

Persistence length calculation from light scattering and intrinsic viscosity of dilute semiflexible polyimide solutions with different degree of imidization

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Abstract

We have derived the translation diffusion coefficient and the intrinsic viscosity formula adopting the Kholodenko's theory using 3+1 dimensional Dirac propagator in the Kirkwood and Riseman scheme. We also performed static light scattering experiments and intrinsic viscosity measurement of dilute solutions of polyimides with different rigidities. In the framework of Kholodenko's theory, we can easily measure the persistence length of polyimide. We prepared five different polyamic acids and polyimides with different degree of imidization by controlling imidization temperatures. From experimental results, we obtained molecular weights and persistence lengths according to the Kholodenko's plot. The molecular weight and the intrinsic viscosity decreased and then increased with the imidization temperature but the persistence length increased monotonically and then leveled off. The persistence lengths calculated from intrinsic viscosities showed very good agreement with those from light scattering experiments.

Keywords: translation diffusion coefficient, Kholodenko's theory, rigidity

1. Introduction

Attempts to describe the polymer, solvent, temperature, and molecular weight dependence of the intrinsic viscosity have stimulated the development of many fundamental models for polymer structure and dynamics. Polymer dynamics still remain as an unexplained and active area of research. The bead-spring model proposed by Rouse and Zimm (RZ) and the bead-rod model by Kirkwood and Riseman (KR), *namely*, pearl-necklace polymer model, now become the theoretical standard for describing polymer dynamics in the limit of strong hydrodynamic interaction (non-draining limit) in dilute solutions (Doi and Edwards, 1986; Yamakawa, 1971). A few works focused on the improvement of numerical solution of the KR theory (Auer and Gardner, 1955a, 1955b; Tschoegl, 1963) because the exact analytic solution did not exist, and sought a more plausible distribution function because the usual Gaussian function had, physically speaking, the equal probability of chain walk in space, so that we could

not eliminate possibility of intersection of chain segment. However, almost all recent theories have been based on the theories of RZ and KR and derived by taking into account additional parameters (Yamakawa, 1974, 1985, 1986; Kholodenko, 1998; Winkler and co-workers, 1994, 1997). Many researchers have concentrated on the degree of draining indicating to what extent the fluid drains through the outer periphery of polymer and on the excluded volume effect with which the dimensional expansion of a chain can be incorporated in order to mimic real chains. The theories of Yamakawa and his co-workers (1974, 1985, 1986) let us understand the dynamics of polymer chains in a solution. Other theories, e.g., the optimized Rouse and Zimm theory (ORZ) (Perico and Guenza, 1985, 1986), utilized the basic concept of RZ scheme. However, we still have difficulty in establishing a relation between the macroscopic hydrodynamics of a polymer solution and the molecular structures of polymer even for a flexible linear polymer.

Recent attention has been paid to challenging problems associated with semiflexibility. A semiflexible polymer has chain flexibility between complete flexibility (flexible coil) and rigidity (rod-like). Theories have been developed for semiflexible polymers by using the more reliable probability function and the self-avoiding chain walk model which ensure more accurate prediction of hydrodynamic properties with the application of a preaveraging approx-

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imation (Kholodenko, 1998). In fact, it is difficult to know clearly how the chain flexibility (or rigidity) of the semiflexible polymer is connected quantitatively with the specific microscopic parameter, *e.g.* trans-gauche bending energy. Many physicists often use the concepts of the persistence length q or the Kuhn statistical segment length a_K for the chain flexibility. Before mentioning the persistence length, we will briefly discuss about the Kratky-Porod (KP) model which takes into account the bending energy of the contour. The purely phenomenological bending parameter γ in this model equivalent to the energy of bending rod can effectively describe the conformational properties of semiflexible polymer. The configurational partition function is given with the curvature vector $\mathbf{u}(s) = \partial \mathbf{r} / \partial s$ as

$$Z = \int \exp \left[-\frac{\gamma}{2kT} \int_0^L \left(\frac{\partial \mathbf{u}}{\partial s} \right)^2 ds \right] d\{\mathbf{r}\} \quad (1)$$

Together with the rigid constraint $|\partial \mathbf{u} / \partial s| = 1$, it is called as a *wormlike* chain. Here we can define a parameter of length scale, that is, the persistence length in terms of the bending force constant γ or $q = \frac{\gamma}{kT}$. Because of the above constraint, most of the equilibrium and dynamic properties are not analytic. Harris and Hearst (1966, 1967) were the first to consider analytically tractable model using the Hamiltonian principle under the rigid constraint. However, this single constraint model cannot reproduce the result of the KP chains. Recently, Winkler and co-workers (1994, 1997) derived a mathematically tractable model using the maximum entropy principle and obtained the structural and dynamical properties of linear polymers with any degree of stiffness. The theory allows one to obtain the equilibrium distribution function for a system of mass points under three major constraints. The chain distribution function was derived and the corrected preaveraging Ronte-Prager tensor for Oseen tensor was used. For all these theories, however, we have to consider the following points: firstly, concerning the chain rigidity, all the above theories utilize the Benoit and Doity (BD) theory to correlate the light scattering experimental data of the radius of gyration and the persistence length. However, we cannot identify the direct contribution of the chain rigidity to the distribution of chain segment in this scheme. Secondly, the velocity field is both long ranged and singular at the origin, *namely*, the singularity is a consequence of idealizing a physical particle as a mass point and has to neglect the diameter of the particle. For a real polymer, the semiflexible nature which one would possibly prefer to neglect, may markedly affect the local dynamic property of the polymer chain and cause the short distance divergence, even if the polymer as a whole looks rather flexible. Thus, the definition of chain rigidity such as Eq.(1) has always failed for small distance along the contour line (Kroy and Frey, 1997).

Kholodenko's theory (1990, 1992, 1993) of semiflexible polymers used the analogy between the walk of Dirac particle and the semiflexible polymer chain is applied to the chain with an arbitrary order and matches well with the known results of fully flexible coil and rigid rod cases. More recently, Cho and Chung (1999) extended the theory to the hydrodynamic. Some attractive feature of the Kholodenko's work is that the chain rigidity and cut-off scale in the usual continuous treatment are no longer questionable. The persistence length in Kholodenko's theory is exactly matched for that of a computer simulation (He and Windle, 1995) and the cut-off length scale is incorporated automatically by the recent work of 3+1 dimensional calculation for all range of chain rigidity (Cho and Chung, 1999). Although they are limited to the case of a simple linear polymer, their potential achievement is unquestionable because of the rapid development of computing power.

The light scattering method has been the most powerful one to study the polymer solution since Debye and his co-workers made a pioneering work after Rayleigh (Yamakawa, 1971). We performed the light scattering experiment based on the Kholodenko's theory in order to study the effect of imidization of polyamic acid on the conformational change and the hydrodynamic property. The method was similar to the old-fashioned static light scattering but the analysis on the persistence length was rather new.

2. Theory

The full derivations of the Kholodenko's theory of 3+1 Dirac propagator are shown in our previous work (Cho and Chung, 1999). Here we summarize the results briefly.

The mean square end-to-end distance $\langle R^2 \rangle$ (Kholodenko, 1993) and the mean reciprocal end-to-end distance $\langle R^{-1} \rangle$ (Cho and Chung, 1999) are given by

$$\langle R^2 \rangle = 2qL \left[\coth \left(\frac{3L}{2q} \right) - \frac{2q}{3L} \right] \quad (2)$$

$$\langle R^{-1} \rangle = \frac{3}{2q} \frac{I_0(3L/2q)}{\sinh(3L/2q)} \quad (3)$$

where I_0 is a Bessel function of the second kind and L is the contour length of a polymer. We note that the persistence length, q , in Kholodenko's theory is somewhat different from the one defined by a bending force constant. It is defined as the average distance parallel to the first projection of chain segment. We have shown that the intrinsic viscosity $[\eta]$ for the semiflexible polymer is given in an implicit form using the KR and Kholodenko's scheme. The equations for the calculation of persistence length from intrinsic viscosities are so complicated that they are not shown here (refer to Cho and Chung, 1999).

At this point, we would like to mention about the benefit for the Kholodenko's analysis of the persistence length from light scattering measurement. The light scattering measurements usually required the sample fractionation for scattering intensity in order to make sure of the precise dependence on the molecular weight. When polymolecularity is involved for the Kholodenko's theory, we are free from the tedious sample fractionation procedure. In order to show the independency of the scattering function on the molecular weight distribution, the z -average of the theoretical expression of the scattering function is calculated using the same manner of Hickl and co-workers (1997), such as

$$S(k, q) = \frac{\int_0^\infty dL s(k, L, q) w(L) L}{\int_0^\infty dL w(L) L} \quad (4)$$

where $w(L)$ is the weight fraction of the chains having the contour length L . The scattering function of an arbitrary flexibility for an infinitely dilute solution, $s(k, L, q)$ was given analytically by Kholodenko (1993)

$$s(k, L, q) = \frac{2}{z} \left[I_{(1)}(z) - \frac{1}{z} I_{(2)}(z) \right] \quad (5)$$

where ; $I_{(n)}(z) = \int_0^\infty dt t^{n-1} g(t)$, $n = 1, 2$; $z = 3L/2q$

$$g(t) = \begin{cases} \frac{1}{E} \frac{\sinh(Et)}{\sinh t} & k \leq \frac{3}{2q} \\ \frac{1}{\hat{E}} \frac{\sinh(\hat{E}t)}{\sinh t} & k > \frac{3}{2q} \end{cases}$$

$$\text{and } E = \sqrt{1 - \left(\frac{2q\mathbf{k}}{3}\right)^2}, \quad \hat{E} = \sqrt{\left(\frac{2q\mathbf{k}}{3}\right)^2 - 1}$$

where \mathbf{k} is scattering vector and $k = \sqrt{\mathbf{k}^2}$. In all subsequent calculations the Schulz-Zimm distribution has been used as

$$w(L) = \frac{L^\sigma}{\Gamma(\sigma+1)} r^{\sigma+1} \exp(-rL) \quad (6)$$

Here $r = (\sigma + 1)/L_w$, where σ is the parameter characterizing the polydispersity of chains, $\sigma = [L_w/L_n - 1]^{-1}$, L_w and L_n is the weight-average and number-average contour length of the chain respectively. For polycondensation polymers, the typical value of polydispersity is 2, therefore, $\sigma = 1$. From the Kholodenko's theory of semiflexible polymer, the excluded volume effect can be mimicked by the appropriate choice of the persistence length. These data are used for the calculation of the persistence length using Eq. (5). According to the discussions of Kholodenko (1993), it is helpful to plot $Lk^2S(k, q)$ as a function of k . The effect of polydispersity for $Lk^2S(k, q)$ versus q is shown in Fig. 1 using Eqs. (4), (5) and (6). There is little difference between $L_w/L_n = 1$ and $L_w/L_n = 2$. Thus, we can use the Kholodenko's plot to obtain the persistence length. without the polydispersity problem from now on. In

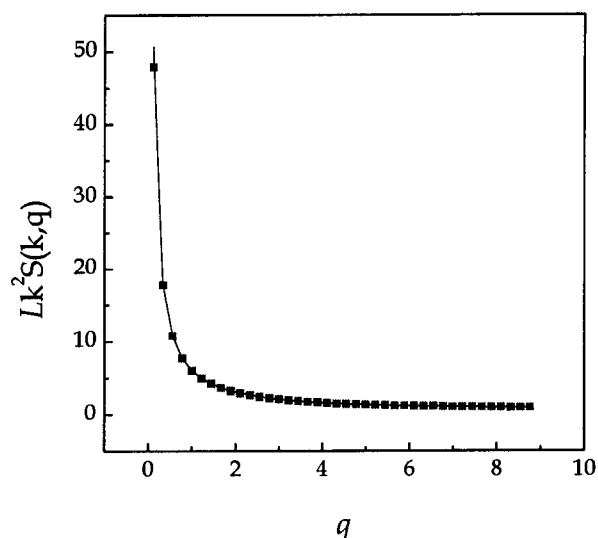


Fig. 1. The kholodenko's plot for sample 3 with polydispersity 1 (line) and 2 (filled symbol). Little difference is observed.

conclusion, the usual Kratky plot and the normalized Kratky plot given by Krigbaum and Bresford (1988) are not most convenient way to obtain the persistence length of polymer chain.

2. Experimental

2.1. Sample preparation

We have tested four partially imidized polyamic acid samples and one fully imidized polyimide. Firstly, the polyamic acid was prepared from 4,4'-(hexafluoro-isopropylidene) diphthalic anhydride (6FDA) and N,N' -bis(4-aminophenyl) isophthalamide (APIA) (Table 1). 6FDA was purchased from Aldrich Co.. APIA was synthesized as follows: N,N' -bis(4-nitrophenyl) isophthalamide was obtained from isophthaloyl chloride and 4-nitroaniline. 0.1 mole of isophthaloyl chloride (20.3 g) and 0.2 mole of 4-nitroaniline (27.6 g) were dissolved in 200 ml of THF and stirred for 5 h under nitrogen atmosphere below 5°C. The solution was poured into water and washed several times. N,N' -bis(4-nitrophenyl) isophthalamide obtained was hydrogenated in isopropanol at 80°C with 10% Pd/C dropping

Table 1. The monomers used for the preparation of polyamic acid

	4,4'-(hexafluoro-isopropylidene) diphthalic anhydride (6FDA)
	N,N' -bis(4-aminophenyl) isophthalamide (APIA)

hydrazine monohydrate. The slurry was obtained and dissolved in DMF. It was filtered to remove Pd/C solid with methanol. When the solution was distilled in vacuum, white crystallite (APIA) was obtained. NMR spectrum of APIA and its chemical structure are shown in Fig. 2.

The polyamic acids were prepared by dissolving the equal moles of 6FDA and APIA in DMF and stirring under nitrogen atmosphere for 12 h. These monomers were used after drying in vacuum oven for 24 h. The total content of monomers was ca. 15 wt% concentration. Polyamic acid films were made on silicon wafer by the spin coating and thermally imidized in nitrogen atmosphere. The degree of imidization was controlled by the imidization of polyamic acid at different imidization rate and temperature. Sample 0 is a fully polyamic acid sample. Four partially imidized samples (sample 1-4) and fully imidized sample (sample 5) were prepared. Polyamic acid film was cast and carefully dried at 60°C at which it was not imidized. Because the imidization proceeded mainly over 150°C, four samples (1-4) were partially imidized at 150, 200, 250, 300°C for 1h, respectively. Fully imidized sample (5) was prepared from sample 4 after imidization at 350°C for 5 minute. All samples except sample 5 were easily dissolved in DMF but sample 5 was dissolved in DMF at an elevated temperature. The peak around 1510 cm⁻¹ (aromatic C-C stretching) is used as a reference because it is independent of bond orientation change during imidization (Fig. 3). The peak 1365 cm⁻¹ peak (imide C-N stretching) intensity is compared with that at 1510 cm⁻¹ to calculate the degree of imidization because it is not affected by any interference during the cure. No further increase at 1510

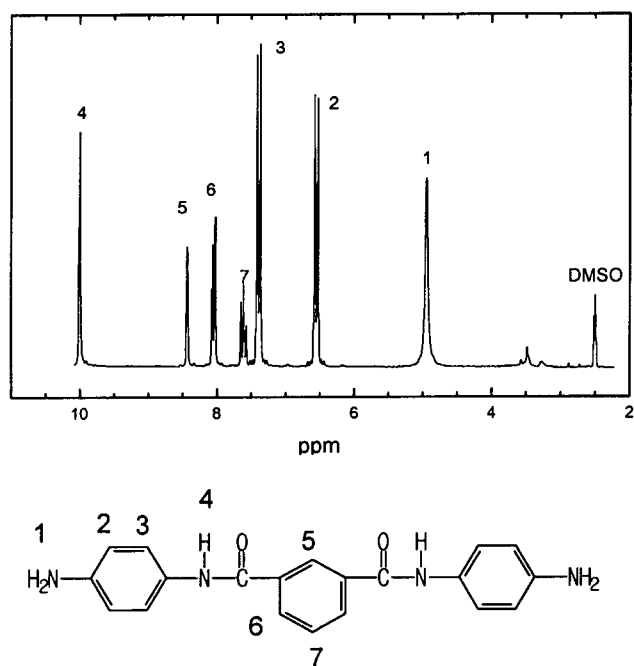


Fig. 2. H-NMR spectrum of synthesized APIA.

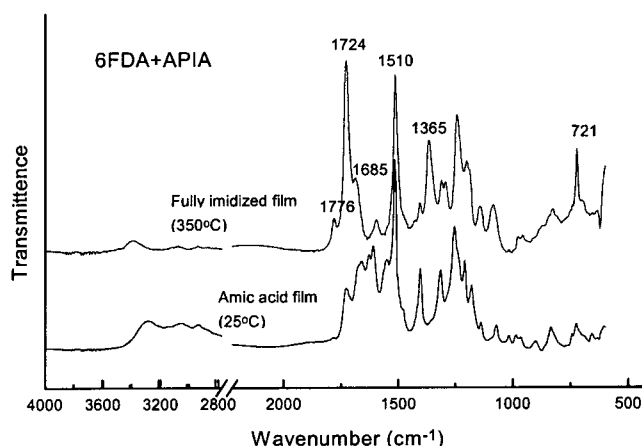


Fig. 3. IR spectra of polyamic acid and polyimide from 6FDA-APIA. The degree of imidization for each sample is listed in Table 2.

cm⁻¹ peak height is observed after the curing at 300°C for 5 minute.

All samples were dissolved in DMF again and diluted to the desired concentrations by adding pure DMF. For polyamic acid, the electrolytic effect affected the internal rotation in short segmental scale not in the long scale nor the aggregation with other chains with a small amount of amine residue (Bessonov, 1987). Thus, DMF was vacuum-distilled and filtrated prior to use to get rid of amine residue to prevent the electrolytic effect. Four or five solutions with different concentrations were prepared for each polymer. The concentration ranged from ca. 0.5×10^{-3} g/cm³ to 3×10^{-3} g/cm³. All specimens were filtered through 0.2 μm syringe filters prior to measurement and UV tests were conducted in order to correct the concentration changes after filtration. The refractive index variation with respect to the concentration, dn/dc for each solution was measured with a differential refractometer and given in Table 2. The values of dn/dc were relatively low compared with the usual polyamic acid and polyimide due to the presence of fluoromethylene group between phenylene of 6FDA.

Viscosities were measured by using a Kennon-Fenske

Table 2. Characterization of polyamic acid, polyimide and its intermediate derivatives and their hydrodynamic properties from 6FDA-APIA.

Sample number	0	1	2	3	4	5
Imidization Temperature	-	150°C	200°C	250°C	300°C	350°C
Imidization degree [%] ^a	0.0	28.5	78.0	93.0	99.4	100
dn/dc [ml/g]	0.144	0.151	1.611	1.571	0.157	0.154

$$a. \frac{(A_{1364}/A_{1510})_{sample}}{(A_{1364}/A_{1510})_{imide}} \times 100, \%$$

type viscometer. Five solutions with different concentrations were prepared for polyamic acid and polyimides as used in the light scattering experiments.

2.2. Static light scattering experiment

The detailed experimental procedures were similar to the usual static light scattering experiment (Krigbaum and Sasaki, 1981), but we could obtain the persistence lengths of the samples with the measurement of the scattered intensity at a fixed angle with aids of new analysis of Kholodenko (shown in the theory section). The light intensity scattered from each of pure solvent (DMF) and standard solvent (benzene) was read in milli-voltage (mV) from a digital oscilloscope. The excess intensity of the solution $[(I_{90} - I_s)R_{st}/I_{st}]$ was obtained where the indices s and st denote the solvent and the standard solvent and R_{st} is the Rayleigh ratio of the standard solution. The correction factor R_b of value $15.8 \times 10^{-6} \text{ cm}^{-1}$ for R_{st} was determined by Coumou (1960) at the wavelength of 632 nm. The basic procedure for determining the scattering function was given in the reference (Bresford and Krigbaum, 1991).

3. Results and Discussion

3.1. Molecular weight and intrinsic viscosity measurement

Molecular weights of the samples are determined by light scattering method at a fixed angle. For a conventional static light scattering experiment, the Zimm plot is used to determine the average molecular weight and the second virial coefficient (Doi and Edwards, 1986). The dimensional information of the polymer chain is also obtained as a measure of radius of gyration by Kratky plot. Zimm plot is obtained if we measure the excess scattered intensity. The polyamic acid samples, even their fully imidized one, were rather flexible, so that we measured the excess scattered intensity at 90° for various concentrations using the following equation:

$$\frac{cK}{2I_{90}} = \frac{1}{M_w} + 2A_2c \quad (7)$$

where c is the concentration of the solution, A_2 is the second virial coefficient, and K is the optical constant given by

$$K = \frac{4\pi^2 n_s^2}{N_A \lambda_o^4} \left(\frac{dn}{dc} \right)^2 \quad (8)$$

where n_s is the refractive index of pure solvent, λ_o the wavelength of laser source, and dn/dc the differential index of refraction of the solution. However, the above equation is not true for all cases. Studies on light scattering in polystyrene solutions showed the existence of a threshold concentration below which a horizontal section is observed on the $cK/2I_{90}$ vs. c relation (Eskin and Bara-

novska, 1977). Thus, in order to obtain the accurate data, we have to prepare the polymer solution under the concentration of 10^{-2} g/cm^3 (D'yakonova and co-workers, 1986). Plotting the excess intensity versus concentration, we can measure the molecular weight of polymer and second virial coefficient A_2 . The measured A_2 values are high enough (order of $10^{-3} \text{ g}^2 \cdot \text{cm}^3 \cdot \text{mol}$) to assume that DMF is the good solvent for all the samples. Of course, the value for polyamic acid is the largest and slowly decreases with imidization. Based on Eq. (7), we plotted the measured $cK/2I_{90}$ versus concentration c . The molecular weight and the second virial coefficient were obtained from the intercept of the ordinate and the slope, respectively (Fig. 4)

The intrinsic viscosities of prepared samples are shown in Fig. 5(a) and (b) via imidization temperature and the

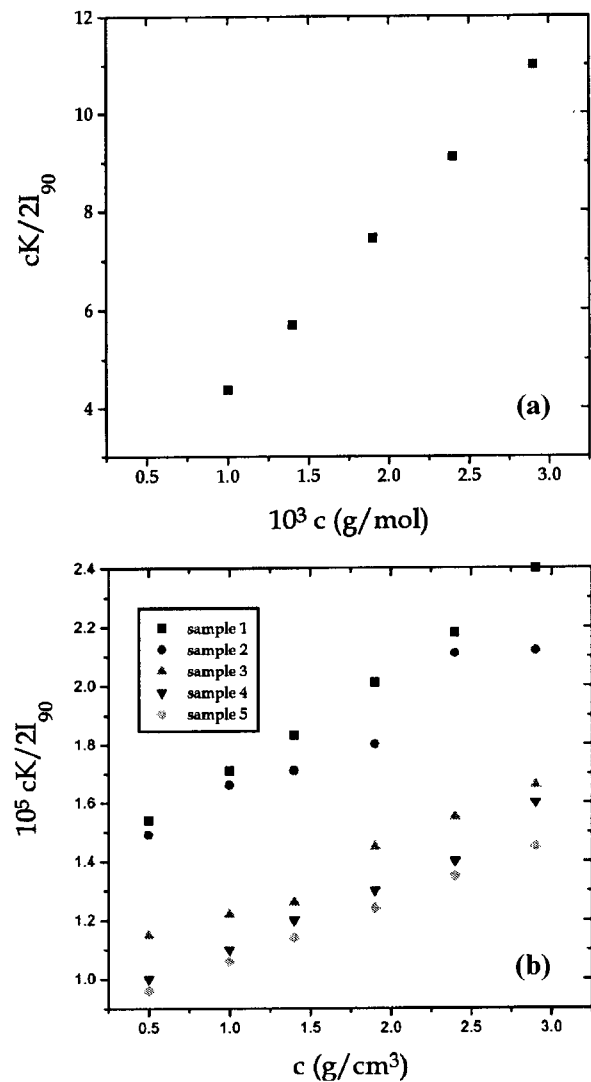


Fig. 4. (a) $\frac{cK}{2I_{90}} = \frac{1}{M_w} + 2A_2c$ versus c for sample 0. The estimated molecular weights for each samples are listed in (b) versus c for sample 1-5. The estimated molecular weights for each samples are listed in Table 3.

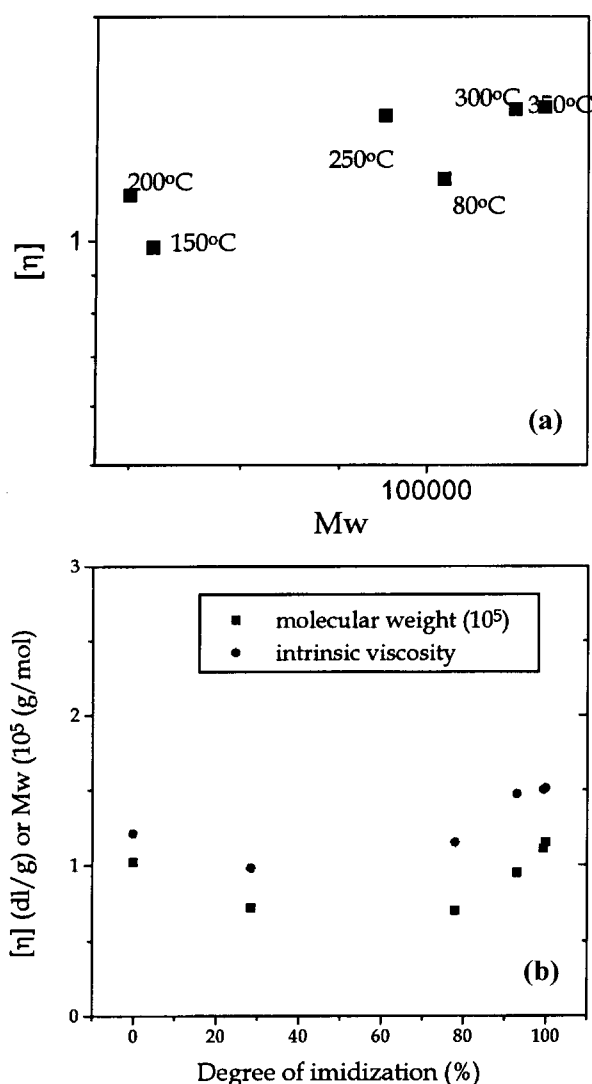


Fig. 5. (a) Intrinsic viscosity versus imidized temperature (b) Intrinsic viscosity and molecular weight change with respect to degree of imidization.

degree of imidization, respectively and tabulated in Table 3. All samples shows relatively high flexibilities because it has meta linkage in the main chain and has a low value of exponent of Mark-Howink equation. In Fig. 5(a), the intrinsic viscosity change with respect to the imidization temperature is very similar to the one reported earlier by Young and Escott (1990). The decrease in the molecular weight at relatively low temperature is attributed to thermal instability and high susceptibility to the oxygen in diamine. And then, the intrinsic viscosity of polymer solution increases as the degree of imidization or the midization temperature is increased. Young and Escott concluded that the change of intrinsic viscosity attributed to the molecular weight increase. From this observation, we recognize that there is a distinct change in the molecular weight and the persistence length between samples cured at low temper-

ature (sample 1 and 2) and at high temperatures (sample 3, 4, 5 and 6).

3.2. The persistence lengths of polyamic acids with different degree of imidization

It is worth mentioning another advantage of the Kholodenko's plot. We only performed the scattering measurement at one angle position for the Kholodenko's plot, so that the error and the tuning involved in rotating photo multiplier tube (PMT) can be avoided. Using intrinsic viscosity and molecular weight data, we can expect the persistence length based on the theory derived in the previous section. In Table 3, a significant increase in the persistence length and the molecular weight of the polymers cured above 200°C is observed. It is recognized from this fact that the conformational change occurs with the increase in chain rigidity and molar mass during the imidization process and affects the hydrodynamic properties of the solutions of polyamic acid and polyimides. Although there was a change in molecular weight and persistence length, we could not observe the sudden transition from a flexible coil to a rigid rod. The transition was expected for the polyimide with high rigidity as was predicted by computer simulation for insoluble polyimide.

The persistence lengths listed in Table 3 show that further imidization above 200°C does not affect the chain conformation very much and molecular weight of the sample. The scattering function was calculated from Eq. (5) by measuring the excess scattered intensity of the solution. Kholodenko's plot (Kholodenko, 1993), $Lk^2S(k,q)$ versus q , is shown in Fig. 6. All lengths are normalized by the average segmental length of polyimide 0.904 nm. Because the polymers have high molecular weights, L values for all the samples exceed 200. The persistence lengths calculated from the measured intrinsic viscosity and the light scattering are also listed in Table 3. There is an excellence agreement between the persistence lengths determined from the light scattering and intrinsic viscosity.

From our experiments and calculations, we recognize that the change of the intrinsic viscosity with respect to imidization temperature is mainly attributed to the change of molecular weight but the conformational change is also significant when we compare the persistence lengths of relatively low and high degree of imidization. However, the molecular weight and persistence length of relatively high degree of imidization samples show little changes.

4. Conclusion

We measured the chain rigidity (persistence length) and molecular weight by light scattering based on the Kholodenko's calculation and intrinsic viscosity. In order to prevent from the complexity in sample preparation and polydispersity effect, we used the Kholodenko's plot to

Table 3. Measured and calculated values of polyamic acid and various polyimides

Sample number	0	1	2	3	4	5
Imidization Temperature	-	150°C	200°C	250°C	300°C	350°C
Imidization degree [%] ^a	0.0	28.5	78.0	93.0	99.4	100
M_w [g/mol]×10 ³	102	72	70	95	111	115
[η] [dl/g]	1.21	0.98	1.15	1.47	1.50	1.51
q [nm] ^b	2.91	3.18	3.80	4.01	3.95	3.98
q [nm] ^c	2.5	2.8	4.0	4.2	4.2	4.2

$$a. \frac{(A_{1365}/A_{1510})_{sample}}{(A_{1365}/A_{1510})_{imide}} \times 100, \%$$

b. Best fitting data from the intrinsic viscosity data

c. Obtained from the Kholodenko's plot of light scattering.

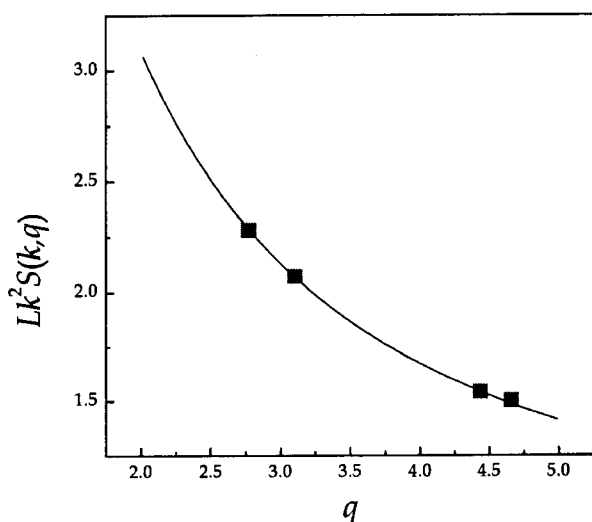


Fig. 6. Kholodenko's plot for determining the persistence lengths of polyamic acid and its intermediate derivatives. The obtained persistence lengths from scattering data at 45° were listed in **Table 3**.

obtain the persistence length from the scattering function. On the other hand, the theory for the intrinsic viscosity was also used in order to obtain the persistence length to be compared with the value determined from the light scattering measurement. Excellent agreement between the persistence lengths determined from two different methods confirm the validity of the theory. This also supports the practical usefulness of our calculation. The conformation change of polyamic acid solution during the cure was tested to elucidate the relationship between the chain conformation and rheological properties. The change of molecular weight and persistence length of polyamic acid derivatives with different degree of imidization was observed when plotting the intrinsic viscosity data and molecular weight versus the degree of imidization.

We have performed the experiments for static and

hydrodynamic properties of semiflexible polymer solution more precisely and developed the (analytic) theory and computer simulation method to take into account all possible factors in order to predict the properties of polymer solution accurately. Particularly, Kholodenko's theory using 3+1 dimensional Dirac propagator may be a valuable analytic framework to understand the behavior of polymer solution covering from fully flexible coil to rigid rod because the theory fits the experimental results irrespective of polydispersity. Moreover, it provides a convenient experimental procedure for measuring persistence length directly related to the structural prediction by the computer simulation.

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