Poly[terephthaloyl-1-(2-aminoethyl)piperazine]연쇄의 굴곡성

하 헌 승* · 이 동 주

인하대학교 고분자공학과 · *국방과학연구소 소재4실

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Semiflexible Chain Behavior of
Poly[terephthaloyl-1-(2-aminoethyl)piperazine]

Hun-Seung Ha* and Dong-Choo Lee

Dept. of Polymer Science and Engineering, Inha University Inchon, 402-751, Korea

*Agency for Defence Development, P. O. Box 35, Daejon, 300-600, Korea

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요 약 : Poly[terephthaloyl-1-(2-aminoethyl)piperazine](PTAP)의 분별시료들에 대한 극한점성도계수를 측정하여 주사슬의 유연성 변화를 검토하였다. 분별시료들의 수평균 분자량 범위는 1.33×10^4에서 9.88×10^4 g/mol이었고, 본성점도는 25℃, m-cresol용액을 사용하여 측정하였다. 이들 값으로부터 PTAP의 입체적 분자형태가 분자량 증가에 따라 반굴곡성 형태로부터 확장된 coil형으로 변하는 것을 확인하였으며 Bohdanecky이론에 근거한 worm-like cylinder의 model parameter값들을 산출한 결과 persistence length(q)값이 4.35nm, 단위 contour length당 분자량(M_L)이 260nm⁻¹, 및 root평균 양말단간 거리[$(\langle \overline{R^2} \rangle_0/M)^{1/2}$]값이 1.830×10^{-1} nm인 것으로 밝혀졌다.

Abstract : Intrinsic viscosities [η] of poly[terephthaloyl-1-(2-aminoethyl)piperazine](PTAP) in m-cresol at 25℃ were determined for well fractionated samples ranging in number average molar mass from 1.33×10^4 to 9.88×10^4 g/mol. The measured values of [η] indicated the chain conformation of PTAP to change continuously from a semiflexible chain to a long extended coil with an increase in molar mass. Viscometric data analysis on the basis of Bohdaneckey theory for worm-like cylinders yielded values 4.35nm, 260nm⁻¹, and 1830×10^{-4}nm which were assigned to the persistence length, the molar mass per unit contour length, and the root mean square end to end distance, respectively.

INTRODUCTION

The poly[terephthaloyl-1-(2-aminoethyl)piperazine](PTAP) is an aromatic polyamide-piperazine whose repeating unit is constituted with planar p-phenylene and piperazine ring. With this heterochain polyamide, it is easy to expect that the main chain can exhibit features predictable for stiff chains due to the partial double bond character of amide linkage. However, in case where an accurate molecular characterization of this type of polymers is concerned, the lack of solubility of the polymers has been the major problem.

The purpose of this study, therefore, is to eva-

luate those important conformational characteristics of the piperazine polyamide which has been molecular designed so as to enhance the solubility in more common organic solvents by introducing ethylene groups into the main chain of polymer.

Seven PTAP fractions covering a moderate range of molar mass were examined by osmometry and viscometry. Analysis of viscosity data in terms of current theory[1] for worm-like cylinder gives that the chain conformation of PTAP is semiflexible but changes continuously from semiflexible to extended coil with an increase of molar mass.

EXPERIMENTAL SECTION

Polymer

The PTAP samples were prepared by low temperature polycondensation[2] of terephthaloyl chloride and 1-(2-aminoethyl)piperazine in chloroform at $-5°C$. The preparation of low molar mass PTAP. sample was carried out by the method of Katz.[3]

Polymers obtained were purified by several cycles of dissolution-precipitation with dichloromethane/methanol mixture as good solvent and acetone as precipitant. Finally, polymers were dried under reduced pressure at room temperature for 48 hrs. Spectral characterization of the purified polymer was consistent with the assigned structure.

Solubility Test

The ability of a solvent to dissolve a definite amount of polymer at given temperature was estimated by close visual examination to ensure the absence of any undissolved material. Powders were tested for solubility at 2% concentration(w/w) in various solvents. Tests were conducted with 28 kinds of organic solvents and some of the selected results were listed in Table 1.

Fractional Precipitation

The fractional precipitation of polymer from the dilute solution was carried out by a conventional procedure starting with 0.8wt% of solution at 20°C. An addition of precipitant up to the first cloudiness

Table 1. Solubility Behavior of Poly[terephthaloyl-1-(2-aminoethyl)piperazine] in Various Solvents at 20°C

No.	Solvent	δ (cal/cm^3)$^{1/2}$	24 hr	48 hr
1	n-Hexane	7.3	IN	IN
2	Acetone	9.9	IN	IN
3	Chloroform	9.3	PS	PS
4	Acetic Acid	10.1	SOL	SOL
5	m-Cresol	10.2	SOL	SOL
6	DMAc	10.8	SOL	SOL
7	NMP	11.3	SOL	SOL
8	DMSO	12.0	SOL	SOL
9	DMF	12.1	PS	PS
10	Benzylalcohol	12.1	SOL	SOL
11	Ethanol	12.7	SW	SW
12	Methanol	14.5	SW	SW
13	Ethylene glycol	14.6	SW	SW
14	TFE		SOL	SOL
15	DCM/Methanol(50/50, 70/30, 85/15 vol%)		SOL	SOL

IN : Insoluble, SW : Swelling, PS : Partly soluble, SOL : Soluble.   DMAc : N, N-Dimethylacetamide, NMP : N-Methyl-2-pyrrolidinone, DMSO : Dimethylsulfoxide, DMF : N, N-Dimethylformamide, TFE : 2, 2, 2-Trifluoroethanol, DCM : Dichloromethane.

was followed by thermal dissolution through cooling and reequlilibration at 20°C. After settling overnight, the dilute phase was separated from the concentrated phase. The fractions thus obtained were successively precipitated and dried under reduced pressure. Mixed solvent composed with dichloromethane and methanol(85/15 vol%) was used as good solvent, and n-hexane as precipitant.

Viscometry

Dilute solution viscosity was measured in an Ubbelohde suspended level type viscometer for which kinetic energy correction was negligible. The temperature control was ± 0.01°C at 25°C. Values of intrinsic viscosity [η] were obtaind by treating the data of reduced and inherent viscosity on the basis of both Huggins[4] and Kraemer equations.[5]

Osmometry

Osmotic pressures of selected sample fractions were measured in benzyl alcohol at 30℃ by employing the Wescan Model 310-104 osmometer fitted with S & S AC 61 membrane. The equlibration was established usually within 30 minutes. Plots of reduced osmotic pressure against polymer mass concetntration for PTAP yielded number-average molar mass($\overline{M}_n$) and osmotic second virial coefficient.

Determination of Theta-Composition

The θ-composition was determined by cloud-point titration method.[6] Polymer solutions of different concentration at constant temperature were titrated with a precipitant until the first sign of turbidity. The volume fraction ϕ_3^i of precipitant to give the first cloud point is then plotted against the logarithm of the volume fraction ϕ_2^i of the polymer at cloud point. An extrapolation of the straight line to the axis of 100% of polymer yielded the composition of solvent-precipitant θ-mixture at the given temperature. The solvent-precipitant system used was dimethylacetamide-acetone at 25℃.

Partial Specific Volume

The partial specific volume($\overline{v}$) of the polymer was computed from the value of buoyancy factor, which was estimated from the slope of a plot of solution density against polymer concentration. Densities of polymer solution and solvent at 25℃ were measured by employing volume calibrated pycnometer(30ml. capacity). The solvent used was m-cresol.

RESULTS AND DISCUSSION

Solubility Behavior

Table 1 shows the solubility behavior of PTAP in some of selected organic solvents. It appeared that the PTAP revealed tendencies of dissolution in such a group of active solvents which have very high dipole moment or strong protic character. The optimum values of solubility parameter for the dissolution are ranged from 10.1 to 12.1 $(cal/cm^3)^{1/2}$.

From the viewpoint that PTAP is a sort of aromatic polyamides and hence may have high crystallinity, dissolution is expected to be possible only with a few highly polar solvents. But, contrary to this expectation, solvents like benzyl alcohol and mixed solvent of dichloromethane-methanol are appeared as good-solvent, as Table 1 exhibits. The uniquely enhanced solubility of PTAP is considered to be attributed to the higher entropy state of the polymer chains resulting from the flexible ethylene linkages. The greater disorder should facilitate solvation of the polymer chains.

It is also noteworthy that the PTAP can be dissolved in a mixed solvent constituted with various composition of dichloromethane and methanol, as described above, both of which are precipitants for the PTAP suggests that the mixed solvent system has great possibility of cosolvency.

Number Average Molar Mass($\overline{M}_n$) and Second Virial Coefficient(A_2)

Fig. 1 shows the plots of reduced osmotic pressure against concentration for PTAP fractions in benzyl alcohol at 30℃. The data points for each fraction are closely fitted by a straight line and al-
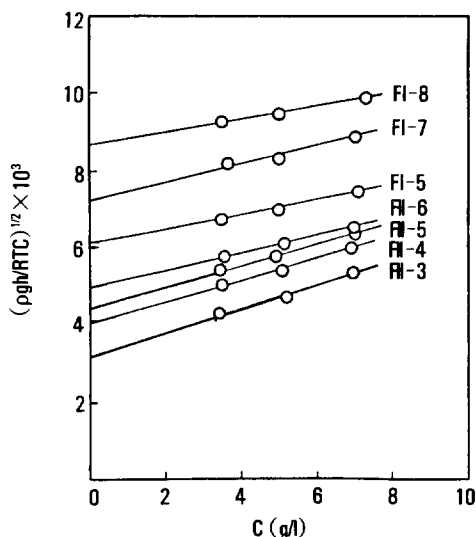

Fig. 1. Reduced osmotic pressure as a function of polymer mass concentration for PTAP in benzylalcohol at 30℃.

Table 2. Values of $\overline{M}_n$, A_2 and $[\eta]$ for the Fractionated Samples of Poly[terephthaloyl-1-(2-aminoethyl) piperazine]

Code No.	$[\eta]^a$ (dl/g)	$\overline{M}_n \times 10^{-4}$ (g/mol)	$A_2 \times 10^{4}$ ^{b} (dl mol g^{-2})
F I-5	1.22	2.70	2.386
F I-7	0.86	1.90	2.387
F I-8	0.66	1.33	2.935
F II-3	3.15	9.88	2.030
F II-4	2.40	6.25	2.334
F II-5	1.80	4.88	2.427
F II-6	1.59	3.92	2.183

^{a} Intrinsic viscosity, m-cresol, 25 ± 0.01°C

^{b} Osmotic second virial coefficient, benzylalcohol, 30°C.

Fig. 2. Log-log plot of osmotic second virial coefficient vs. $\overline{M}_n$ for poly[terephthaloyl-1-(2-aminoethyl)piperazine].

low us to evaluate the accurate values of $\overline{M}_n$ and A_2. The values of $\overline{M}_n$ and A_2 evaluated from the intercepts and slopes of the indicated straight lines are summarized in Table 2. The highest value of $\overline{M}_n$ found was 9.88×10^4 and the lowest was 1.33×10^4 g/mole. The span of molar masses appeared in Table 2 is considered somewhat narrow for more correct estimation of overall conformation due probably to its failure to take into account the possible difference of molecular shape between oligomer and high molar mass homologues, and hence it seems proper to regard the conformational characteristics evaluated here as pertinent to the part encompassed within the limit of molar masses listed in Table 2.

As Table 2 reveals, values of A_2 show no appreciable difference in their magnitude between fractions, and are appeared even larger than those for flexible polymers in good solvents.[7] Furthermore, double-logarithmic plots of A_2 against $\overline{M}_n$, as is illustrated in Fig. 2, shows the trend that A_2 is slightly lower for higher $\overline{M}_n$, and yields an empirical relationship between A_2 and $\overline{M}_n$ as :

$$A_2 = 1.8 \times 10^{-2} \, \overline{M}_n^{-0.22} \quad (1)$$

Following recent theories,[8,9] A_2 for a linear flexible polymer in a good solvent decreases with an increase in molar mass of polymer. Particularly, in case where A_2 is determined over a very wide ra-

nge of molar mass, it has been found that the plots of log A_2 against log $\overline{M}_n$ are not linear but followed a convex-downward curve with an asymptotic slope of -0.20. Refering to this well established statement, those results described above imply that the molecular shape of PTAP is the one quite different from the flexible polymer, at least.

Theta-composition of Mixed Solvent

Since that the accurate detection of precipitation temperature in a single solvent was found impossible within the experimentally possible region, the method using cloud point titration under constant temperature has been employed.

Fig. 3 illustrates the concentration dependences of acetone (precipitant) at the cloud points on the logarithm of volume fraction ϕ_2^i of PTAP in dimethylacetamide(DMAc) at 25°C.

Extrapolations of the concentrations of precipitant to the 100% of polymer intersected at one point without regard to the molecular size, yielding ϕ_3 as 0.225 within the error range of ± 0.5%. The θ-composition thus found for the system of DMAc-acetone at 25°C was 0.745 : 0.225 by volume fraction.

Intrinsic Viscosity[η]

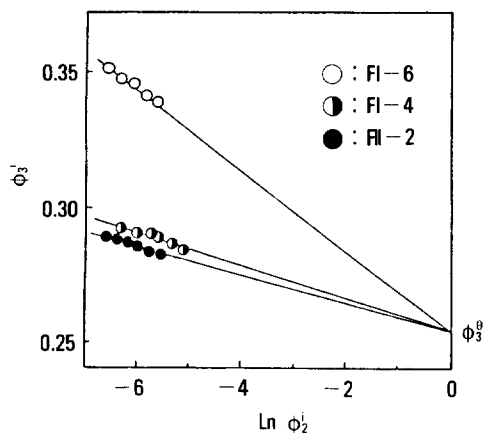Fig. 4 shows an example of $[\eta]$ determination by plotting simultaneously the reduced and inhe-

Fig. 3. Dependence of the volume fraction ϕ_3' of the precipitant acetone on the logarithm of the volume fraction of poly[terephthaloyl-1-(2-aminoethyl)piperazine] in DMAc at 25℃.
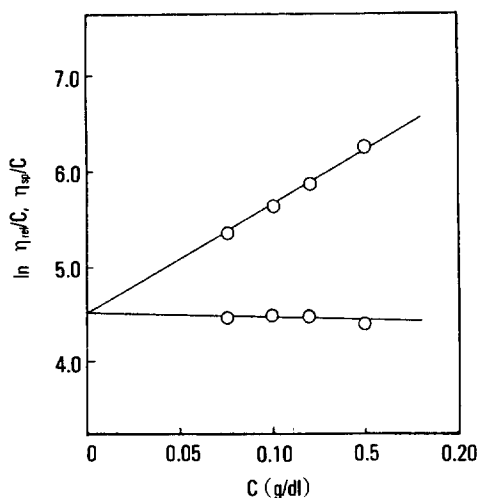

Fig. 4. Plot of η_{sp}/C and ln η_{rel}/C vs. C poly[terephthaloyl-1-(2-aminoethyl)piperazine] in m-cresol at 25℃.

rent viscosity against concentration and extrapolating to a common intercept. Those values thus obtained for all the fractions in m-cresol at 25℃ are summarized in Table 2, and the selected values of [η] are plotted double logarithmically against $\overline{M}_n$ in Fig. 5. The plotted points are fitted by a smooth curve convex upward. The slope of the curve is about 0.86 for $\overline{M}_n$ lower than 2.7×10^4 and about
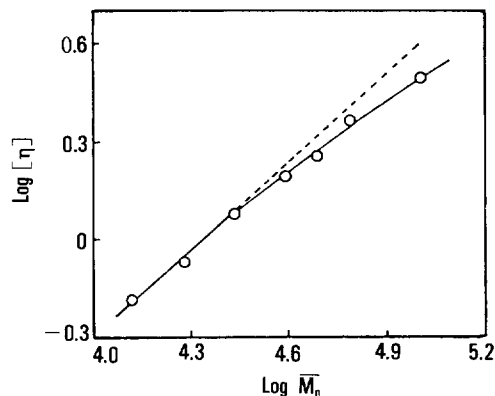

Fig. 5. Log-log plot of [η] vs. $\overline{M}_n$ for poly[terephthaloyl-1-(2-aminoethyl)piperazine] in m-cresol at 25℃.

0.73 for higher $\overline{M}_n$. This change in slope suggests that the PTAP molecule has somewhat stiff character in the lower molar mass range but approaches to an extended coil as $\overline{M}_n$ increases. This charactristic dependence of [η] on molar mass does not seem explainable in terms of the theory of flexible polymers which are subject to excluded volume effects. Thus the viscosity data obtained may be taken as an evidence for a semiflexible nature of the PTAP molecule.

Determination of Worm-like Chain Parameters

The semiflexible nature of the PTAP chain apparent from the experimental data presented above may be ascribed to the hindrance of internal rotation of each repeating unit about the amide bond. In order to visualize the stiffness of the chain, it has been attempted to analyze the viscosity data in terms of the theory for the worm-like cylinder model.

The theory proposed by Yamakawa et al.[10,11] for intrinsic viscosity of an unperturbed worm-like cylinder capped with two hemispheres at its ends contains three parameters, M_L (the molar mass per unit contour length), q(the persistence length), and d(the cylinder diameter). Recently, Bohdaneky[1] showed a simplified version of the Yamakawa theory as :

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

with

$$A_\eta = A_o \ M_L \ \Phi^{-1/3} \tag{3}$$
$$B_\eta = B_o \ \Phi^{-1/3} \ (\langle\overline{R}\rangle_o^2/M)^{-1/2} \tag{4}$$

where M is the molar mass of the cylinder and Φ ($=2.87\times10^{23}\text{mol}^{-1}$) is the universal viscosity function. Both parameters A_o and B_o are known functions of d/2q and can be described by

$$A_o = 0.46 - 0.53 \ \log \ d_r \tag{5}$$
$$B_o = 1.00 - 0.0367 \ \log \ d_r \tag{6}$$

where $d_r (=d/\lambda^{-1})$ is the reduced diameter. Since B_o is a very weak function of d_r, it can be replaced in the first approximation by the numerical constant 1.05.[1] Thus the slope of the plot of $(M^2/[\eta])^{1/3}$ against $M^{1/2}$ yields B from which the unperturbed mean square end to end distance $(\langle\overline{R}\rangle_o^2/M)$ can be estimated.

On the other hand, the intercept A is depended on both d_r and M_L, and hence in order to estimate either of these quantites, one of them must be known. An assumption, proposed by Tsujii et al.,[12] that the hydrodynamic volume occupied by 1g of the worm-like cylinder is equal to the partial specific volume of the polymer molecule allows us to compute d_r by the relationships given below :

$$d_r^2/A_o = (4 \phi/1.215\pi N_A)(v/A)B^4 \tag{7}$$

where N_A is the Avogadro's number, and

$$\log \ dr^2/A_o = 0.173 + 2.158 \ \log \ d_r \ (d_r \le 0.1) \tag{8}$$

$$\log \ dr^2/A_o = 0.795 + 2.78 \ \log \ d_r$$
$$(0.1 \le d_r \le 0.4) \tag{9}$$

With d_r thus calculated, M_L can be obtained respectively from the slope and intercept of the plot of $(M^2/[\eta])^{1/3}$ vs. $M^{1/2}$. Once the M_L and $(\langle\overline{R}\rangle_o^2/M)$ are determined, then the values of q, d, and Kuhn statistical segment length(λ^{-1}) can easily be calculated by employing those definitions listed below, respectively :

$$\lambda^{-1} = (\langle\overline{R}^2\rangle_o/M)M_L \tag{10}$$
$$q = (1/2) \lambda^{-1} \tag{11}$$
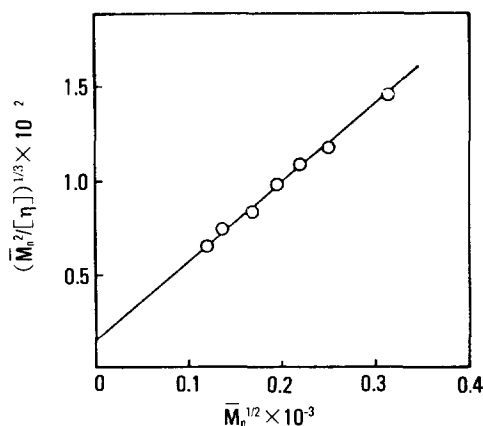$$d = \lambda^{-1} \ dr \tag{12}$$

Fig. 6. Plot of $(\overline{M}_n^2/[\eta])^{1/3}$ vs. $\overline{M}_n$ for poly[terephthaloyl-1-(2-aminoethyl)piperazine].

Table 3. Comparison of Conformational Parameters of Worm-Like Cylinder Model for Various Polymers

Polymer	Solvent	$(\langle\overline{R}^2\rangle_o/M)^{1/2}$ $\times 10^4$ nm	M_L, nm	q, nm	d, nm	viscosity data from Ref.
Schizophyllan	water	—	1900	137	1.6	13
PCBL[a]	DMF	—	1450	38	0.58	14
PHIC[b]	hexane	—	680	41	1.3	15
Poly(TPDP)[c]	m-cresol	1897	290	5.25	—	16
PTAP	m-cresol	1830	260	4.35	—	this study
Polystyrene	benzene	695	—	—	—	17

[a] Poly(ε-carbobenzoxy-L-lysine)

[b] Poly(n-hexylisocyanate)

[c] Poly(terephthaloyl-trans-2,5-dimethylpiperazine)

Data treatment according to eq. (2) is illustrated in Fig. 6. The data points are fitted a straight line, which gives 183.76 and 4.048 for A_η and B_η, respectively. Treatments of these data with those relationships described above yielded model parameters which are summarized in Table 3 together with values of other stiff chain polymers for the comparative purpose. Clearly, all the values of conformational parameters of PTAP listed in Table 3 are found to be quite lower than the parameters exhibited by polymers known as the typical stiff chain molecules such as schizophyllan,[13] PCBL,[14] and PHIC.[15] This implies strongly that the main chain of PTAP does not take the form of rigid rod. Meanwhile, a close observation of the data in Table 3 between PTAP of this study and poly-(TPDP), which is known as semi-flexible chain polymer,[16] confirms the increased chain flexibility of PTAP, but not as much as the typical coil molecules (polystyrene) exhibit.

CONCLUSION

The values of conformational parameters of PTAP listed in Table 3 can describe fairly well the dimensional and hydrodynamic properties in m-cresol over the range of molar masses studied. Data analysis in terms of worm-like cylinder model suggested that the PTAP in m-cresol behaves like a semiflexible chain. The change in conformation from stiff chain to extended coil-like one as the molar mass increases is considered to be attributed to the increased freedom of rotation about the C-C single bond of ethylene group introduced. This introduction of ethylene linkage into the backbone chain does not only change the overall molecular shape but also enhance the solubility of PTAP in organic solvents.

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