurada viscosity exponent, which changes from 0.51 to 1.35 depending on solvent condition and side chain structure. However, it is known that the Mark−Houwink−Sakurada equation is not correct over a large molecular weight range; in other words, the exponent changes with molecular weight.[15−17] Therefore, this exponent is not necessarily the most appropriate measure for the stiffness. In this connection the global conformation of a stiff polymer is well represented by the wormlike chain of Kratky and Porod[18] with the persistence length *q* as a stiffness parameter. The persistence length is thus a better measure for stiffness, which may be correlated more directly with molecular models which may be used for theoretical treatments of electrooptical properties. However there is no systematic, accurate determination of persistence length on chiral polysilanes. In the present study, we have chosen two chiral polysilylenes presented in Figure 1, poly{*n*-hexyl-[(*S*)-2-methylbutyl]silylene} (PH2MBS, **1**) and poly{*n*-hexyl-[(*S*)-3-methylpentyl]-silylene} (PH3MPS, **2**). This is because they exhibit largely different electrooptical and global properties,

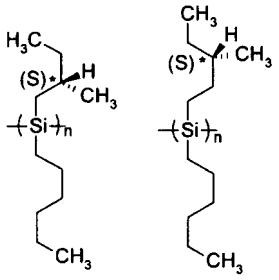

Figure 1. Polysilylenes investigated.

namely, while the former shows almost no optical activity change with temperature, the latter shows a remarkable temperature dependence of optical activity; the global conformation of the former is suggested to be much closer to rodlike than the latter,[7] which appears to be almost random coil as other polysilylene so far investigated.[19−21] For a quantitative discussion, we need their stiffness values, which are obtained by analyzing their global properties such as light scattering radii, intrinsic viscosities, etc. by the standard procedures.[15−17]

Experimental Section

For this purpose, a number of well-fractionated samples covering wide molecular weight ranges were prepared for PH2MBS by repeated fractional precipitation and for PH3MPS by gel permeation chromatography. Their molecular weights were determined by light scattering and/or sedimentation equilibrium according to the established procedures and their intrinsic viscosities were determined. The partial specific volume and specific refractive index increment were measured for both polymers under necessary solvent conditions, with the

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Table 1. Partial Specific Volumes and Specific Refractive Index Increments for Poly{*n*-hexyl-(2-methylbutyl)silylene} (PH2MBS) and Poly{*n*-hexyl-(3-methylpentyl)silylene} (PH3MPS) in Isooctane

polymer	temp/°C	d*n*/dc/cm^3 g^{-1} (λ/nm)	v/cm^3 g^{-1}
PH2MBS	20	0.197 (546)	
		0.181[a] (546)	1.049
PH3MPS	25	0.172 (546)	
	25	0.162 (633)	1.113

[a] The value for fraction 3. λ: wavelength of incident light.

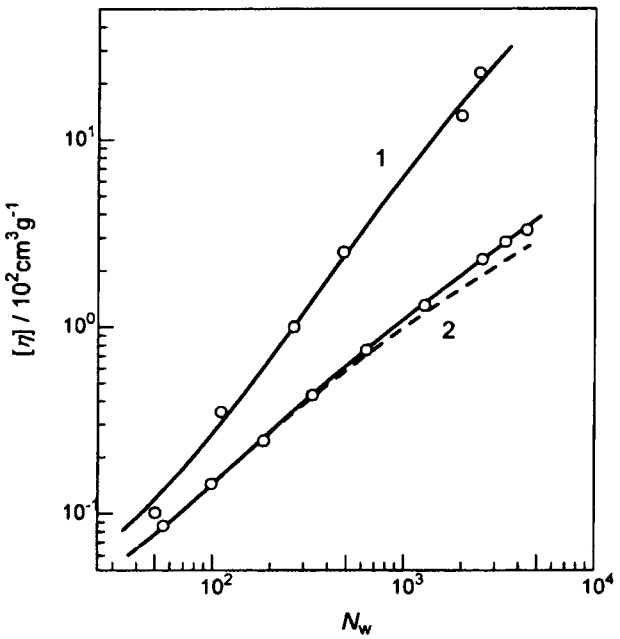

Figure 2. Double-logarithmic plots of $[\eta]$ against N_w for poly{*n*-hexyl-[(*S*)-2-methylbutyl]silylene} (PH2MBS, **1**) at 20 °C and for poly{*n*-hexyl-[(*S*)-3-methylpentyl]silylene} (PH3MPS, **2**) at 25 °C in isooctane. Key: solid curves, theoretical values[15] for the wormlike cylinder model with $q = 85$ and 6.2 nm and $d = 2.0$ nm for the two polymers; dashed curve, for the unperturbed wormlike cylinder.

results presented in Table 1. All the manipulations were done avoiding degradation by room light. The experimental details will be presented in a forthcoming publication[22] along with the temperature dependence of the global properties and chiro-optical properties.

Results and Discussion

Figure 2 shows double-logarithmic plots of intrinsic viscosity $[\eta]$ vs N_w for PH2MBS at 20 °C and PH3MPS in isooctane at 25 °C. To compare the two polysilylenes on the same basis, the molecular weight M_w is converted to the number N_w of Si atoms per molecule by $N_w = M_w/M_o$, where M_o is the molar mass per Si atom and $[\eta]$ is referred to zero shear rate. It is seen that the value of $[\eta]$ at each fixed N_w is larger for PH2MBS than for PH3MPS and the slope of the plot is about 1.3 for PH2MBS, whereas that for PH3MPS is about 0.8. These slope values are compared favorably with the preliminary values reported by Fujiki,[7] confirming his conclusion that PH2MBS is much stiffer than PH3MPS. Figure 3 shows the light scattering radii $\langle S^2\rangle_z^{1/2}$ of these polysilylenes in the same solvent conditions; the slopes of the plots are 0.83 and 0.56, respectively, for PH2MBS and PH3MPS. Thus, these data are consistent with the viscosity data. However, when examined more precisely, the data points in Figure 2 do no follow exactly a

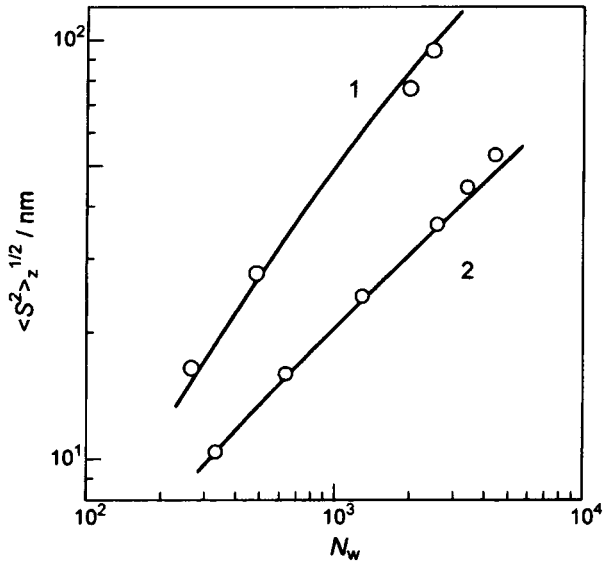

Figure 3. Molecular weight dependence of light scattering radius $\langle S^2\rangle_z^{1/2}$ for poly{*n*-hexyl-[(*S*)-2-methylbutyl]silylene} at 20 °C and for poly{*n*-hexyl-[(*S*)-2-methylpentyl]silylene} at 25 °C in isooctane. Key: solid curves, theoretical values[15] calculating the same parameters as those used in Figure 2.

Table 2. Molecular Characteristics of Poly{*n*-hexyl-[(*S*)-2-methylbutyl)]silylene}} (PH2MBS)

	$M_w/10^3$		A_2[a]			$[\eta]/10^2$
sample	LS	SED	LS	SED	$\langle S^2\rangle_z^{1/2}$/nm	cm^3 g^{-1}
1−1	456		7.0		94.2	22.8
1−2	368		5.0		76.4	13.4
1−3	89	88.5 (1.21)[b]	6.2	6.4	27.6	2.51
1−4	48.9	46.3 (1.33)	5.5	6.3	16.4	1.00
2	20.4	21.4 (1.25)	6.7	6.8		0.350
3	9.25	8.94 (1.14)		9.0		0.101

[a] In units of 10^{-4} mol g^{-2} cm^3. [b] Values in parentheses: M_z/M_w. LS: light scattering. SED: sedimentation equilibrium.

straight line over the entire N_w range examined; the slope for PH2MBS is as large as 1.5 at the lowest N_w but tends to decrease below 1.3 at large N_w, but that for PH3MPS changes from 0.90 to 0.77. It is noted however that even the slope values for PH3MPS are nearly the same as or larger than those reported for achiral polysilylenes with linear alkyl side chains.[19−21] Thus, there is no doubt that the chiral β- and γ-branched pendant groups make the polysilylene chains stiffer.

Table 2 summarizes the data for PH2MBS.[23] In this connection Miller and Michl[2] noted that the reported molecular weights mostly obtained by GPC based on polystyrene standard would be largely in error and must be checked by absolute molecular weight determination supplemented with viscosity. The situation is more or less the same, and their notion is justified by the present data, which reveal the chain dimension of polysilylene depends remarkably on polymer, so does the GPC calibration curve as well. In addition, Table 2 shows that the four lower molecular weight fractions were studied by both light scattering and sedimentation equilibrium, giving essentially the same molecular weights within experimental errors. This guarantees the validity of our procedure, providing an absolute molecular weight standard. It is seen that A_2 is rather large, indicating that isooctane is a good solvent for this polymer, which permits this rodlike polymer dissolving in it. It was found that the molecular weight distribution is reasonably narrow from the M_z/M_w values from sedimentation

equilibrium ranging between 1.14 and 1.33. For samples 2 and 3, the light scattering data were corrected for optical anisotropy according to the standard procedure,[17] yielding the optical anisotropy factor δ of 0.0068 and 0.0121. No such correction was necessary for PH3MPS as will be shown in the forthcoming article.

To discuss the stiffness in a quantitative terms, we use the wormlike cylinder model, which is characterized by the contour length L, diameter d, and persistence length q, where L is related to the molecular weight M by $L = M/M_L$, with M_L being the mass per unit length. For $[\eta]$ all these parameters are important, but d is of negligible importance for $\langle S^2 \rangle_Z$. In principle, these parameters are determined by fitting data for $[\eta]$ and $\langle S^2 \rangle$ as functions of M to the respective theoretical equations. However, in practice, this is impossible unless data covering a wide N range down to oligomers are available. For poly(dihexyl silylene) is proposed two models, all trans-planar and 7_3 helix model.[2,3,24,25] Since the all trans-planar model is stabilized only in the solid state, the 7_3 helix is more probable in solution. Therefore, we estimate M_L assuming the 7_3 helix; M_L is 935 nm^{-1} for PH2MBS and 1005 nm^{-1} for PH3MPS. It has been shown that this is a rather good approximation to a variety of stiff polymers.[17] The solid curves in Figure 2 represent the theoretical values of $[\eta]$, which fit best the data, where a small excluded-volume correction[17] is applied to the PH3MBS curve; the dashed curve is for the unperturbed chain with q of 6.2 nm. The persistence length q is 85 and 6.2 nm for PH2MBS and PH3MPS, respectively, with d being about 2.0 nm for both polymers. It is surprising that the q of these polymers differ by a factor of 14 despite the location of the methyl group on the side chain differing only one carbon atom, i.e., β-carbon and γ-carbon. This is because the methyl groups on the β-carbon atom interact more strongly with the neighboring side chains and the main chain, thus giving rise to the internal rotation about the Si−Si bonds to a helical conformation of a given screw sense. On the other hand, in PH3MPS, such interactions are weaker than in PH3MPS because the methyl groups are removed by one carbon atom more from the main chain and easy to avoid such interactions. In passing it is noted that PH2MBS is the stiffest single-chain polymer except for polypeptides in the α-helical conformation.[17] In Figure 3, solid curves represent the theoretical values for $\langle S^2 \rangle$ calculated using the same wormlike chain parameters. For both polymers, the data points appear closely to the theoretical curves; the polydispersity of the samples used has no serious effect on $\langle S^2 \rangle_z$.

Similar steric effects are also found in chiral poly(alkyl isocyanate)s; poly[(*R*)-2,6-dimethylheptyl isocyanate] is almost entirely left-handed and nearly rodlike (q = 76 nm),[26] but stereospecifically deuterated poly(hexyl isocyanate)s, at the α- and β-carbons, are partially right-handed and left-handed, respectively,[26−30] and moderately stiff (q = 40 nm). Thus, in both stiffness and optical activity, polyisocyanates[26−30] are similar to polysilylenes, but the latter are unique in that their electronic structures are correlated closely with the stiffness. In fact, PH3MPS reacts more sensitively toward external stimuli in that both q and Kuhn's dissymmetry ratio g_{abs} show remarkable temperature changes.[13,22] It is shown that the g_{abs} value of PH3MPS depends remarkably on molecular weight, which will be analyzed to provide basic molecular parameters.[22] Statistical mechanical theories based on the linear Ising model,[26,31−33] when modified to individual polymers, may be used for this purpose. Results from such analyses are expected to help develop a theory on polysilylenes based on a more general model taking into account their structural feature, which explains both aspects, thus exploiting the atomic-molecular level mechanism behind.

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