Dilute-Solution Behavior of a Rigid Polymer, Poly[*trans*-bis(tributylphosphine)- platinum 1,4-butadiynediyl]

Masanori MOTOWOKA, Takashi NORISUYE, Akio TERAMOTO,
and Hiroshi FUJITA

*Department of Polymer Science, Osaka University,
Toyonaka, Osaka, 560 Japan.*

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ABSTRACT: Poly[*trans*-bis(tributylphosphine)platinum 1,4-butadiynediyl] (PPBD) in heptane at 25°C was studied by viscosity and sedimentation velocity measurements over a range of weight-average molecular weight M_w from 7×10^3 to 1.4×10^5 . Although the chemical structure of PPBD suggests a very rigid nature of the chain, the measured value 1.1 for the exponent in the Mark–Houwink–Sakurada $[\eta]$ (intrinsic viscosity)– M_w relation indicated an appreciable flexibility of the chain. The data for $[\eta]$ and sedimentation coefficient as functions of M_w were analyzed by the Yamakawa–Fujii theories for a wormlike cylinder, yielding $M_L = 810 \pm 60 \text{ nm}^{-1}$, $q = 13 \pm 3 \text{ nm}$, and $d = 1.2 \pm 0.3 \text{ nm}$, where M_L is the molecular weight per unit contour length, q is the persistence length, and d is the diameter of the cylinder. The flexibility of PPBD indicated by this q value is comparable to that of cellulose nitrate which is known to be a typical stiff polymer.

KEY WORDS Dilute Solution / Poly-yne Polymer / Poly[*trans*-bis(tributylphosphine)platinum 1,4-butadiynediyl] / Rigid Polymer / Wormlike Chain / Persistence Length / Intrinsic Viscosity / Sedimentation Coefficient /

Recently, Hagihara and his coworkers^{1–4} have synthesized new poly-yne polymers containing platinum metal atoms in the main chain. Poly[*trans*-bis(tributylphosphine)platinum 1,4-butadiynediyl](PPBD) is a linear polymer of repeat units consisting of a platinum atom of square planar configuration and a conjugated butadiyne (see Figure 1). The present paper reports a molecular characterization of this polymer by viscometry and ultracentrifugation.

From ³¹P NMR measurements Hagihara *et al.*^{2,3} concluded that the two phosphorus atoms attached to each platinum atom in the PPBD chain are in the *trans* configuration. This finding together with the rigid nature of the butadiyne portion suggests that the PPBD chain should assume a rodlike conformation in solution. In fact, as evidence consistent with this suggestion, Hagihara *et al.*⁴ found that intrinsic viscosities $[\eta]$ for a PPBD sample in various

solvents were essentially independent of solvent (about $1.2 \times 10^2 \text{ cm}^3 \text{ g}^{-1}$) and that the exponent in the Mark–Houwink–Sakurada relation between $[\eta]$ and weight-average molecular weight M_w was close to 1.7. These preliminary results indicate that PPBD can be used as a model substance for investigating rodlike polymers in solution. In contrast with aromatic polyamides, considered model substances for rodlike molecules,^{5–7} PPBD does not involve the problem of difficulty in solubility; Hagihara *et al.* found that it dissolves in a number of common organic solvents. This is a very inviting feature for a solution study of PPBD.

EXPERIMENTAL

Samples

Two samples of PPBD, $f([\eta](\text{heptane}, 25^\circ\text{C}) = 1.2 \times 10^2 \text{ cm}^3 \text{ g}^{-1}, 5 \text{ g})$ and $F([\eta] = 0.27 \times 10^2 \text{ cm}^3 \text{ g}^{-1}, 1.3 \text{ g})$, kindly furnished by Professor Hagihara, were fractionated by fractional precipitation with benzene as a solvent and methanol as a precipitant. Seven fractions were separated from Sample F and sixteen fractions from Sample f. The main appropriate fractions from Sample F were

Figure 1. Repeat unit of PPBD.

subjected to further fractional precipitation. Three fractions were chosen from the resulting products and designated as F-series. Each fraction from Sample f was separated into 5 or 6 parts by using a Sephadex column (Type LH-60; Pharmacia Fine Chemicals, Uppsala, Sweden) with dichloromethane as solvent. The column used was 100 cm in length and 2.5 cm in inner diameter, and the flow rate was about 70 cm³ per hour. The relative viscosity of each solution was adjusted to a value less than 2. The column-separated fractions having nearly identical intrinsic viscosities (in dichloromethane at 25°C) were combined and then refractionated by the same column method. This procedure was repeated twice. Eight appropriate fractions were chosen from the resulting products and designated as f-series. All the 11 fractions were freeze-dried and stored at -20°C until use.

Molecular Weight Determination

The polymer PPBD is yellowish and has an absorption maximum near 380 nm. Because of these properties and the limited amount of each fraction, no light-scattering measurement was feasible. Hence, the sedimentation equilibrium method with heptane at 25°C as a solvent was used to determine the weight-average molecular weights M_w of all the 11 fractions. The measurement was made in a Beckman-Spinco Model E ultracentrifuge equipped with an electronic speed control system.

The specific refractive index increment of PPBD in heptane at 25°C was 0.199 cm³g⁻¹ for light of 546 nm, and its partial specific volumes in both heptane and benzene were 0.776 cm³g⁻¹.

The number-average molecular weights M_n of six fractions of PPBD (f-3 through f-8) were determined by vapor pressure osmometry with benzene as the solvent. A Knauer vapor pressure osmometer thermostated at 45°C was used. The apparatus was calibrated with benzil under the same solvent conditions as for the measurements on polymer solutions.

Viscosity and Sedimentation Velocity Measurements

Intrinsic viscosities of all the 11 fractions of PPBD in heptane and benzene were determined at 25°C by using a capillary viscometer of the Ubbelohde suspended-level type, designed so as to require no corrections for kinetic energy and shear rate. In converting the flow times to relative viscosities, the

correction for the density of solution was made.

Sedimentation coefficients s of seven higher-molecular-weight fractions of PPBD in heptane at 25°C were determined by the conventional peak method. For lower-molecular-weight fractions, no reliable measurement could be made because the schlieren boundary curves rapidly broadened by diffusion.

RESULTS

Figure 2 shows plots of M_{app}^{-1} vs. $\bar{c}$ for PPBD fractions in heptane at 25°C, where M_{app} denotes an apparent molecular weight and $\bar{c}$ is equal to $(c_a + c_b)/2$, with c_a and c_b the polymer mass concentrations at the meniscus and bottom in the ultracentrifuge cell, respectively. The values of M_w and A_2 (second virial coefficient) evaluated from the intercepts and slopes of the indicated straight lines are summarized in Table I, in which the values of M_n determined by vapor pressure osmometry are also given. The ratios of M_w to M_n in the fifth column are

Figure 2. Plots of M_{app}^{-1} vs. $\bar{c}$ for PPBD fractions in heptane at 25°C.

Table I. Numerical results from sedimentation equilibrium and vapor pressure osmometer measurements on PPBD fractions

Fraction	$M_w \times 10^{-4a}$	$A_2 \times 10^{4a}$	$M_n \times 10^{-4b}$	M_w/M_n
	g mol ⁻¹	cm ³ mol g ⁻²	g mol ⁻¹	
F-1	14.1	1.9	—	—
F-2	10.5	1.9	—	—
F-3	7.41	1.9	—	—
f-1	5.26	1.9	—	—
f-2	3.53	2.1	—	—
f-3	2.82	1.9	2.5 ± 0.4	1.2 ± 0.2
f-4	2.06	2.2	2.0 ± 0.1	1.1 ± 0.1
f-5	1.45	—	1.3	1.1
f-6	1.19	—	1.1	1.1
f-7	0.877	—	0.83	1.1
f-8	0.692	—	0.65	1.1

^a Sedimentation equilibrium (heptane, 25°C).^b Vapor pressure osmometry (benzene, 45°C).**Table II.** Numerical results from viscosity and sedimentation-velocity measurements on PPBD fractions

Fraction	$[\eta] \times 10^{-2}$	k'	$[\eta] \times 10^{-2}$	k'	$s_0 \times 10^{13}$	$k_s \times 10^{-2}$
	cm ³ g ⁻¹ (heptane, 25°C)		cm ³ g ⁻¹ (benzene, 25°C)		s (heptane, 25°C)	cm ³ g ⁻¹ (heptane, 25°C)
F-1	1.84	0.42	1.96	0.48	11.8	1.02
F-2	1.45	0.41	1.57	0.42	10.9	0.82
F-3	0.986	0.38	1.03	0.40	9.95	0.62
f-1	0.640	0.42	0.679	0.39	8.82	0.43
f-2	0.414	0.34	0.444	0.38	7.52	0.26
f-3	0.320	0.36	0.327	0.42	6.94	0.17
f-4	0.221	0.43	0.226	0.39	6.25	0.09
f-5	0.168	0.38	0.170	0.44	—	—
f-6	0.133	0.44	0.136	0.46	—	—
f-7	0.0970	0.41	0.0980	0.39	—	—
f-8	0.0778	0.44	0.0785	0.47	—	—

about 1.1, indicating that each fraction of the f-series is fairly narrow in molecular weight distribution.

The values of $[\eta]$ and k' (Huggins constant) for all the fractions in heptane and benzene are summarized in Table II. The values of $[\eta]$ in benzene are slightly but systematically larger than those in heptane over the entire range of M_w studied. Figure 3 depicts double-logarithmic plots of $[\eta]$ as a function of M_w for PPBD in heptane at 25°C. If the solid curve is approximated by a straight line, it gives a slope of 1.1. This value is much larger than those (0.5–0.8)

reported for usual flexible polymers, but significantly smaller than 1.7 expected for long rigid rods,⁸ indicating that the PPBD chain is not completely rigid. The closed circles in Figure 3 show the data reported by Hagihara *et al.*⁴ The slope 1.6 of the line connecting these two points leads to their conclusion that the PPBD chain behaves as an almost rigid rod.

Plots of s^{-1} vs. initial concentration c_0 for PPBD fractions in heptane at 25°C are shown in Figure 4. The values of s_0 (limiting sedimentation coefficient) and k_s (defined by the equation $s^{-1} = s_0^{-1} + k_s s_0^{-1} c_0$)

Figure 3. Molecular weight dependence of $[\eta]$ for PPBD in heptane at 25°C. The closed circles are the data (in tetrahydrofuran at 25°C) of Hagihara *et al.*⁴

obtained from the indicated lines are listed in Table II. Figure 5 shows the s_0 plotted against $\log M_w$. The data points follow a curve slightly concave upward. If the PPBD chain were perfectly rigid, this type of plot should give a straight line. Hence, these data for s_0 also suggest some flexibility of the PPBD chain.

DISCUSSION

Data Analysis

Although from its chemical structure the PPBD

Figure 5. Molecular weight dependence of s_0 for PPBD in heptane at 25°C.

chain is expected to be very stiff, the present experimental data are not consistent with this expectation. The value 1.1 for the viscosity exponent indicates that the chain is only moderately stiff. In order to estimate the chain stiffness, we analyze our data for $[\eta]$ and s_0 using the Yamakawa-Fujii theories^{9,10} for a wormlike cylinder. The method described below is essentially the same as that proposed by Yamakawa and Fujii.¹⁰

The equations of Yamakawa and Fujii may be written

$$\log (M^2/[\eta]) = 3 \log M_L + \log F_1(L/q, d/q) \quad (1)$$

$$\log (3\pi\eta_0 N_A s_0 / 1 - \bar{v}\rho_0)^3 = 3 \log M_L + \log F_2(L/q, d/q) \quad (2)$$

Figure 4. Plots of s^{-1} vs. c_0 for PPBD fractions in heptane at 25°C.

where M is the molecular weight of the polymer, L is the contour length of the polymer chain, q is its persistence length, d is the diameter of the cylinder, N_A is the Avogadro constant, ρ_0 and η_0 are, respectively, the density and viscosity of the solvent, F_1 and F_2 are known functions of L/q and d/q , and M_L is the shift factor defined by

$$M_L = M/L \quad (3)$$

Equations 1 and 2 indicate that $\log(M^2/[\eta])$ and $\log(3\pi\eta_0 N_A s_0 / (1 - \bar{v}\rho_0))^3$ differ from $\log F_1$ and $\log F_2$ by $3 \log M_L$ and that F_1 and F_2 depend on the same arguments. These features can be utilized to evaluate three unknowns q , M_L , and d .

We first plot experimental values of $\log(M_w^2/[\eta])$ and $\log(3\pi\eta_0 N_A s_0 / (1 - \bar{v}\rho_0))^3$ against $\log M_w$ and theoretical values of $\log F_1$ and $\log F_2$ against $\log(L/d)$ for various d/q values. We then displace the plots for $\log(M_w^2/[\eta])$ and $\log(3\pi\eta_0 N_A s_0 / (1 - \bar{v}\rho_0))^3$ by δ_1 in the ordinate direction and at the same time by δ_2 in the abscissa direction and examine whether there is a particular value of d/q for which the displaced plots fall on the theoretical curves of $\log F_1$ and $\log F_2$. Once we find a set of δ_1 , δ_2 , and d/q giving the closest agreement between the experimental and theoretical curves, the values of M_L and d can be calculated from $\delta_1 = 3 \log M_L$ and $\delta_2 = \log(M_L d)$, and then the value of q can be obtained from the value of d/q . In this way, we found that $q = 13 \pm 3$ nm, $M_L = 810 \pm 60$ nm⁻¹, and $d = 1.2 \pm 0.3$ nm. The indicated ranges of error take account of the uncertainties in finding the "best" agreement between experiment and theory. The M_L value of 810 nm⁻¹ is close to 846 nm⁻¹, as estimated from X-ray data on an acetylide complex of platinum.¹¹ If as in our previous papers¹²⁻¹⁴ it is assumed that the hydrodynamic volume occupied by one gram of the wormlike cylinder is equal to partial specific volume $\bar{v}$ of the polymer, the measured value of $\bar{v} = 0.776$ cm³ g⁻¹ together with the calculated value of $M_L = 846$ nm⁻¹ gives $d = 1.18$ nm, which agrees with 1.2 nm estimated from the hydrodynamic data. Another point to note is that $q = 13$ nm is much smaller than the q values of DNA (60 nm)^{9,10,15,16} and poly(isocyanate)s (40 nm),^{10,17,18} but comparable to that of cellulose nitrate (17 nm).¹⁰

Comparison of Experiment and Theory

Figure 6 compares the measured values of $[\eta]$ and s_0 in heptane with the theoretical values calculated

Figure 6. Comparison of measured values (circles) of $[\eta]$ and s_0 with theoretical values (solid lines) calculated from eq 1 and 2 with $q = 13$ nm, $M_L = 810$ nm⁻¹, and $d = 1.2$ nm.

Figure 7. Comparison of experimental and theoretical values of the Scheraga-Mandelkern-Flory parameter β for PPBD in heptane. The parameter values used are the same as in Figure 6.

from eq 1 and 2 with $q = 13$ nm, $M_L = 810$ nm⁻¹, and $d = 1.2$ nm. The computations were truncated at $M_w = 10^4$, below which no theoretical values for F_1 and F_2 were available. The agreement between theory and experiment is satisfactory.

In Figure 7, the experimental and calculated values of the Scheraga-Mandelkern-Flory parameter¹⁹ $\beta (= N_A \eta_0 s_0 [\eta]^{1/3} / 10^{2/3} (1 - \bar{v}\rho_0) M^{3/2})$ are compared. The calculation was made with the same parameter values as in Figure 6. These β values are much smaller than those expected for long rigid rods,¹⁹ again indicating a flexibility of the PPBD chain.

In conclusion, the molecular chain of PPBD can be represented by the wormlike chain model, and it is

not as stiff as concluded by Hagihara *et al.* on the basis of NMR and viscosity data. It is interesting to pursue the factors responsible for the flexibility of the PPBD chain as expressed by the q value of 13 nm obtained in this study.

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