Stiff-Chain Nature of Poly(1-phenyl-1-propyne) in Dilute Solution

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ABSTRACT: Light scattering and viscosity measurements were made on twelve narrow-molecular weight distribution samples of poly(1-phenyl-1-propyne) in toluene and in cyclohexane. In cyclohexane at 36°C, the second virial coefficient A_2 vanished, the mean-square radius of gyration increased linearly with weight-average molecular weight M_w , but the intrinsic viscosity was not proportional to $M_w^{1/2}$. Thus poly(1-phenyl-1-propyne) in cyclohexane at 36°C is an unperturbed semiflexible polymer. A_2 in toluene was positive, indicating significant intermolecular excluded volume effect. However the intramolecular excluded volume effect became appreciable only at M_w higher than 3×10^5 . Analysis of the light scattering and viscosity data in terms of the wormlike chain model gave persistence lengths of 3.8 and 3.9 nm in cyclohexane and toluene, respectively. The Flory viscosity factor in the unperturbed-coil limit was 2.17×10^{23} and $2.35 \times 10^{23} \text{ mol}^{-1}$ in the two solvents.

KEY WORDS Semiflexible Polymer / Wormlike Chain / Persistence Length
/ Stiffness / Flory Viscosity Factor / Excluded Volume Effect / Poly(1-phenyl-1-propyne) / Substituted Polyacetylene /

Masuda and Higashimura^{1,2} have succeeded in polymerizing substituted acetylenes to yield high molecular weight polymers with alternating double bonds along the main chain. Unlike polyacetylene which has virtually no solvent, these substituted polyacetylenes are soluble in ordinary organic solvents and stable in the solid state, thus permitting molecular characterization. Masuda *et al.*^{2,3} found for some substituted polyacetylenes that the viscosity exponent in the Mark-Houwink-Sakurada relation was as large as 1, suggesting that those polyacetylenes would be stiff-chain polymers. They attributed this stiffness to the alternating double bonds on the main chain and bulky side chains attached to it. Therefore, as a continuation of studies on dilute solution properties of stiff polymers,^{4–13} we have chosen one of such polymers, poly(1-phenyl-

1-propyne) (PPP) with the chemical structure shown in Figure 1 and made light scattering, sedimentation equilibrium, and viscosity measurements. This polymer dissolves in toluene (good solvent) and in cyclohexane (poor solvent) and has no absorption for visible light.^{2,3} It seemed interesting to compare its solution behavior with that of polystyrene because of the similarity in chemical structure and solvent between the two polymers. Indeed we found that PPP is brought to the unperturbed state in cyclohexane at 36°C but behaves as a semiflexible polymer.

Figure 1. Repeating unit of poly(1-phenyl-1-propyne) (PPP).

EXPERIMENTAL

Four samples of PPP with different molecular weights were synthesized as described before.³ They were separated into many fractions by repeated precipitation fractionation in benzene-methanol mixtures containing 4,4 thiobis-(6-*tert*-butyl-*m*-cresol), an antioxidant. Appropriate twelve fractions designated A-1 through A-12 were chosen for physical measurements. Just before solution preparation, they were freed from the antioxidant by reprecipitating the polymer from benzene solutions into methanol and freeze-dried from benzene solutions.

Light scattering measurements on eight fractions A-1 through A-8 in toluene at 25°C and in cyclohexane at temperatures between 30 and 45°C were performed on a Fica 50 light scattering photometer with vertically polarized incident light of the 436-nm or 546-nm wavelength following the procedure established.⁸ Data were analyzed by the square-root plot to obtain weight-average molecular weights M_w , second virial coefficients A_2 , and z -average mean-square radii of gyration $\langle S^2 \rangle_z$.

Both cyclohexane and toluene solutions of fractions A-6, A-7, and A-8 exhibited optical anisotropy, so that the optical anisotropy factor δ was estimated for these fractions using the relation^{14,15}

$$\lim_{c \rightarrow 0, \theta \rightarrow 0} (R_{\theta, H_V}/Kc) = 3\delta M_w$$

Here, R_{θ, H_V} is the reduced scattering intensity measured at a scattering angle θ for vertically polarized incident light with the analyzer set in the horizontal direction, K the optical constant, and c the polymer mass concentration. The light scattering data for the three fractions were corrected for the anisotropy effect by the conventional method for Gaussian chains¹⁴ (see Discussion) to obtain M_w , A_2 , and $\langle S^2 \rangle_z$, though the correction was no more than 2% for M_w and $\langle S^2 \rangle_z$ and 4% for A_2 .

Specific refractive index increments at

infinite dilution $(\partial n/\partial c)_0$ were measured on a modified Schulz-Cantow type differential refractometer for solutions of PPP in toluene at 25°C and in cyclohexane at temperatures T (°C) between 30 and 45°C. The values of $(\partial n/\partial c)_0$ in toluene were $0.1861 \text{ cm}^3 \text{ g}^{-1}$ at 436 nm and $0.1656 \text{ cm}^3 \text{ g}^{-1}$ at 546 nm. The values in cyclohexane were determined to be

$$(\partial n/\partial c)_0 = [0.264 + 5.3 \times 10^{-4}(T - 30)] \text{ cm}^3 \text{ g}^{-1} \quad (436 \text{ nm})$$

$$(\partial n/\partial c)_0 = [0.234 + 4.7 \times 10^{-4}(T - 30)] \text{ cm}^3 \text{ g}^{-1} \quad (546 \text{ nm})$$

Sedimentation equilibrium measurements were made for toluene solutions of fractions A-8 through A-12 at 25°C on a Beckman-Spinco model E analytical ultracentrifuge. The partial specific volume of PPP in toluene at 25°C needed to analyze the data was measured to be $0.863 \text{ cm}^3 \text{ g}^{-1}$. Intrinsic viscosities $[\eta]$ were determined by using a four-bulb capillary viscometer or an ordinary capillary viscometer of the Ubbelohde type.

Although PPP was stable in the solid state, its stability in solution was questioned because of its alternating double bonds on the main chain. Therefore viscosity measurements on cyclohexane and toluene solutions were made in order to find a condition whereby possible degradation of the polymer could be avoided; $(\ln \eta_r)/c$ was taken as a measure of molecular weight, with η_r being the relative viscosity of the solution. It was found that in both toluene and cyclohexane $(\ln \eta_r)/c$ decreased at a rate of 0.2%/h for a high molecular weight sample A-2 but at a negligible rate for a lower molecular weight sample (viscosity-average molecular weight = 8×10^4). This shows that higher molecular weight PPP degrades gradually in toluene and in cyclohexane. To minimize effects of degradation on measured properties, all the manipulations from solution preparation to measurement were completed within 12 h, except for sedimentation equilibrium measurements. It took one to two days to complete the

sedimentation experiment. However this experiment was done only for samples with molecular weights lower than 8×10^4 .

RESULTS

Figure 2 shows representative Zimm plots in the square-root form for A-3 in cyclohexane at 36°C and A-4 in toluene at 25°C. Sedimentation equilibrium data for fractions A-8 through A-12 were used to estimate M_w , M_z (the z -average molecular weight), and A_2 . As seen in Table I summarizing the light

scattering and sedimentation data, these samples are essentially monodisperse, with the polydispersity index M_z/M_w being 1.06–1.09. The values of M_w for fractions A-1 through A-8 in the different solvents are seen to agree with each other within 5% and those for fraction A-8 from different experiments, within 2%.

Figure 3 shows the temperature dependence of A_2M_w for three fractions A-3 through A-5 in cyclohexane. For any of these fractions, A_2 is negative at lower temperatures, positive at higher temperatures, and vanishes at 36°C.

Figure 2. Zimm plots in the square-root form for PPP (a) sample A-3 in cyclohexane at 36°C, (b) sample A-4 in toluene at 25°C; R_θ is the reduced scattering intensity measured at a scattering angle θ with a vertically orientec polarizer and no analyzer.

Figure 3. Temperature dependences of A_2M_w for three samples in cyclohexane.

Figure 4. Double-logarithmic plot of A_2 vs. M_w for PPP in toluene at 25°C.

Table I. Results from light scattering and sedimentation equilibrium measurements on PPP samples in cyclohexane (36°C) and toluene (25°C)

Sample	Cyclohexane (36°C)			Toluene (25°C)				
	$M_w/10^4$	$\langle S^2 \rangle_z^{1/2}$ nm	$\delta/10^{-3}$	M_w 10 ⁴	A_2 10 ⁻⁴ cm ³ g ⁻² mol	$\langle S^2 \rangle_z^{1/2}$ nm	$\delta/10^{-3}$	M_z/M_w
(light scattering at 546 nm)								
A-1	145	64.4		145	2.91	69.4		
A-2	126	58.3		132	3.78	67.8		
A-3	61.5	40.7		61.3	3.58	44.5		
A-4	35.0	29.6		37.2	4.31	31.7		
A-5	24.3	26.5		25.8	3.84	27.2		
A-6	14.4	19.6		14.0	4.77	20.8		
(light scattering at 436 nm)								
A-6	14.2	19.2	0.87	14.2	4.82	20.3	1.1	
A-7	9.58	16.4	1.4	10.0	5.46	16.7	1.6	
A-8	5.47	12.3	1.9	5.70	6.05	11.7	2.8	
(sedimentation equilibrium)								
A-8				5.59	6.75			1.06
A-9				4.39	9.50			1.08
A-10				2.82	9.88			1.06
A-11				2.21	10.0			1.09
A-12				1.55	15.7			1.06

Figure 5. Molecular weight dependence of $\langle S^2 \rangle_z^{1/2}$ for PPP in cyclohexane and toluene.

This indicates that PPP is brought to the theta condition in cyclohexane at 36°C, where both inter- and intramolecular excluded-volume effects vanish.* On the other hand, as shown in Figure 4, A_2 in toluene is positive and decreases gradually with increasing molecular

weight as usually found for flexible polymers in good solvents.

Figure 5 shows double-logarithmic plots of $\langle S^2 \rangle_z^{1/2}$ vs. M_w in cyclohexane at 36°C and in toluene at 25°C. The data points in cyclohexane follow closely the straight line of a slope 0.5 indicated. Those in toluene follow this line up to an M_w of about 3×10^5 and then deviate slightly upward from it. Thus the PPP chain in toluene is essentially unperturbed below M_w 3×10^5 and perturbed above it by intramolecular excluded-volume effects; note that A_2 is positive in toluene.

Figure 6 shows double-logarithmic plots of $[\eta]$ vs. M_w in cyclohexane at 36°C and in toluene at 25°C. The data points in cyclohexane follow closely the smooth curve drawn, whose slope decreases from 0.8 to 0.55 with increasing M_w in the M_w range examined. This behavior, along with the square-root dependence of

* For fraction A-8, however, A_2 at 36°C remained positive (about 5×10^{-5} cm³ g⁻² mol). This finding is similar to what has recently observed by Huber and Stockmayer¹⁶ and Konishi *et al.*¹⁷ for low-molecular weight polystyrene samples in cyclohexane, a theta solvent.

Figure 6. Molecular weight dependence of $[\eta]$ for PPP in the two solvents.

Table II. Results from viscosity measurements on PPP samples in cyclohexane (36°C) and toluene (25°C)

Sample	Cyclohexane (36°C)		Toluene (25°C)	
	$[\eta]$	k'	$[\eta]$	k'
	$10^2 \text{ cm}^3 \text{ g}^{-1}$		$10^2 \text{ cm}^3 \text{ g}^{-1}$	
A-1	4.21	0.66	6.32	0.42
A-2	4.13	0.71	6.24	0.42
A-3	2.81	0.62	3.82	0.41
A-4	1.98	0.52	2.40	0.42
A-5	1.40	0.56	1.81	0.38
A-6	1.02	0.55	1.20	0.35
A-7	0.828	0.52	0.938	0.38
A-8	0.546	0.71	0.604	0.41
A-9	0.510	0.51	0.526	0.42
A-10	0.371	0.57	0.384	0.40
A-11	0.297	0.58	0.287	0.44
A-12	0.207	0.73	0.210	0.40

$\langle S^2 \rangle_z^{1/2}$ in Figure 5, indicates that PPP in cyclohexane at 36°C is a semiflexible polymer in the unperturbed state. On the other hand, the data points in toluene appear slightly above the solid curve at M_w lower than 3×10^5 but deviate definitely upward above this M_w . This upswing is due to intramolecular excluded-volume effects as found for $\langle S^2 \rangle_z$. The numerical data for $[\eta]$ and Huggins' constant k' obtained are summarized in Table II.

DISCUSSION

Wormlike Chain Parameters

PPP in cyclohexane at 36°C may be modeled by the wormlike cylinder,¹⁸ which is characterized by three parameters: the contour length L , persistence length q , and diameter d of the cylinder. The mean-square radius of gyration $\langle S^2 \rangle$ of this model chain at the limit of large $L/2q$ is written¹⁴

$$\langle S^2 \rangle = (1/3)qL - q^2 \quad (1)$$

where $L = M/M_L$, with M and M_L being the molecular weight and the molar mass per unit contour length, respectively. Yamakawa, Fujii, and Yoshizaki^{19,20} have derived an expression for $[\eta]$ of the model, which contains M_L , q , and d as the parameters, that is,

$$[\eta] = (2q/M_L)^{3/2} M^{1/2} \Phi(d/2q, M/2qM_L) \quad (2)$$

where Φ is given as a function of $d/2q$ and $L/2q$. A graphical procedure for analyzing experimental data based on this equation is also given.^{19,20} Later Bohdanecký²¹ and Bushin *et al.*²² independently proposed a simple procedure for data analysis using the following approximation to eq 2:

$$(M^2/[\eta])^{1/3} = A + BM^{1/2} \quad (3)$$

with

$$A = A_0 M_L \Phi_\infty^{-1/3} \quad (4)$$

$$B = B_0 (2q/M_L)^{-1/2} \Phi_\infty^{-1/3} \quad (5)$$

where Φ_∞ is the Flory viscosity factor for unperturbed random coils and A_0 and B_0 are given as functions of $d/2q$. We examine whether these theoretical predictions are compatible with the present data for PPP in cyclohexane and allow the stiffness parameter q to be evaluated.

The linear dependence of $\langle S^2 \rangle_z^{1/2}$ on $M_w^{1/2}$ found in Figure 5 shows that the second term in eq 1 is negligible, yielding $\langle S^2 \rangle_z = (1/3)q(M_w/M_L)(M_z/M_w)$. The straight line in Figure 5 along with $M_z/M_w = 1.07$ (the mean value from the sedimentation equilibrium)

Figure 7. Plot of $(M_w^2/[\eta])^{1/3}$ vs. $M_w^{1/2}$ for PPP in cyclohexane at 36°C.

gives $q/M_L = 7.91 \times 10^{-3} \text{ nm}^2$.

Figure 7 displays the $[\eta]$ data in cyclohexane at 36°C according to eq 3. The data points follow closely the straight line indicated, yielding $A = 51 \text{ g}^{1/3} \text{ cm}^{-1}$ and $B = 1.32 \text{ g}^{1/3} \text{ cm}^{-1}$. It is noted that this analysis of light scattering and viscosity data has given two relationships among the three parameters involved and does not allow separate estimates of them. Since $[\eta]$ is rather insensitive to d , we may use an approximate value of d . From the molecular model of PPP chain constructed on the basis of the crystallographic data for polyacetylenes,^{23,24} d was estimated to be $1.1 \pm 0.2 \text{ nm}$. This d value along with the above q/M_L , A , and B values yields the result: $M_L = 480 \text{ nm}^{-1}$, $q = 3.8 \text{ nm}$ and $\Phi_\infty = 2.17 \times 10^{23} \text{ mol}^{-1}$. The solid curve in Figure 8 represents the values calculated from the Yamakawa-Fujii-Yoshizaki theory with these parameter values, which fits the data points well. The uncertainty in d of $\pm 0.2 \text{ nm}$ gives rise to those in M_L of $\pm 20 \text{ nm}^{-1}$ and in q of $\pm 0.1 \text{ nm}$.

As mentioned above, at M_w lower than 3×10^5 PPP in toluene is also in the unperturbed state. Therefore a similar analysis was performed with the $\langle S^2 \rangle_z$ and $[\eta]$ data in toluene in this molecular weight range. The result is: $M_L = 490 \text{ nm}^{-1}$, $q = 3.9 \text{ nm}$, and $\Phi_\infty = 2.35 \times 10^{23} \text{ mol}^{-1}$. The solid line in Figure 5 and the dashed line in Figure 8

Figure 8. Comparison of the measured $[\eta]$ with the theoretical values calculated from the Yamakawa-Fujii-Yoshizaki theory: solid curve, calculated with $q = 3.8 \text{ nm}$, $M_L = 480 \text{ nm}^{-1}$, and $d = 1.1 \text{ nm}$; dashed curve, with $q = 3.9 \text{ nm}$, $M_L = 490 \text{ nm}^{-1}$, and $d = 1.1 \text{ nm}$.

Table III. Molecular parameters of poly(1-phenyl-1-propyne)

Solvent	q	M_L	d	ϵ	Φ_∞
	nm	nm^{-1}	nm		10^{23} mol^{-1}
Cyclohexane	3.8 ± 0.1	480 ± 30	1.1 ^a	2.1	2.17
Toluene	3.9 ± 0.1	490 ± 30	1.1 ^a	2.4	2.35

^a Assumed values.

represent the theoretical values with these parameter values. The agreement between theory and experiment is also satisfactory for M_w below 3×10^5 . The upward deviation of the data points at higher M_w is ascribed to the intramolecular excluded-volume effect. The wormlike chain parameters of PPP thus determined are summarized in Table III. The M_L values obtained are consistent with the structure of PPP whose M_L is 480–530 nm^{-1} when estimated from the above-mentioned crystallographic data for polyacetylenes.^{23,24}

In terms of q , PPP is much more flexible than typical semiflexible polymers such as poly(*p*-benzamide) ($q = 50 \text{ nm}$)²⁵ and poly(hexyl isocyanate) ($q = 21\text{--}42 \text{ nm}$)⁸⁻¹¹ and

Figure 9. Double-logarithmic plot of δ against M_w for PPP in cyclohexane and toluene.

comparable to polyamides containing piperazine rings on the main chain ($q=1.2$ – 6.4 nm).^{4–6} However it is definitely stiffer than polystyrene.¹⁷ It is noted in Table III that Φ_∞ is not a universal constant but depends slightly on solvent. The difference in Φ_∞ is a direct reflection of the finding that while the radii of gyration in the two solvents are essentially the same for M_w below 3×10^5 , the intrinsic viscosities are different. The Φ_∞ values in these solvents are lower than any of the theoretical values so far calculated,^{26–29} but are comparable to those for polyamides.^{4,5}

Nagai¹⁵ was the first to present a theory for the optical anisotropy factor of a wormlike chain with cylindrical symmetry. For relatively flexible wormlike chains, his expression can be written

$$\delta = (2\varepsilon^2 q M_L / 135 M) [1 - 0(q M_L / M)] \quad (6)$$

where ε is defined by

$$\varepsilon = 3(\alpha_1 - \alpha_2) / (\alpha_1 + 2\alpha_2) \quad (7)$$

with α_1 and α_2 being respectively the longitudinal and transverse polarizabilities per unit contour length of the chain. The values of δ in the two solvents are plotted against M_w

Figure 10. Temperature dependences of A_2 , $(\ln \eta_r)/c$, and $\langle S^2 \rangle_z^{1/2}$ in cyclohexane: (○, ○–), $\langle S^2 \rangle_z^{1/2}$; (●), $(\ln \eta_r)/c$. The subscript 36 indicates the quantities at 36°C.

in Figure 9, which reproduces the inverse proportionality predicted by the leading term of eq 6 with reasonable accuracy; we note that the $O(qM_L/M)$ term in eq 6 does not exceed 0.012 in the M_w range studied. The values of $|\varepsilon|$ are estimated to be 2.1 and 2.4 for cyclohexane and toluene, respectively. These values are compared with 2.1 obtained by Sakurai *et al.*¹³ for poly(terephthalamide-*p*-benzohydrazide) in dimethylsulfoxide.

Inter- and Intramolecular Excluded-Volume Effects

Figure 10 shows the temperature dependence of A_2 for fractions A-3 and A-4 in cyclohexane in comparison with those of $\langle S^2 \rangle_z$ and $(\ln \eta_r)/c$. While A_2 changes remarkably with temperature, both $\langle S^2 \rangle_z$ and $(\ln \eta_r)/c$ virtually remain unchanged. Thus for PPP in cyclohexane, the intermolecular excluded volume changes remarkably with temperature, but the intramolecular excluded volume is essentially negligible. This is a typical feature of a

semiflexible polymer,¹² which reflects the fact that even though each segment has a finite excluded volume, it has no chance to meet with other segments on the same chain because of the stiff nature of the chain. Cellulose diacetate in 2-butanone³⁰ and poly(phenylsilsesquioxane) in ethylene dichloride³¹ are known to exhibit similar behavior. In spite of the similarity in structure and solvent, PPP is contrasted with polystyrene, for which both effects are closely correlated. In toluene PPP undergoes both the inter- and intramolecular excluded-volume effects; the latter effect becomes appreciable at $M_w \sim 3 \times 10^5$, but is not so detailed as to permit quantitative analysis.

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