Solution Characterization of the Novel Organometallic Polymer Poly(ferrocenyldimethylsilane)

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ABSTRACT: A series of four well-defined poly(ferrocenyldimethylsilane) (PFS) samples spanning a molecular weight range of approximately 10,000–100,000 g mol^{-1} was synthesized by the living anionic polymerization of dimethyl[1]silaferrocenophane initiated with *n*-BuLi. The polymers possessed narrow polydispersities and were used to characterize the solution behavior of PFS in tetrahydrofuran (THF). The weight-average molecular weights (M_w) of the polymers were determined by low-angle laser light scattering (LALLS), conventional gel permeation chromatography (GPC), and GPC equipped with a triple detector (refractive index, light scattering, and viscosity). The molecular weight calculated by conventional GPC, with polystyrene standards, underestimated the true value in comparison with LALLS and GPC with the triple detection system. The Mark–Houwink parameter a for PFS in THF was 0.62 ($k = 2.5 \times 10^{-4}$), which is indicative of fairly marginal polymer–solvent interactions. The scaling exponent between the radius of gyration and M_w was 0.54, also consistent with marginal polymer–solvent interactions for PFS in THF. © 2000 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 38: 3032–3041, 2000

Keywords: polyferrocene; light scattering; solution properties; organometallic

INTRODUCTION

It is well known that subtle changes in the chemical architecture of an organic polymer can have a dramatic effect on the physical properties of the material. On the basis of the rich variety of coordination geometries available, the incorporation of transition metals into the main chain of a polymer is, therefore, of considerable interest. In addition, the presence of metallic elements can be expected to introduce other unusual and potentially useful physical and chemical properties.[1,2]

Ring-opening polymerization (ROP) of strained [1]ferrocenophanes provides a convenient route to novel high molecular weight poly(ferrocenes) such as poly(ferrocenylsilanes) (Scheme 1).[3,4] These materials are currently attracting interest as, for example, electroactive and charge dissipation materials and as precursors to shaped magnetic ceramics and nanostructures.[4] Although many aspects of the properties of the ring-opened poly(ferrocenes) have been well studied, a paucity of information is currently available on their solution behaviour.[3,4] To date, we have reported light scattering results for three thermally ring-opened polyferrocenes: poly(ferrocenyldibutylsilane), poly(ferrocenylmethylphenylsilane), and poly(ferrocenyldibutylgermane).[5] In each case, low-angle laser light scattering (LALLS) was used to determine the molecular weight of a representative sample. We found that in each case gel permeation chromatography (GPC), calibrated with polystyrene (PS) standards, underestimated the weight-average molecular weight (M_w) by about 30% in comparison with the value determined by

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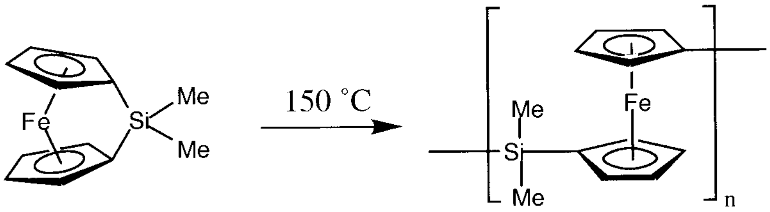


Scheme 1

LALLS. We attributed the differences in the molecular weights to differences in the coil dimension of polyferrocene in tetrahydrofuran (THF) in comparison with polystyrene.[4,5]

The discovery that the silicon-bridged [1]silaferrocenophanes undergo living anionic ROP with organolithium initiators has allowed the preparation of well-defined poly(ferrocenylsilanes) with controlled molecular weights and narrow polydispersities.[6,7] These materials are excellent candidates with which to further investigate the solution behavior of poly(ferrocenes). In addition to LALLS and conventional GPC, a new GPC detector available from Viscotek allowed us to determine many of the fundamental parameters defining the solution properties of a polymer easily. These fundamental constants defining a polymer–solvent system have not been reported before for any poly(ferrocenylsilanes). We were able to determine an absolute molecular weight, the intrinsic viscosity, and the radius of gyration (R_g) for poly(ferrocenyldimethylsilane) (PFS). Because the polymers synthesized had such narrow polydispersities, we were also able to determine the Mark–Houwink parameters of the polymer.

EXPERIMENTAL

Equipment and Materials

n-Butyllithium (1.6 M) in hexanes and dimethyldichlorosilane were purchased from Aldrich. Me_2SiCl_2 was distilled prior to use. Distilled water was degassed prior to use. THF, hexanes, diethyl ether, and tetramethylethylenediamine (TMEDA) were distilled from Na/benzophenone under prepurified N_2 immediately prior to use. All reactions and manipulations were carried out under an atmosphere of prepurified N_2 with either a standard Schlenk line or a glove box (Vacuum Atmospheres).

The 200-MHz ^1H NMR spectra were recorded on a Varian Gemini 200 spectrometer with deuterated benzene as the solvent in all cases.

Molecular weights were determined by GPC with a Waters Associates 2690 separation module that had as components an inline solvent degasser, a High Performance Liquid Chromatography (HPLC) pump, and an autosampler. The separation module was equipped with a Waters 410 differential refractometer as the concentration detector and, connected in parallel, a Viscotek T60A dual detector consisting of a right-angle laser light scattering detector with a laser source of 670 nm and a four-capillary differential viscometer. Software from Viscotek was used to analyze the data. Columns from Polymer Laboratories with pore sizes of 5×10^2, 1×10^4, and 1×10^5 Å were used with THF as the eluent at a flow rate of 1.0 mL/min. Polystyrene standards purchased from Aldrich and Viscotek were used for calibration.

Absolute molecular weights were determined by LALLS performed on a Chromatix KMX-6 instrument at a wavelength of 632.8 nm and a scattering angle of 6–7°. Measurements were carried out at room temperature with a metal cell 4.93 mm long. Each solution was filtered three times through a MILEX filter with an average pore size of 0.2 μm before injection into the cell. The refractive index increment (*dn/dc*) of the polymer solutions was obtained with a Chromatix KMX-16 differential refractometer operating at a wavelength of 632.8 nm. The instrument was calibrated with NaCl solutions.

Synthesis of Dimethyl[1]silaferrocenophane Monomer

Over a period of 5 min, neat Me_2SiCl_2 (9.2 mL, 76 mmol, 20% excess) was added dropwise to a suspension of 20.0 g of dilithioferrocene · TMEDA (64 mmol) in 400 mL of diethyl ether at −76 °C. The reaction was allowed to warm to room temperature overnight; over this time, the color changed from orange-yellow to red. The solvent, excess Me_2SiCl_2, and TMEDA were removed by vacuum (10^{-3} mmHg) over 24 h, and hexanes were added. The solution was filtered to remove LiCl, and the hexanes were removed. The product was vacuum-sublimed (10^{-3} mmHg) onto a cold probe (5 °C) at room temperature, yielding 12.3 g (80% yield) of red, crystalline [1]silaferrocenophane.

^{1}H NMR (200 MHz, C_6D_6, δ): 0.51 (s, 6H, Me), 4.08 (t, $J_{\text{H-H}} = 1.7$ Hz, 4H, cyclopentadienyl ring), 4.48 (t, $J_{\text{H-H}} = 1.7$ Hz, 4H, cyclopentadienyl ring) ppm.

Further purification was necessary to obtain a monomer of sufficient purity to be initiated anionically. This process consisted of repetitive sublimation plus recrystallization from hexanes until no spurious peaks appeared in the ^{1}H NMR spectrum with the vertical scale increased 20 times relative to the Me (0.51 ppm) peak. This cycle was usually repeated a minimum of three times. The reaction could be easily scaled up to produce about 80 g of monomer.

Anionic ROP of the [1]Silaferrocenophane with BuLi

Before the anionic polymerization of the [1]silaferrocenophane was attempted, the purity of the THF was confirmed. To a volume of THF that was the same as that used for the subsequent reactions (8 mL), a few milligrams of 1,10-phenanthroline was added as an indicator. *n*-BuLi was then added dropwise until the solution turned slightly pink. In successful polymerizations, this volume (10 μL) was less than the minimum initiator volume to be used. The synthesis of PFS_{40} is presented as a typical anionic reaction. In the glove box, 83 μL of 1.24 M *n*-BuLi (1.03×10^{-4} mol) in hexanes was added quickly to a stirred solution of 0.996 g of [1]silaferrocenophane (4.11×10^{-3} mol) in THF (8 mL) at room temperature. After 50 min, the solution changed from red to deep amber. A few drops of degassed water were added, and the solution was precipitated into hexanes. The hexanes were decanted, and the product was isolated and dried under vacuum (10^{-3} mmHg) for 24 h to yield 0.966 g of PFS (97% yield). For PFS_{100}, 33 μL of 1.24 M *n*-BuLi was added to 1.002 g of [1]silaferrocenophane, yielding 0.962 g of PFS. For PFS_{150}, 22 μL of 1.24 M *n*-BuLi was added to 1.005 g of [1]silaferrocenophane, yielding 0.965 g of PFS. For PFS_{200}, 17 μL of 1.24 M *n*-BuLi was added to 0.997 g of [1]silaferrocenophane, yielding 0.987 g of PFS.

^{1}H NMR (200 MHz, C_6D_6, δ): 0.54 {s, $[(\eta\text{-}C_5H_4)_2FeSiMe_2]_x$}, 4.10 (s, cyclopentadienyl ring), 4.26 (s, cyclopentadienyl ring) ppm.

LALLS Measurements

Static light scattering experiments in the low-angle regime were used to determine the M_w. The M_w was obtained from the Rayleigh–Debye relationship in the limit of the low scattering angle:[8]

$$Kc/R_\theta = 1/M_w + 2A_2c \tag{1}$$

where c is the concentration of the polymer, R_θ is the measured excess Rayleigh ratio, A_2 is the second virial coefficient, and K is an optical constant defined as

$$K = [4\pi^2n^2/N_0\lambda_0^4](dn/dc)^2 \tag{2}$$

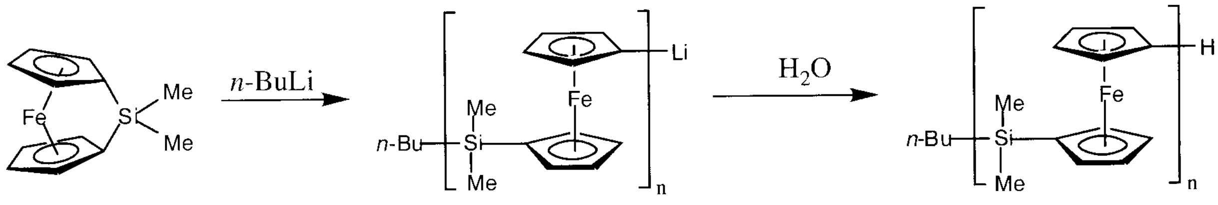
where n is the refractive index of the solvent, λ_0 is the wavelength of the laser light in vacuum, N_0 is Avogadro's number, and *dn*/*dc* is the refractive index increment of the polymer in THF. Refractive index increment measurements were carried out at five different concentrations in THF at 23 °C. A value of $dn/dc = 0.1960$ mL/g was obtained.

Molecular Weight Measurements with Triple Detection and GPC

Triple detection Size Exclusion Chromatography (SEC^3) was utilized with GPC to determine the molecular weight and intrinsic viscosity. The refractive index concentration profile, the Rayleigh ratio at 90°, and the intrinsic viscosity were measured simultaneously over the molecular weight distribution. The intrinsic viscosity was measured with a four-capillary differential viscometer directly:[9]

$$[\eta] \cong \eta_{sp}/c = 4\Delta P_s/(P_i - 2\Delta P_s) \tag{3}$$

where $[\eta]$ is the intrinsic viscosity, η_{sp} is the specific viscosity, ΔP_s is the differential pressure across the bridge, and P_i is the inlet pressure. The Rayleigh ratio measured at 90° is related to M_w by $R_\theta = KcM_wP_\theta$ at infinite dilution, where P_θ is the particle scattering function. Both $[\eta]$ and P_θ are functions of the molecular size, and the theoreti-



Scheme 2

cal relations are known for a given shape in solution. The relationship between R_g, R_h, and $[\eta]$ is[10]

$$R_h = \left[\frac{3}{4\pi}\left(\frac{[\eta]M}{0.025}\right)\right]^{1/3} \tag{4}$$

$$R_g = \left(\frac{1}{6}\right)^{1/2}\left(\frac{[\eta]M}{\Phi}\right)^{1/3} \tag{5}$$

where Φ is the Flory viscosity constant. P_θ is defined as

$$P_\theta = \frac{2}{X^2}\left[e^{-X} - (1 - X)\right] \tag{6}$$

where

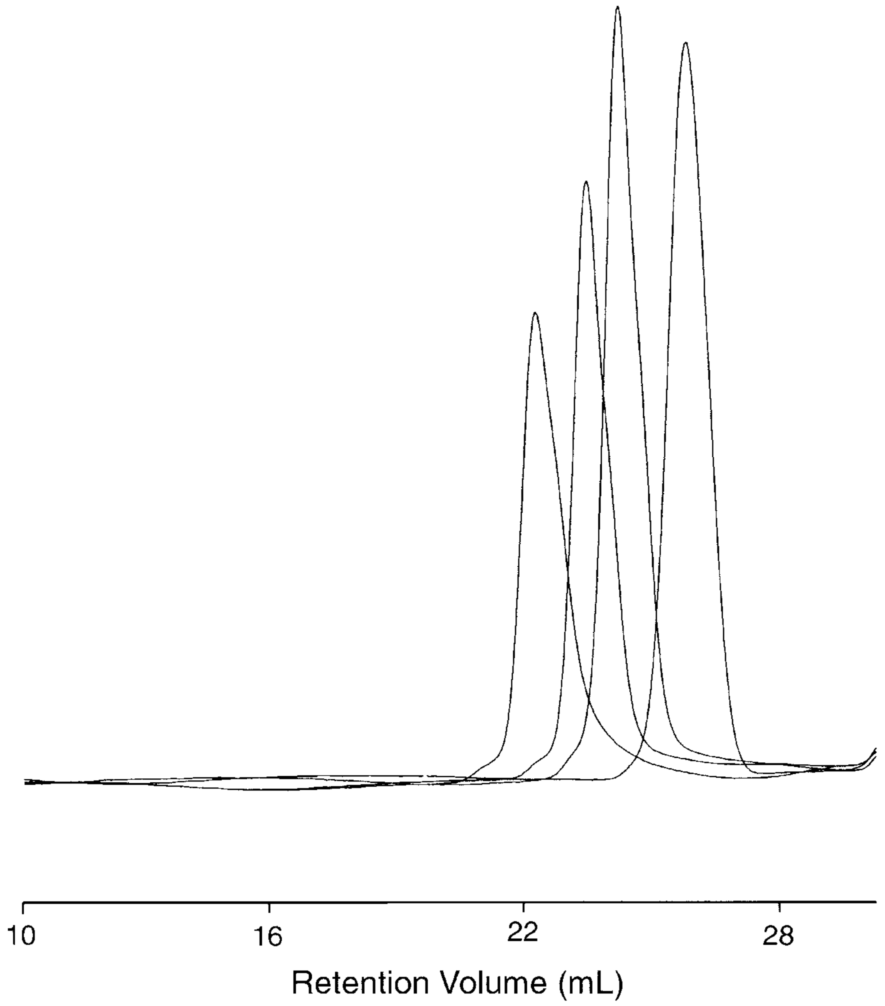


Figure 1. Conventional GPC traces in THF of PFS samples prepared by anionic ROP.

Table I. Characteristic Data for PFS

Sample	M_w[a]	M_w[b]	PDI[b]	M_w[c]	M_w[d]	PDI[d]	$[\eta]_w$[d]	$R_{g,z}$[d]	$R_{h,z}$[e]
PFS_{40}	9,680	8,300	1.06	8,800	9,640	1.03	0.0791	2.98	2.29
PFS_{100}	24,200	23,400	1.06	26,500	27,300	1.03	0.153	5.26	4.03
PFS_{150}	36,300	36,800	1.06	46,500	42,800	1.03	0.221	6.88	5.28
PFS_{200}	48,400	69,200	1.11	95,800	92,500	1.05	0.326	10.1	7.78

[a] Predicted from the reaction stoichiometry.

[b] Polydispersity index calculated with conventional GPC (calibrated with PS standards).

[c] Determined by LALLS.

[d] Calculated with GPC equipped with a Viscotek triple detector (refractive index, viscosity, and light scattering).

[e] $R_g/R_h = 1.3$ from the model used in eqs 3 and 4 (M_w, g/mol; $[\eta]$, dL/g; $R_{h,z}$ and $R_{g,z}$, nm).

$$X = \left(\frac{4\pi n_0 R_g}{\lambda_0}\right)^2 \sin^2(\theta/2) \qquad (7)$$

and λ_0 is the incident wavelength. These relations assume a random-coil conformation in solution for the macromolecule.[9] R_g and M_w were iteratively calculated to 0° across the molecular weight distribution. The refractive index increment of the polymers was determined with the refractive index detector. We found the value of dn/dc for PFS_{40} through PFS_{200} to be 0.185, 0.183, 0.193, and 0.181 mL/g, respectively. These values are the same within the experimental error of the technique.

RESULTS AND DISCUSSION

Anionic ROP of [1]Silaferrocenophane

The ROP of dimethyl[1]silaferrocenophane was initiated with varying amounts of n-BuLi (see Scheme

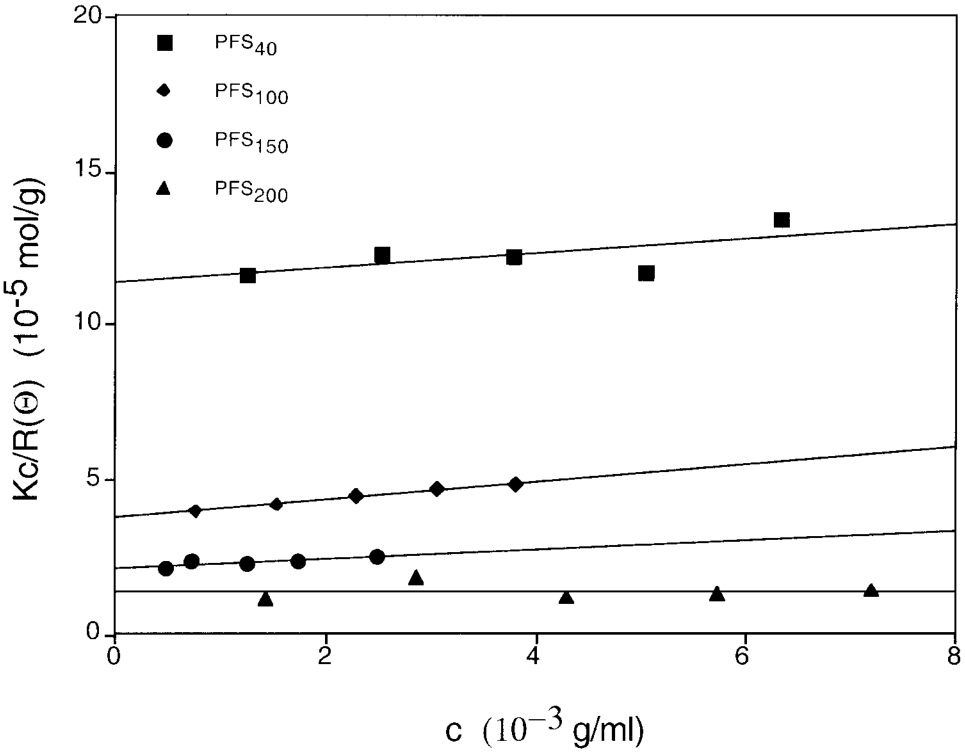


Figure 2. LALLS results for the series of PFS samples prepared by anionic ROP. Statistical errors in the data points are smaller than the symbol size.

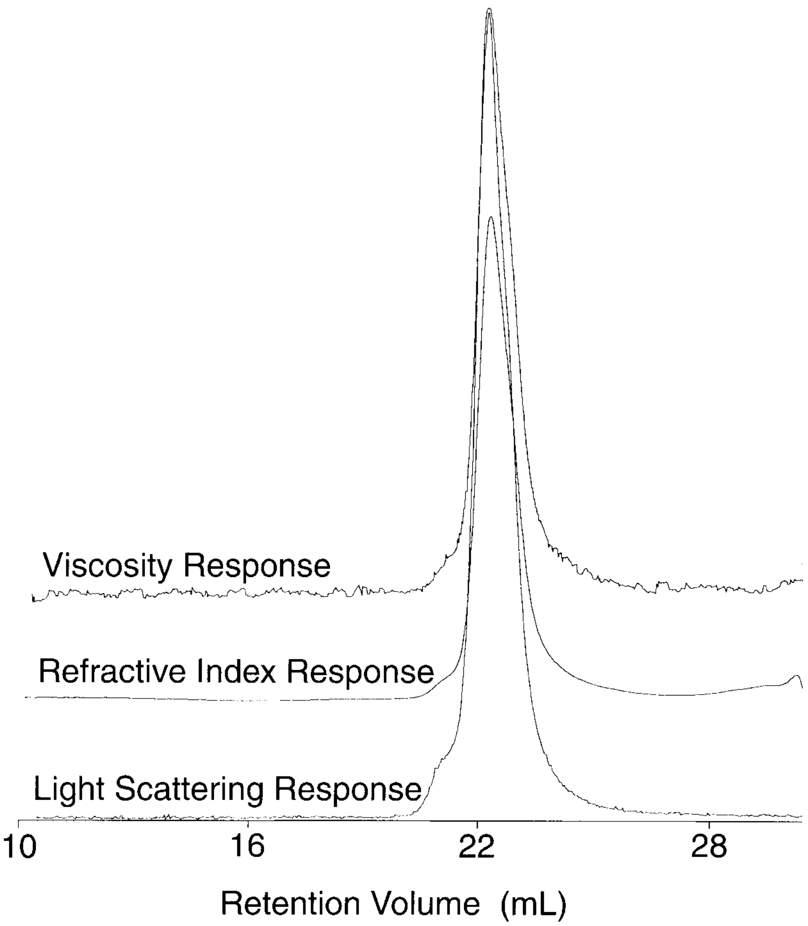


Figure 3. GPC trace of PFS_{200} showing the response of the triple detector system.

2) to produce a series of homopolymers with narrow polydispersities and differing chain lengths, as previously described.[6,7] We varied the molecular weight of PFS between 9000 and 95,000 g/mol by varying the initiator/monomer ratio between 1/40 and 1/200. The GPC refractive index trace of the polymers is presented in Figure 1. The series of homopolymers was used to characterize the molecular weight and solution properties of PFS in THF. The results are summarized in Table I and are discussed in subsequent sections.

Molecular Weight Determination of PFS by LALLS

An accurate determination of the molecular weight of a polymer is one of the most basic and important aspects in characterizing a new material. Static light scattering provides an absolute method of determining the molecular weight of a polymer.[8] LALLS results for the PFS series prepared by anionic polymerization is presented in Figure 2. The data were fit to eq 1, and the molecular weight for each sample was calculated from the inverse of the intercept. The molecular weights were 8800 ± 500, 26,500 ± 400, 46,500 ± 2000 and 95,800 ± 5000 g/mol for PFS_{40} through PFS_{200}, respectively. The results are summarized in Table I.

There is a clear discrepancy when the molecular weight determined by LALLS is compared to the value predicted from the reaction stoichiometry. The higher the degree of polymerization, the greater the apparent overestimation of the molecular weight determined by LALLS. Further complicating the interpretation of the data are the results from conventional GPC, calibrated with polystyrene standards, which more closely match the predicted molecular weight. As discussed next, the molecular weight determined by LALLS is correct, and the discrepancy probably arose from impurities in the reaction mixture, which quickly consumed a fixed amount of *n*-BuLi before

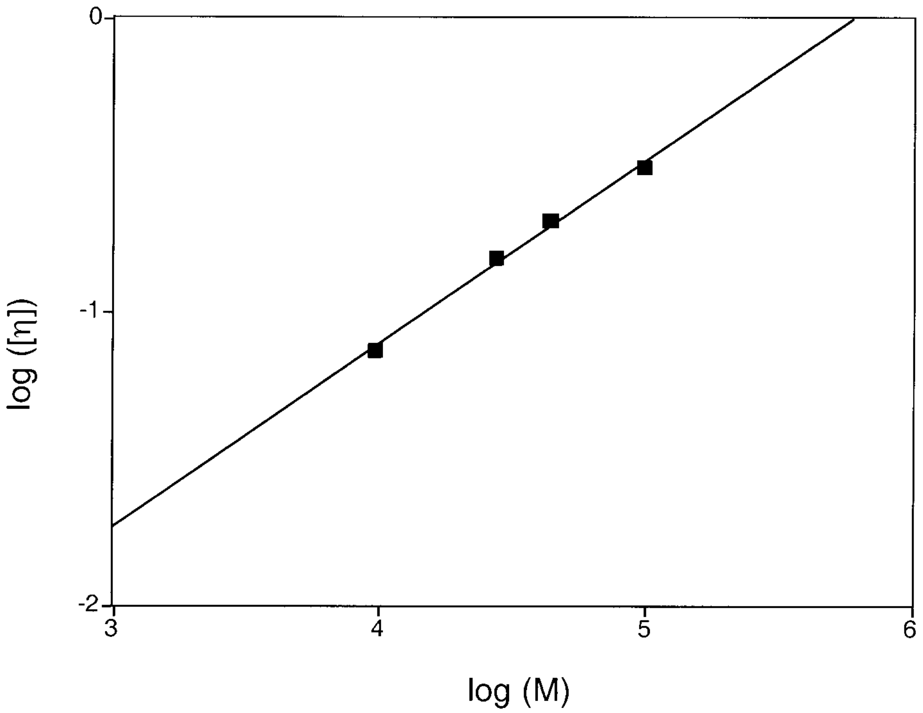


Figure 4. Mark–Houwink plot for PFS.

initiation could occur. As the amount of initiator decreased to increase the degree of polymerization, the effect became more dramatic, giving rise to polymers with higher molecular weights than predicted.

Comparison with the Molecular Weight Determined by GPC

GPC is a common method used to determine the molecular weight of polymers. GPC is a size exclusion technique that separates polymer molecules on the basis of their effective hydrodynamic size. The technique is simple and fast, providing not only an estimation of the molecular weight but also a measure of the molecular weight distribution of the sample. The difficulties arise in quantifying the molecular weight obtained. The most commonly employed method is to calibrate the GPC against secondary standards of known molar mass with a narrow distribution. The molecular weight determined, however, is relative to the standards used for calibration. The recent availability of reliable online light scattering and viscosity detectors has made it possible to easily and accurately determine the molecular weight across the entire molecular weight distribution of the polymer.

In Figure 3, there is an overlay of the GPC traces measured with a Waters 410 refractive index detector and a Viscotek T60A dual light scattering and viscosity detector for PFS_{200}. The results calculated for the series of homopolymers are tabulated in Table I. There is excellent agreement between the molecular weight calculated with GPC coupled with triple detection and the results obtained with LALLS.

Determination of the Mark–Houwink Parameters for PFS

Using the molecular weight determined by GPC with the triple detection system and the viscosity measured directly with the four-capillary viscometer, we generated a Mark–Houwink plot for PFS. The Mark–Houwink parameters are constants for a given polymer–solvent system. They were determined from the intercept ($\log k = -3.6 \pm 0.1$) and the slope ($a = 0.62 \pm 0.03$) in Figure 4, which was fit to the expression $[\eta] = kM^a$. Generally, a lies between 0 and 0.5 for branched polymers, between 0.5 and 0.8 for flexible chains, between 0.8 and 1.0 for stiff molecules, and between 1.0 and 1.7 for highly extended macromolecules.[11] For flexible chains, a is a measure of the thermodynamic interaction between the polymer and the

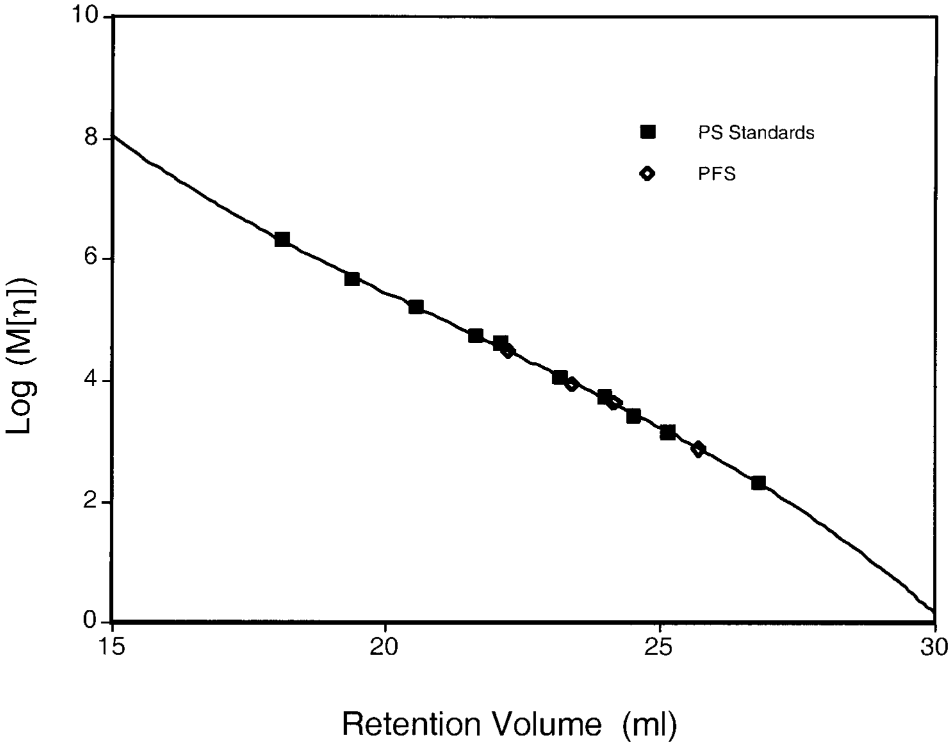


Figure 5. Universal calibration curve generated from polystyrene standards. The curve is fit to the closed squares (polystyrene).

solvent. It takes a value of 0.7–0.8 in good solvents and a value of 0.5 under θ conditions. For PFS, the polymer–solvent interaction was marginal because a was 0.62. We can compare this value to the Mark–Houwink parameter for polystyrene in THF. Using a series of polystyrene standards with the same instrument under the same conditions, we determined a to be 0.72.[12] As anticipated, THF is a good solvent for polystyrene. We are now in a position to rationalize why conventional GPC so dramatically underestimates the molecular weight of PFS. GPC resolves the molecular weight distribution by separating the polymer on the basis of its hydrodynamic volume. The random-coil conformation of PFS is more compact in THF than polystyrene because the interaction with the solvent is not as favorable. Therefore, for two random coils of the same molecular weight, PFS will elute more slowly from the size exclusion column and will have a lower apparent molecular weight. In addition, PFS is denser than polystyrene (1.3 g/cm^3 vs 1.05 g/cm^3), and this will also be a contributing factor to the underestimation of the molecular weight by conventional GPC.

Comparison with Universal Calibration

Grubisic et al.[13] were the first to demonstrate that a universal calibration curve could be generated for the peaks in a GPC experiment to determine the molecular weight of a polymer sample. They found that all polymers they investigated lay on this curve for a wide variety of different architecture. One derives the calibration curve by plotting log ($[\eta]M$) against the retention time, measured with the same instrument and columns for which the curve is going to be used. The calibration method is universal because $[\eta]M$ is proportional to the hydrodynamic volume, the basis for separation in GPC. We were curious to see if PFS would also lie on a universal calibration curve generated for our GPC.

Figure 5 is a universal calibration curve generated from polystyrene standards (closed squares). The line is fit to these data points, whereas the data for PFS are overlaid on the graph (open diamonds). Log ($[\eta]M$) for PFS falls directly on the universal calibration curve in every case, providing further validity for our determined molecular weight and intrinsic viscosity.

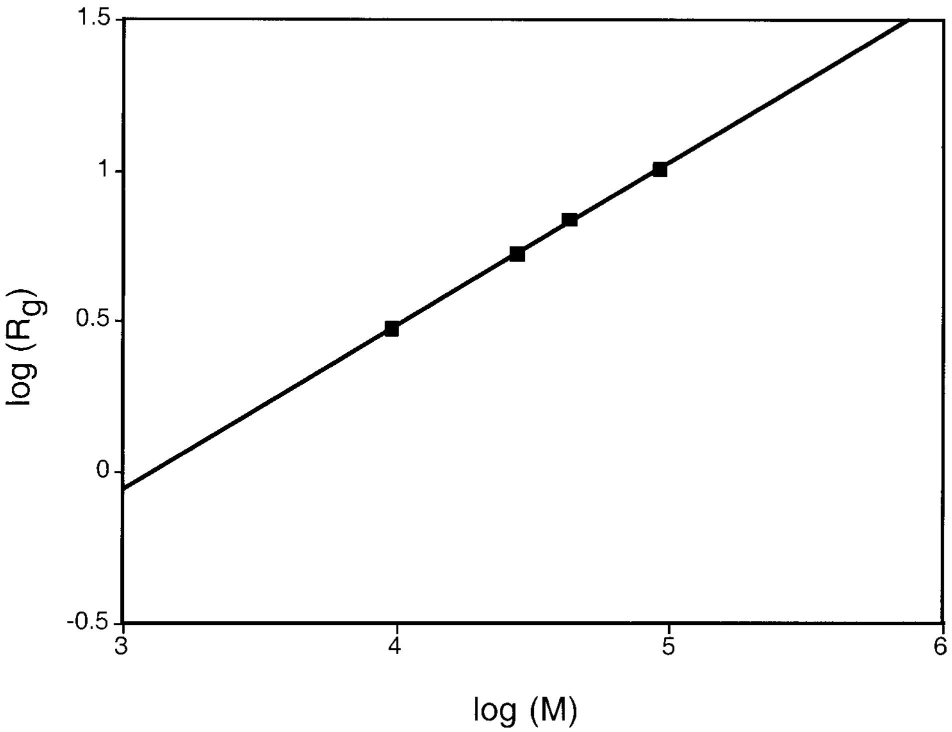


Figure 6. Dependence of R_g with molecular weight for PFS.

Relationship between the Molecular Weight and R_g

R_g is also calculated by the software of the GPC triple detection system. An advantage of this method is that R_g can be determined for values much lower than those that can be measured by the angular dependence of the light scattered in a light scattering experiment. In fact, we were also unable to obtain reliable measurements of R_h with our dynamic light scattering instrument in the concentrations used for LALLS because of the relatively low output power of our He–Ne laser. The scaling relation between the molecular weight and R_g is given by the expression $R_g \sim M^{\nu}$, where ν is the scaling exponent and ranges between ½ for θ conditions and ⅗ for a good solvent for the polymer. In Figure 6, log (R_g) is plotted against log (M). The plot is linear, and from the slope we calculated the value of ν to be 0.54 ± 0.01. This value is indicative of marginal thermodynamic interaction between PFS and THF, agreeing well with the calculated Mark–Houwink parameter.

SUMMARY

Four samples of PFS were synthesized by living anionic polymerization. The absolute molecular weight of each of the polymer samples was determined with LALLS. The molecular weight was also calculated with conventional GPC calibrated with polystyrene standards and GPC with a triple detection system. The molecular weights determined with LALLS and the triple detection GPC were in excellent agreement. Conventional GPC underestimated the molecular weight of poly(ferrocenylsilanes). This was understood through a comparison of the Mark–Houwink parameters of PFS with those of polystyrene. PFS had a more compact random-coil conformation in THF than polystyrene, indicating that the polymer–solvent interactions were not as favorable for PFS as for PS. This inference was confirmed by the finding that the exponent in the $R_g \sim M^{\nu}$ relationship was equal to 0.54, a value typical of a polymer in a fairly marginal solvent.

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