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Poly(organophosphazene) 고립연쇄의 분자형태 : 2. Poly[bis(phenylphenoxy)phosphazene] 고립연쇄의 분자형태

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Molecular Dimension of Poly(organophosphazene) : 2. Unperturbed Molecular Dimension of Poly[bis(phenylphenoxy)-phosphazene]

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요 약 : Poly[bis(phenylphenoxy)phosphazene](PBPPP)를 합성하고 분별하였으며, 분별시료들에 대한 분자특성을 용액론적 방법으로 결정하였다. 분별시료들의 분자량범위는 8.3×10^4에서 176×10^4 g/mol이었다. Cyclohexanone 50℃에서 배제체적효과가 사라졌으며, 이 θ-상태에서 본성점도는 $M^{1/2}$에 비례하지 않았다. 이것으로 미루어 PBPPP분자는 반굴곡성 분자특성을 갖는 것으로 판단되었다. Cyclohexanone 60℃에서 분자량 8.7×10^5 g/mol 이하의 분자들은 A_2가 양의 값이었으나 근본적으로 비섭동상태이었으며 분자량 8.7×10^5 g/mol 이상에서는 섭동상태이었다. Yamakawa와 Fujii의 wormlike cylinder 이론에 의한 비섭동 PBPPP 분자의 persistence length, q는 4.2 nm 및 shift factor, M_L은 1300 nm^{-1}이었다. $\alpha_\eta^3=\alpha_s^{1.79}$의 관계와 Flory-Fox식을 이용하여 관성반경, $\langle S^2\rangle$ 값을 계산하였고, Benoit-Doty의 식을 이용, n_k^c값 80을 산출하였다. Cyclohexanone 60℃에서 $n_k^c > 80$에서는 배제체적효과가 나타났으며 이때 binary cluster integral, β 값은 77.6×10^{-24} cm^3로서 확장된 coil형 연쇄의 거동을 보였다. 이상의 모든 실험적 결과로 PBPPP분자는 근본적으로 반굴곡성 분자특성을 취하나, 저분자량측에서는 막대형의 경직성을 나타내고 분자량이 증가할수록 배제체적효과에 의하여 유연해지는 분자특성을 지닌 것으로 밝혀졌다.

Abstract : Molecular characterization by dilute solution technique was made on those well fractionated samples of poly[bis(phenylphenoxy)phosphazene](PBPPP) ranging in number-average molar mass $\overline{M}_n$ from 8.3×10^4 to 176×10^4 g/mol. In cyclohexanone at 50℃, the excluded volume effect vanished and the intrinsic viscosity under theta condition was not proportional to $M^{1/2}$. In cyclohexanone at 60℃, it is found that the molecules are found to be unperturbd below $\overline{M}_n=8.7\times10^5$ g/mol even they have positive value of second virial coefficient, and perturbed above it. When modeled by the wormlike cylinder, the unperturbed PBPPP chain was characterized by a persistence length q=4.2

nm and a molar mass per unit contour length $M_L = 1300\ nm^{-1}$. Values of the radius-expansion factor α_s for the PBPPP fractions were calculated on the basis of the relation $\alpha_\eta^3 = \alpha_s^{1.79}$. The mean square radius of gyration $\langle S^2 \rangle$ data, being computed with the combination of α_s values and Flory-Fox expression, was treated in terms of Benoit-Doty theory to yield 80 for the critical segment number n_K^c. The binary cluster integral β found at above $n_K^c = 80$ in perturbed state was $77.6 \times 10^{-24}\ cm^3$, which suggests the chain is flexible but expanded. All the experimental result so far obtained indicated that the overall chain conformation of PBPPP is essentially semiflexible and changes continuously from a short rod to a long expanded coil with an increase in molar mass.

INTRODUCTION

In recent years, intensive studies of polyphosphazenes with various kinds of side groups have been performed experimentally with respect to their synthesis, reactivities, and solid state properties.[1~4] The wide potential in newer functions such as biocompatibility, electric or photoconductivity, and the side chain liquid crystallinity together with the well-known useful properties including lower T_g, flame retardance, stability to UV radiation, and the reasonably high thermal stability, is some of the reasons that this type of polymer is being extensively investigated.

Basically, the physical properties exhibited by this polyphosphazene can be understood in terms of inherent skeletal flexibility, with specific physical or chemical characteristics imposed by the side groups. The most striking effect exerted by the side group is the conformational change of the phosphazene backbone chain which, in turn, leads to the variation of the physical properties of the polymer.

Thus, from both the theoretical and experimental points of view, the molecular characterization and particularly the evaluation of the conformational characteristics of such polymers having specific side groups are considered to be the essential procedures not only to obtain a better understanding of the structure-property relationship but also to provide a basis for more perfect molecular design to produce a new functional materials. Theoretical analysis and experimental data, however, for the conformational characteristics of polyphosphazenes are yet few.

In the present work, it has been attempted to synthesize poly[bis(phenylphenoxy)phosphazene] (PBPPP) and to evaluate its conformational characteristics quantitatively. A variety of dilute solution techniques have been used for the molecular characterization and those results obtained are interpreted in terms of the existing theories for the chain conformation[8,18~21,30,31] to offer a quantitative description on the molecular dimension for the given polymer chain.

EXPERIMENTAL SECTION

Polymer

The PBPPP was synthesized by the procedure described by Allcock and coworkers.[9] The hexachlorocyclotriphosphazene(13 g)(HCTP), purified by recrystallization and sublimation, was thermally polymerized in a sealed evacuated tube at 250 ± 1.0℃ until the molten viscous reaction mixture lost its fluidity. The poly(dichlorophosphazene) (10.2 g)(PDCP) thus obtained was dried under reduced pressure to remove the unreacted HCTP and then dissolved in 200 ml of dry benzene. To this PDCP solution was added slowly the solution of THF-sodium biphenyloxide prepared by refluxing the mixture of 150 ml THF, 47.6 g of 4-hydroxybiphenyl, and 5.5 g of metallic sodium for 21 hrs. After the whole reaction mixture was kept for 23 hours at 61-64℃ with vigorous stirring, the mixture was cooled to 45℃ and acidified by adding 6% HCl solution. The polymer was then precipitated by pouring the reaction mixture into a large quantity

of methanol, filtered, and dried under reduced pressure. All polymers were subjected to Soxhlet extraction with methanol(one day) and n-heptane (one day) to remove any residual salts and low molar mass species. Further purification of the polymer, achieved by successive cycles of solubilization in hot benzene and precipitation into methanol, yielded white solid product.

All the reactions and treatments involving the use of PDCP were carried out in dry nitrogen atmosphere.

I.R. Spectroscopy

Infrared spectra of PBPPP and HCTP were obtained with the use of a JASCO Model A-102. KBr pressed pellet technique was used. Calibration was made by means of the usual polystyrene film.

Solubility Test

The solubility of the polymer to those common organic solvents was tested by placing about 0.1 g of the polymer in 10 ml of desired solvent and observing the transparency of the system visually. The system was shaken throughout the test period and the temperature was raised from room temperature to 60℃ with specified time interval. Table 1 shows the results of solubility test.

Fractionation

The fractionation of PBPPP was carried out by the column elution technique. The polymer was deposited on glass beads(dia.=0.5 mm) packed in a column and successive elution was carried out with liquid of increasing solvent power. The composition gradient was varied from 100% of nonsolvent to 100% of good-solvent with time. The polymer molecules were transferred to the top of the column, being eluted by the liquid mixture which passes through the column upward under constant temperature. A fixed amount of eluted fraction was collected, and the polymer was recovered by solvent vaporization.

The solvent system used for the good- and nonsolvent was cyclohexanone and n-haptane, respectively. The temperature of the column was controlled to keep 60℃ by circulating hot water. The schematic diagram of the fractionation results is illustrated in Fig. 2.

Table 1. Solubility Behavior of PBPPP in Various Solvents.

Solvents	$(cal/cm^3)^{1/2}$	Temp.(℃)			
		30	40	50	60
n-heptane	7.4	i	i	i	i
cyclohexane	8.2	i	i	i	i
carbontetrachloride	8.6	i	i	i	
toluene	8.9	i	i	i	i
THF	9.1	i	i	sw	sw
benzene	9.2	i	i	sw	sol
chloroform	9.3	i	i	sw	sw
MEK	9.3	i	i	i	
chlorobenzene	9.5	i	i	sw	sol
1,2-dichloroethane	9.8	i	i	i	i
acetone	9.9	i	i	i	
cyclohexanone	9.9	i	ps	sol	sol
1,4-dioxane	10.0	i	i	i	i
pyridine	10.7	i	sw	sol	sol
dimethylsulfoxide	12.0	i	i	i	i
DMF	12.1	i	i	i	sol
methanol	14.5	i	i	i	

i : insoluble, sw : swelling, ps : partialy soluble, sol : soluble.

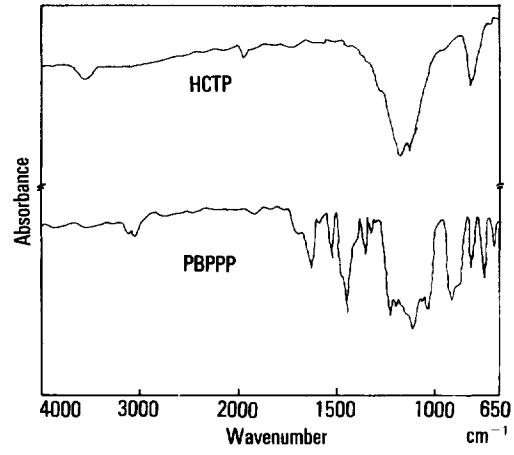


Fig. 1. IR spectra of HCTP and PBPPP.

Viscometric Measurement

An Ubbelohde suspended level type of viscometer

	Sample code	Weight(g)	$[\eta]^{a)}$(dl/g)
F-PBPPP (10g)	F-1	0.2153	
	F-2	0.3414	
	F-3	0.4016	
	F-4	0.5943	
	F-5	1.0275	0.0076
	F-6	0.6075	
	F-7	0.2028	
	F-8	0.0522	
	F-9	0.0163	
	F-10	0.0105	
	F-11	0.0686	0.0150
	F-12	0.0280	
	F-13	0.0741	
	F-14	0.0596	0.0420
	F-15	0.1279	0.1664
	F-16	0.1727	0.3200
	F-17	0.8865	0.6900
	F-18	0.5350	1.0000
	F-19-a	0.3216	1.0700
	F-19-b	0.3678	1.1960
	F-19-c	0.8566	1.3320
	F-19-d	0.4634	1.4680
	F-19-e	0.0438	
	F-20	0.3871	1.7610

Fig. 2. Fractionation results of PBPPP by column elution method.
a) Value of [η] in cyclohexanone at 60.0℃.

was employed to measure the flow times of solvent and PBPPP solution at the given temperature controlled within ± 0.05℃.

A simultaneous extrapolation to infinite dilution of the plot of η_{sp}/C and $\ln \eta_{rel}/C$ versus concentration, as usual, yielded the values of intrinsic viscosity from the common intercept and Huggins constant from the slope.

Membrane Osmometry

Osmotic pressure of solutions of PBPPP in freshly distilled and degassed cyclohexanone was measured with a Wescan Model 310-104 fitted with semipermeable membrane RC 51. The measuring temperature was 52.3℃

Experimental values of reduced osmotic pressure was plotted against concentrations(0.2-1.0 g/dL) and extrapolated to infinte dilution. The number average molar mass $\overline{M}_n$ and second virial coefficient A_2 were determined from the intercept and slope, respectively.

Determination of Theta Temperature

The theta temperature of the PBPPP-cyclohexanone system was determined by the phase equilibrium method.

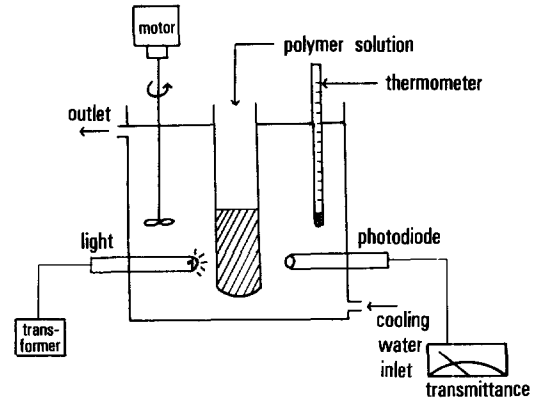


Fig. 3. Schematic diagram of the turbidimeter.

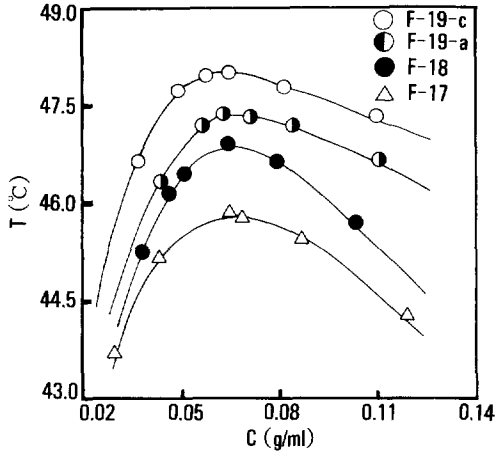


Fig. 4. Phase diagram of PBPPP fractions.

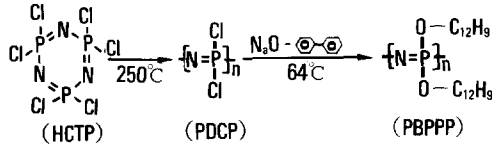
The cloud point was measured for a number of different concentrations of a PBPPP fraction of known $\overline{M}_n$ with temperature variation. Four polymer fractions were selected for the measurement. The first sign of cloudiness of the solution was detected by a turbidimeter(Fig. 3) which was designed to monitor the change of intensity of the light transmitted through the solution. The critical precipitation temperatures T_C were then determined from the phase diagram as the maximum points of each plot of the precipitation temperature versus the concentration(Fig. 4). The plot of T_C^{-1} vs. $M^{-1/2}$ yielded theta temperature from its inter-

cept.[10]

RESULTS AND DISCUSSION

Synthesis and Characterization

The synthetic pathway is outlined in Scheme 1. The PDCP, prepared by the thermal polymerization of the cyclic trimer HCTP, was allowed to react with the sodium salt of 4-hydroxybiphenyl to give a white solid state polymer, PBPPP. The maximum conversion to polymer was 54.3% and the $\overline{M}_n$ value of unfractionated polymer was 7.5×10^5 g/mol.



Scheme I

The I. R. spectroscopy was the main method used for the structure proof. The I. R. spectra of PBPPP shown in Fig. 1 reveals no evidence of chlorine at 1300 cm^{-1} but shows an intense absorption band at 1240 cm^{-1}(-P-N-), which is characteristics of a high polymeric phosphazene skeleton.[9,11] The weak peak at 3020 cm^{-1}(Ar, CH), the strong peaks at 1210 cm^{-1}(P-O-C, Aryl) and 1470 cm^{-1} (Aro., -C=C-) confirm qualitatively that the chlorine atoms in PDCP are replaced by the aromatic side groups.

Due its poor solubility to those common organic solvents at room temperature, solution state NMR spectra could not be obtained.

The solubility behavior of PBPPP has been examined over a wide range of organic solvents whose solubility parameters range from 7.4 to 14.5 $(cal/cm^3)^{1/2}$. As the Table 1 shows, the polymer is found to be insoluble in most of the organic solvents with some exceptions of polar solvent at relatively high temperature. This result is tentatively ascribed to the microcrystallinity due possibly to the liquid crystalline type side group stacking behavior which can be originated by a restricted conformational reorientation of backbone chain as a consequence of the steric hindrance associated with the rigid biphenyl groups. A similar effect was observed by Allcock and coworkers[11] for the polyphosphazene containing phenylazophenoxy unit. They concluded the insolubility of such polymers was due to their high degree of microcrystallinity.

In order to avoid the tailing effect, fractional solution technique, which involves extracting fractions of increasing molar mass by use of a series of eluents of increasing solvent power, was employed. As the diagram illustrated in Fig. 2, 24 fractions were obtained. On the basis of both the weights fractionated and [η] values of respective fractions, it can be concluded that the fractionation itself is conducted fairly well. The temperature was controlled carefully to avoid the degradation of polymer.

Attempts to obtain the size exclusion chromatograms of the polymer fractions have been unsuccessful. The analysis was attempted on commercial Styragel column at a variety of temperatures above 60℃ and concentrations(DMF or cyclohexanone), but in almost all cases an anomalous behavior like severe tailing, nonreproducibility, or distortion of chromatogram was observed suggestive of an adsorption type of interaction between the polymer and the packing materials.

Fig. 5 shows the reciprocal square root molar mass dependence of critical temperature for the

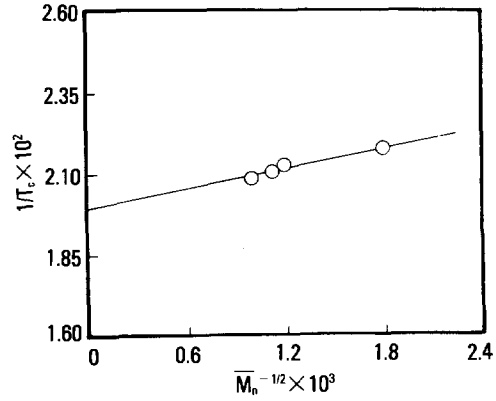


Fig. 5. Plot of $1/T_c$ vs. $\overline{M}_n^{-1/2}$.

four fractions of different molar mass. All the experimental points fall nicely on a straight line and the extrapolation to the infinite molar mass yielded theta temperature as 50 ± 0.05℃ in cyclohexanone, where both inter- and intramolecular excluded volume effects vanish.

Fig. 6 illustrates the square root of reduced osmotic pressure as a function of concentration at 52.3℃ in cyclohexanone for some of the polymer fractions selected. Values of $\overline{M}_n$ and A_2 were obtained from the intercept and slope respectively and summarized in Table 2. The $\overline{M}_n$ range found is considered to be wide enough to examine the molecular characteristics of the given polymer. A_2 values in Table 2 show the usual increasing trend with decreasing molar mass but the average value of A_2 is appeared as quite small than a flexible polymer exhibits. This low value of A_2 is considered to be an evidence of the inherent stiffness of the chain.

Fig. 7 is illustrated a representative Huggins and Kraemer plots for the fraction F-19-c in cyclohexanone at 60℃. From the common intercept and slope of the Huggins plot, [η], and Huggins constant, k′, were calculated, respectively. The data thus obtained from the selected fractions both at theta temperature T_θ and 60℃ are also listed in Table 2.

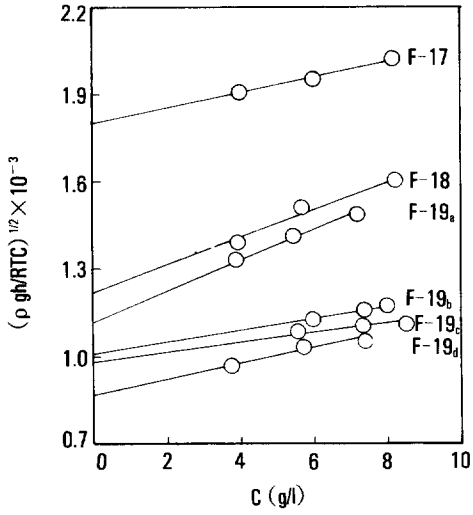


Fig. 6. Plots of $(\rho gh/RTC)^{1/2}$ vs. C of PBPPP in cyclohexanone at 52.3℃.

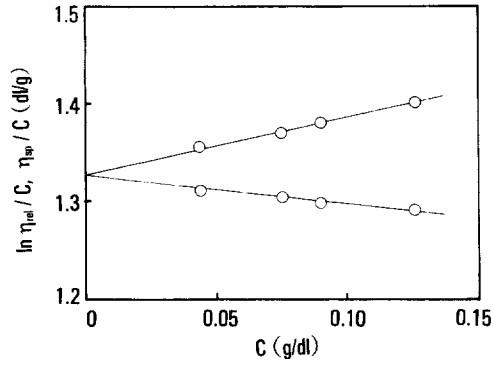


Fig. 7. Huggins & Kraemer plots for the polymer PBPPP in cyclohexanone at 60℃.

Table 2. Molecular Characteristics of PBPPP Molecules

Sample code	$\overline{M}_n/10^5$ (g/mol)	$A_2/10^4$ (ml · mol · g^{-2})	$[\eta]^{a)}$ (ml · g^{-1})	k′	$[\eta]^{b)}$ (ml · g^{-1})	α_η^3
F-20	17.6	0.42	176	0.52	151	1.17
F-19^{d}	13.0	0.50	147	0.45	130	1.31
F-19^{c}	10.1	0.27	133	0.29	121	1.10
F-19^{b}	9.4	0.31	120	0.26	112	1.07
F-19^{a}	7.8	1.80	107	0.23	105	1.02
F-18	7.0	1.30	100	1.01	99	1.01
F-17	3.0	1.05	69	0.73	67	1.03
F-16	0.83	1.63	31	0.81	29	1.07

a) Intrinsic viscosity at 60℃ in cyclohexanone.

b) Intrinsic viscosity at theta condition.

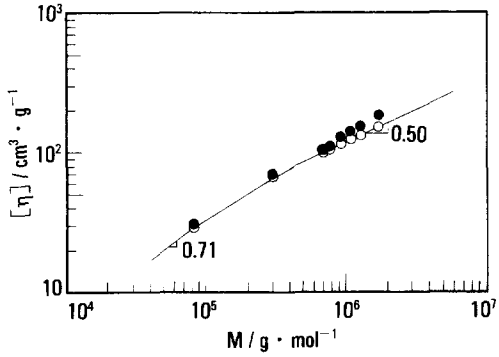


Fig. 8. Molar mass dependence of [η] for PBPPP samples in cyclohexanone at T_θ(○) and 60℃(●).

Fig. 8 shows the conventional double logarithmic plots of [η] versus $\overline{M}_n$ in cyclohexanone at T_θ and 60℃. The data point at T_θ follow closely the smooth curve drawn, whose slope decreases from 0.71 to 0.5 with increasing molar mass in the $\overline{M}_n$ range examined. This behavior suggests that the molecules of low molar mass have a finite chain stiffness in the unperturbed state.[12] On the other hand, those data points at 60℃ appear slightly above but follow the solid curve at $\overline{M}_n$ lower than 8.7×10^5 g/mol and then deviate definitely upward from the curve. This implies that the PBPPP chains in cyclohexanone at 60℃ is essentially unperturbed below this $\overline{M}_n$ even if they have positive value of A_2 and perturbed above this $\overline{M}_n$ by intramolecular excluded volume effect. Although the value of Mark-Houwink exponent 0.71 is found lower than 0.8 which is known as the asymptotic value to be assumed by the random coil polymer, those facts that the [η] is not proportional to $M^{1/2}$ as expected for a rod and that the chains of low molar mass at 60℃ follow the unperturbed chain behavior may be taken as the reflection of a finite stiffness of the PBPPP chain.

Furthermore, according to recent experimental studies of excluded volume effects in flexible polymers, the relation between $A_2M/[\eta]$ and $[\eta]/[\eta]_\theta$ follows a universal curve, which traces the typical data for flexible polymers as shown in Fig. 9 by the thin line.[13,14] Values of $A_2M/[\eta]$ of PBPPP in Fig. 9 appear far below the universal

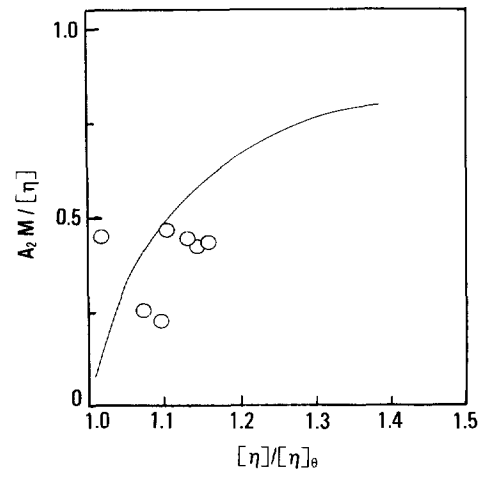


Fig. 9. Dimensionless quantity of $A_2M/[\eta]$ plotted against $[\eta]/[\eta]_\theta$ for PBPPP in the cyclohexanone.

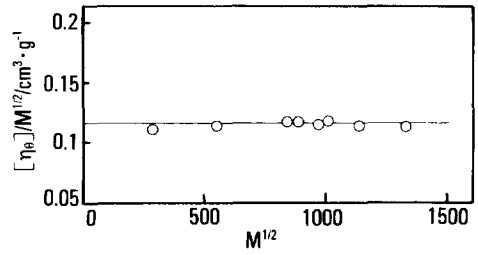


Fig. 10. Stockmayer-Fixman-Burchard plots for PBPPP in cyclohexanone at 50℃.

curve, being a strong support for the suggestion of finite stiffness of PBPPP chains. Consequently, it has been attempted to examine whether the equilibrium and hydrodynamic data for the PBPPP obtained can be interpreted in terms of semiflexible chain theory.

Estimation of Unperturbed Dimension

Fig. 10 shows the $[\eta]_\theta$ data plotted according to the Stockmayer-Fixman plot.[15] Assuming the Flory's viscosity factor in the unperturbed state, Φ_o, to be 2.5×10^{23} mol^{-1}, a value of 1.03×10^{-17} cm^2 was obtained for $\langle S^2\rangle_o/M$ from the ordinate intercept of the straight line. Here, $\langle S^2\rangle_o$ is the unperturbed radius of gyration. This value is comparable with 1.26×10^{-17} cm^2 of poly(isophthaloyl-trans-2,5-dimethylpiperazine) which is known as wormlike chain.[16]

Another thing to note is that the slope of line in Fig. 10 approaches to zero which means the theta condition established above is fairly accurate.

Dimensional Parameters from the Wormlike Cylinder Model

The PBPPP molecule in cyclohexanone at 50℃ may be modeled by the wormlike cylinder,[17] which is characterized by three parameters : persistence length q, diameter d of the cylinder, and the shift factor M_L defined by the ratio of molar mass M to the contour length L. Yamakawa and coworkers[17~19] derived an expression for $[\eta]$ of the model, which contains M_L, q, and d as the parameters, and later Bohdanecky[20] proposed a simple procedure for data analysis using the following approximation to the original equation of Yamakawa and coworkers :

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

with $$A_\eta=A_0 M_L \Phi_0^{-1/3} \quad (2)$$

$$B_\eta=B_0(2q/M_L)^{-1/2}\Phi_0^{-1/3} \quad (3)$$

where Φ_0 is the Flory viscosity factor for unperturbed random coil, and A_0 and B_0 are given as functions of reduced diameter d_r which is defined by $d_r=d/\lambda^{-1}$ where λ^{-1} is Kuhn statistical segment length.[20] The value of d_r was estimated as 0.25 from the unperturbed molecular dimension determined by the Stockmayer-Fixman method and the diameter d=2.06 nm is approximated from the molecular model of PBPPP chain constructed on the basis of the data on X-ray diffraction analysis of PDCP.[21]

Fig. 11 shows the $[\eta]_\theta$ data plotted against $M^{1/2}$ according to equation 1). The experimental points fall closely on the straight line, yielding $A_\eta=160$ $g/^{1/3}$ cm^{-1} and $B_\eta=2.0$ $g^{1/3}$ cm^{-1}. These values, in turn, gave q=4.2 nm and $M_L=1300$ nm^{-1}.

The solid line in Fig. 12 represents the theoretical plot, drawn by $[\eta]$ values computed with the same values of above q and M_L by employing an equation of $[\eta]$ for the wormlike chain proposed by Yamakawa and coworkers[18] :

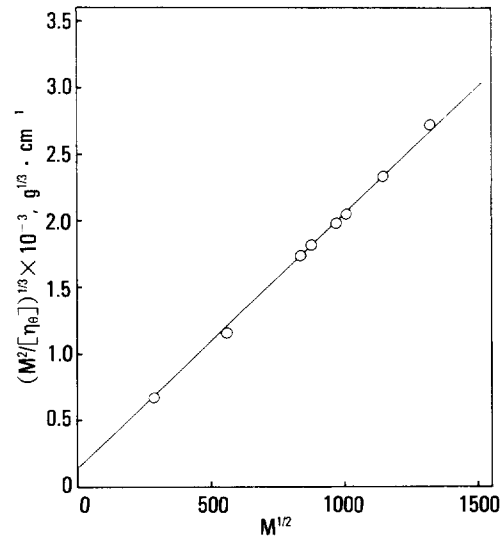


Fig. 11. Plot of $(M^2/[\eta])^{1/3}$ vs. $M^{1/2}$ for PBPPP in cyclohexanone at 50℃.

$$[\eta]=(\Phi_0 L^{3/2}/M)[1/(1-\sum_{i=1}^{\infty} C_i L^{-i/2})] \quad (4)$$

where M is the molar mass, L is the contour length, and C_i is the coefficient which is independent of L. The theoretical line fits the experimental points fairly well, which confirms the semiflexible character of PBPPP molecule in unperturbed state.

A similar treatment of the data obtained from the low molar mass fractions at 60℃ yielded q=4.8 nm and $M_L=1280$ nm^{-1}. This consistence of dimensional parameters with those of theta state is a strong proof that the molecules of molar mass below than 8.7×10^5 g/mol are essentially free from excluded volume effect due to the short chain effect, even though they are not in the theta condition.

The wormlike chain parameters obtained for the PBPPP are summarized in Table 3 together with data associated with other unperturbed wormlike chains. A comparison of q values listed in Table 3 makes it clear that PBPPP is much more flexible than those typical semiflexible polymer like Schizophyllan and poly(hexylisocyanate) and comparable to polyamide containing piperazine ring in the

Table 3. Dimensional Parameters of PBPPP and Other Unperturbed Wormlike Polymers

Polymers	Solvents	Temp.(℃)	q(nm)	M_L(nm^{-1})	d(nm)[g]
Schizophyllan[a]	0.01 N NaOH	25	150	2170	
PHIC[b]	hexane	25	42	715	
PTDP[c]	trifluoroethanol	25	6.4	350	
PBPPP	cyclohexanone	50	4.2	1300	2.06
PPP[d]	cyclohexane	36	3.8	480	1.10
	toluene	25	3.9	490	1.10
PC[e]	THF	25	1.8	260	
Polystyrene[f]	cyclohexane	T_e	1.10	390	

[a] Ref. 25). [b] Poly(hexylisocyanate), Ref. 26). [c] Poly(terephthaloyl-trans-2,5-dimethylpiperazine), Ref. 27). [d] Poly(1-phenyl-1-propyne), Ref. 12). [e] Bisphenol A polycarbonate, Ref. 14). [f] Ref. 28). [g] Values calculated from the molecular model.

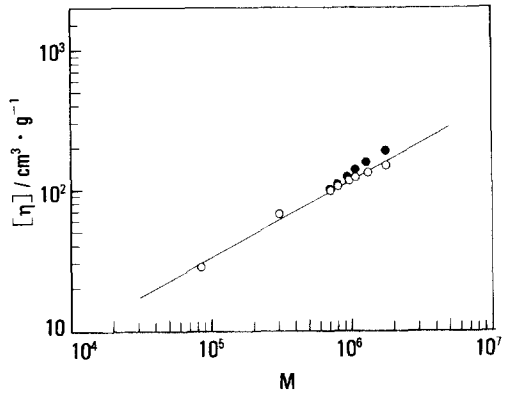


Fig. 12. Comparison of the measured $[\eta]_\theta$(○) and $[\eta]^{60℃}$(●) with the theoretical values computed from the Yamakawa-Fujii theory : solid line, calculated with q=4.2 nm, M_L=1300 nm^{-1}, and d=2.06 nm.

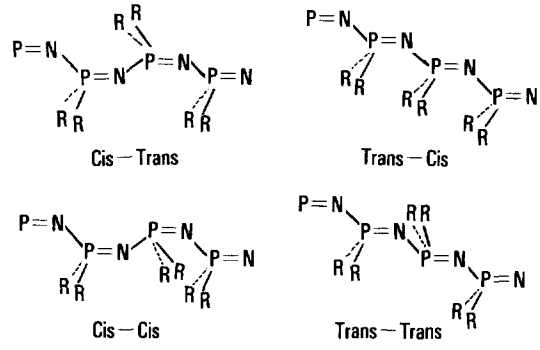


Fig. 13. Four probable conformational model of PBPPP.

main chain or polyacetylene attached with phenyl side group, but definitely stiffer than polycarbonate or polystyrene.

On the basis of the chemical structure and conformational parameters so far obtained, it can be concluded that the chain rigidity of the PBPPP molecule arises from the severely restricted conformational reorientation of backbone chain due mainly to the strong steric interference acting between those rigid biphenyl groups. It is reasonable therefore to suggest that the most preferable conformational structure taken by PBPPP molecule is the cis-trans type which is illustrated in Fig. 13.

Excluded Volume Effect

The deviations of measured $[\eta]$ from the Yamakawa-Fujii's theory, as is shown in Fig. 12, are, mainly, a consequence of volume exclusion between chain segments. To make this volume effect to be expressed quantitatively, it has been attempted to analyze the data in terms of Benoit-Doty theory.[22] As is known well, however, the excluded volume effect is less sensitive with $[\eta]$ than radius of gyration.[29] Thus, the need arises primarily for obtaining data of radius of gyration. Unfortunately, since it was impossible to conduct experiments to obtain radius of gyration directly due to the unusual solubility behaviour of PBPPP, an indirect method involving viscosity expansion factor, α_η, and radius expansion factor, α_s, is used for the estimation of radius of gyration.

Recently, from an extensive study on the experimental evidence against the two-parameter theory, Miyaki[23] proposed a reliable relation between α_η and α_s as follows :

$$\alpha_\eta^3=\alpha_s^{1.79} \quad (-0.2 < \log \alpha_s^3 < 0.3) \tag{5}$$

With combination of this relation with the well known Flory-Fox expression[24] for intrinsic viscosity,

$$[\eta]=6^{3/2}\Phi(\langle S^2\rangle/M)^{3/2}M^{1/2} \tag{6}$$

where $\langle S^2\rangle$ is the mean square radius of gyration and $\Phi=\Phi_o(\alpha_\eta/\alpha_s)$,[3] values of radius of gyration for the respective polymer fractions were possible to estimate by using the data of α_η^3 listed in Table 2. The results are summarized in Table 4.

Fig. 14 shows the molar mass dependence of $\langle S^2\rangle^{1/2}$ at T_θ and 60℃. As was the case of double logarithmic plots of $[\eta]$ versus molar mass, the data points in cyclohexanone at 60℃ deviate upward from the straight line of slope 0.5 at higher molar mass.

Benoit-Doty's expression for $\langle S^2\rangle$ of the Kratky-Porod wormlike chain[22,29,30] may be written as

$$\langle S^2\rangle/(2q)^2=n_k/6-1/4+1/4\ n_k-(1/8\ n_k^2)\ [1-\exp(-2n_k)] \tag{7}$$

where $n_k=M/(2qM_L)$ (8)

with M the molar mass of the chain. The quantity n_k is the number of Kuhn statistical segments in the chain. A reduced mean square radius of gyration $\langle s^2\rangle/(2q)^2$ should be a universal function of n_k if equation (7) holds. Thus, in Fig. 15 is illustrated the double logarithmic plot of $\langle S^2\rangle/(2q)^2$ against n_k with q=4.2 nm, and $M_L=1300\ nm^{-1}$. The plotted points for n_k below 80 fall closely on the solid line which represents equation (7). This is the strong evidence that the polymers in this range are not perturbed by excluded volume effect and their statistical radii obey equation (7). In the region of n_k around 80, however, the data points start to deviate upward from the solid line and follow the dashed line indicated. It is resonable therefore to assume that this deviation is attributed to the volume effect. Thus, the critical segment number n_k^c, defined as the n_k at the intersec-

Table 4. Values of α_s and Root Mean Square Radius of Gyration

Sample code	α_s	$\langle S^2\rangle^{1/2}$ (nm.)	$\langle S^2\rangle_o^{1/2}$ (nm.)
F-20	1.089	45.36	41.64
F-19-d	1.071	38.35	35.81
F-19-c	1.054	33.88	32.14
F-19-b	1.039	31.78	30.54
F-19-a	1.011	28.42	28.12
F-18	1.006	26.75	26.60
F-17	1.017	17.90	17.61
F-17	1.038	9.01	8.68

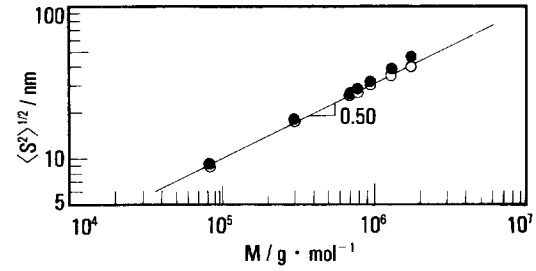


Fig. 14. Molar mass dependence of $\langle S^2\rangle^{1/2}$ of PBPPP in cyclohexanone at T_θ(○) and 60℃(●).

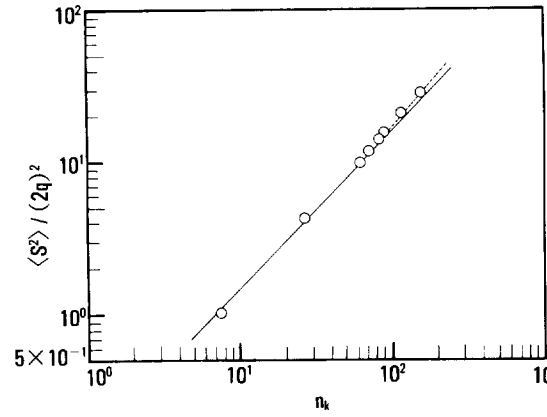


Fig. 15. Reduced mean square radii of gyration plotted against the number of Kuhn statistical segment of PBPPP in cyclohexanone at 60℃. $n_k^c=80$

tion of the dashed and solid line in Fig. 15, for the onset of volume effect of PBPPP in cyclohexanone is 80 which corresponds to molar mass 8.7×10^5 g/mol.

Quite recently, from the combination of the Yamakawa-Stockmayer perturbation theory for the radius expansion factor of a wormlike bead chain and the Domb-Barett equation[32] for a flexible chain, Kitagawa and coworkers[16] proposed an equation of the following form to estimate the excluded volume parameter B :

$$\langle S^2\rangle/M = 1.53(q/3M_L)(3/2\pi)^{3/5}B^{2/5}(M/2qM_L)^{1/5} \quad (9)$$

$$\text{with} \quad B=\beta/2qb^2 \quad (10)$$

where β is the binary cluster integral for a pair of beads and b is the spacing of two adjacent beads along the chain contour. Fig. 16 shows the $\langle S^2\rangle$ data for molar mass above 8.7×10^5 g/mol. The indicated solid line, drawn with q=4.2 nm and M_L= 1300 nm^{-1}, yielded 0.118 for B. Taking b in equation (10) to be 0.28 nm, the contour length per monomer, 77.6×10^{-24} cm^3 of β value is resulted, which is larger than $20\text{-}40\times10^{-24}$ cm^3 reported for the typical flexible polymers in good solvents.[8] Although enough information is not available at present to make clear why cyclohexanone acts as so good solvent for PBPPP, it would be worth considering that the molecules of PBPPP in perturbed state at higher range of molar mass are expanded. This can also be taken as an evidence of semiflexible nature of the PBPPP chain.

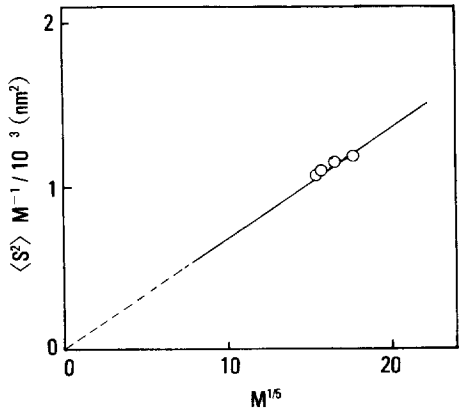


Fig. 16. Plot of $\langle S^2\rangle/M$ vs. $M^{1/5}$ for high molar mass fractions of PBPPP in cylohexanone at 60℃.

CONCLUSION AND REMARKS

A variety of fundamental dilute solution techniques has been used for the molecular characterization of well fractionated poly[bis(phenylphenoxy)phosphazene]. The analyses of intrinsic viscosity data in terms of wormlike cylinder model yield dimensional parameters as 4.2 nm for q and 1300 nm^{-1} for M_L, which implies the polymer molecules are essentially semiflexible.

In the state of non-theta condition, the polymer molecules of low molar masses reveal the unperturbed chain behavior due to the chain stiffness. With values of above q and M_L, it is found that the critical segment number n_k^c, the onset of excluded volume effect, is 80 which corresponds to molar mass 8.7×10^5 g/mol. From the reduced excluded volume parameter B=0.118 obtained at higher range of molar mass ($\overline{M}_n > 8.7\times10^5$ g/mol), a value of 77.6×10^{-24} cm^3 for β, the binary cluster integral between a pair of beads, is estimated. This means the molecules of higher molar masses are flexible but quite expanded under perturbed state.

Finally, it must be pointed out that the conclusion state above is considered to be less definitive because the most of the measured values are used without correction for the polydispersity. The anomalous behavior of solubility makes the experiment of GPC or light scattering impossible, but those facts that the fractionation has been conducted with great care and the good agreement between experimental and theoretical values of intrinsic viscosity make the conclusion on overall conformation and their dimensional parameters to be held as they stand.

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