Helical Structural Change in Poly((4-carboxyphenyl)acetylene) by Acid−Base Complexation with an Optically Active Amine

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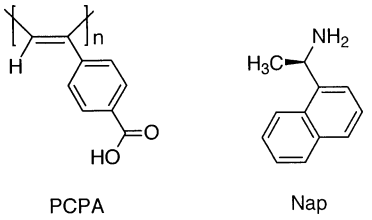
ABSTRACT: The acid−base complexation of poly((4-carboxyphenyl)acetylene) with an optically active amine [(*R*)-(+)-1-(1-naphthyl)ethylamine] not only induces strong circular dichroism (CD) but also changes the molecular weight dependence of the intrinsic viscosity in dimethyl sulfoxide. From the intrinsic viscosity data, we have determined the chain stiffness parameter (the persistence length) and have estimated from this parameter the average standard deviation of the internal rotation angle around the single or double bond of the polyacetylene chain to be 21 and 15° before and after the complexation, respectively. The reduction of the torsional fluctuation may arise from the steric hindrance among the amines complexed with the carboxy pendants which makes the internal-rotation energy well steeper for the polyacetylene backbone. The reduction is however not as remarkable as the change in CD due to the complexation. We conclude that the remarkable CD behavior arises from a drastic change in population of the right- and left-handed helices of the polymer, and the helical conformation of the complex is still imperfect.

Introduction

The synthesis of helical polymers with controlled helix sense has aroused considerable interest in polymer[1] and supramolecular chemistry[2] in recent years not only because of their interesting structures as observed in various biopolymers but also because of their possible applications in materials science, chemical sensing, and enantioselective adsorbents.[1a,3] The helical polymers have usually been prepared either by polymerization of optically active monomers[1c,f,h,k] or by asymmetric polymerization of achiral or prochiral monomers with chiral catalysts or initiators.[1a,j] Therefore, the helix sense can be controlled by chiral substituents covalently bonded to the polymer main chain or kinetically during the polymerization. Recently, Yashima et al. reported that macromolecular helicity with a predominantly one-handed helix can be induced in optically inactive poly(phenylacetylenes) bearing various functional groups at the phenyl group.[4−6] For instance, poly((4-carboxyphenyl)acetylene) (PCPA) forms a one-handed helical conformation upon complexation with chiral amines or amino alcohols in dimethyl sulfoxide (DMSO)[4] and amino acids in water,[5] thus exhibiting an induced circular dichroism (ICD) in the π-conjugated main chain region of the polymer in solution. A similar drastic CD change was also attained in a helical poly(phenylacetylene) having a β-cyclodextrin[7] upon inclusion complexation with chiral and achiral guest molecules. Even without any specific interactions between the polymer and small chiral molecules, an excess one-handed helix can be induced in optically inactive helical polymers in optically active solvents[1c,f] or by chiral doping;[8] a nematic liquid crystal phase in concentrated helical polymer solutions can be transformed into a cholesteric one by chiral doping, where the intermolecular interaction is just the van der Waals type.[8] Those interesting phenomena are based on the high sensitivity of helical polymer conformations to a chiral environment.[1c,f]

Chart 1. Structures of PCPA and Nap



So far, those induced helical conformations have been investigated by circular dichroism (CD), optical rotation, or cholesteric pitch measurements. Although these quantities are convenient for measuring the excess one-handedness (right- and left-handed helices) in the helical polymer main chain, they cannot distinguish disordered achiral conformation from the racemic mixture of helical conformations. For example, the intense ICD in PCPA induced by complexation with optically active amines or amino alcohols in DMSO is evidence of the helical conformation of PCPA after the complexation, but it cannot give us information regarding whether the PCPA chain assumes a disordered or racemic helical conformation before the complexation nor how regular is the helical conformation after the complexation.

In this study, we have investigated the conformation of PCPA in DMSO before and after complexation with an optically active amine, (*R*)-(+)-1-(1-naphthyl)ethylamine (Nap), from a different aspect by viscometry and

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ultracentrifugation. The molecular weight dependence of the intrinsic viscosity obtained was analyzed by a routine procedure to estimate the helix pitch (or the chain contour length per monomer unit) and the chain stiffness (or the persistence length). On the basis of these results, we estimated the degrees of torsional fluctuation in the helical structure in solution before and after the complexation and compared them to elucidate how the chiral amine complexed with the carboxy groups of PCPA affects the helical conformation or the backbone internal rotation energy of PCPA. The present viscometric results combined with the previous CD ones should be useful in understanding the significant nature of the helical structure of PCPA in solution.[4,5]

Experimental Section

Materials. Anhydrous DMSO (water content < 0.005%) was purchased from Aldrich and stored under nitrogen. (*R*)-(+)-1-(1-Naphthyl)ethylamine (Nap) was kindly supplied from Yamakawa Chemical (Tokyo, Japan), distilled under reduced pressure, and stored under nitrogen. (*R*)-(+)-1-(1-Naphthyl)-ethylamine hydrochloride (Nap·HCl) was prepared by bubbling hydrochloric acid gas generated from the reaction of concentrated sulfuric acid with concentrated hydrochloric acid into a dry toluene solution of Nap (13.2 g/400 mL) and purified by recrystallization from acetone−water (27/1, v/v).

PCPA Samples. Cis−transoidal PCPA was synthesized by the polymerization of (4-carboxyphenyl)acetylene with $[Rh(nbd)_2]ClO_4$ (nbd = norbornadiene) in the presence of diethylamine (sample 1) or NaOH (sample 2) in water at 30 °C according to the previously reported method.[5a] Two original samples, 1 and 2, were divided into seven and eight fractions, respectively, by repeating the fractional precipitation using DMSO as the solvent and toluene as the precipitant. The concentrated phase separated at each precipitation step was diluted with DMSO and poured into toluene to reprecipitate a fraction. The reprecipitated fraction was washed with toluene several times and dried in a vacuum for ca. 1 week at room temperature. In the following, the fractions obtained from the original samples 1 and 2 are denoted as Fr-1-1 to Fr-1-7 and Fr-2-1 to Fr-2-8, respectively. Among those, seven fractions were chosen for the following experiments. In addition, two unfractionated PCPA samples (named S-3 and S-4) were also used for viscosity measurements.

Because DMSO is a hardly volatile solvent, a small amount of the solvent DMSO remained in each dried fraction, which was estimated by proton NMR (a Varian VXR-500S spectrometer). Concentrations of the test solutions of each fraction used in the following experiments were calculated by taking the amount of the remaining DMSO into account.

Proton NMR also gave us information about the stereoregularity of each PCPA fraction (see Supporting Information). For higher molecular weight fractions recovered from lower toluene-content solutions, the proton resonances were sharp, indicating that the fractions retain the cis−transoidal structure.[4,5] However, for lower molecular weight fractions recovered from toluene-rich solutions, the resonances were broad and the cis−transoidal structure may be partly transformed into the trans−transoidal structure in those fractions during the fractionation process.

Sedimentation Equilibrium. DMSO solutions of seven PCPA fractions were studied by sedimentation equilibrium, using a Beckman-Coulter Optima XL-I ultracentrifuge, equipped with a Rayleigh interferometer with 675 nm light emitted from a diode laser. The temperature was chosen to be 25 °C, and aluminum 12 mm double-sector cells were used. The height of the solution column was adjusted to ca. 1.5 mm, and the rotor speed was chosen in the range from 12 800 to 25 700 rpm depending on the molecular weight. The data were analyzed by the established method[9,10] to obtain the weight-average molecular weight M_w and the second virial coefficient A_2.

For fraction Fr-1-1, M_w and A_2 were also measured in DMSO containing 0.34 M Nap and 0.02 M of its hydrochloric acid salt (Nap·HCl). The original solution was dialyzed against the mixed solvent for 4 days with stirring, and the dialyzed solution was diluted to prepare the test solutions with different concentrations. The dialysis was effected using a Visking gel−cellophane membrane and dialyzer as described elsewhere.[11]

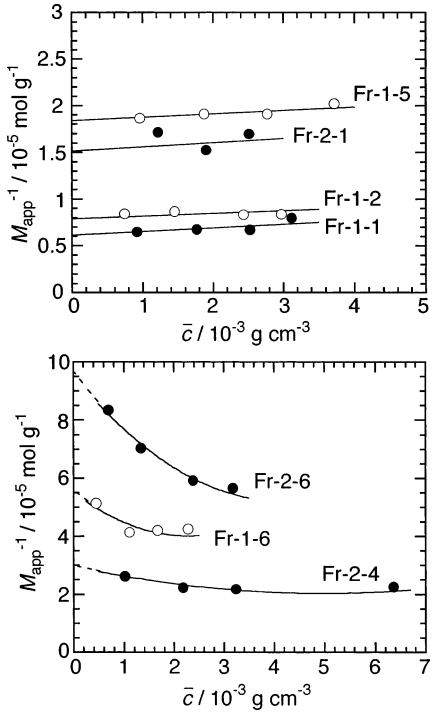

Figure 1. Plots of M_{app}^{-1} vs $\bar{c}$ for seven PCPA fractions in DMSO at 25 °C.

Densitometry and Refractometry. Densities ρ and excess refractive indices Δn of the DMSO solutions of PCPA (Fr-1-1) were measured at 25 °C as a function of the polymer concentration c to obtain $\partial\rho/\partial c$ and $\partial n/\partial c$ (at constant pressure) necessary to analyze sedimentation equilibrium data. While the former measurement was made with an oscillation U-tube densitometer (Anton-Paar, DMA5000), the latter measurement was performed with a differential refractometer (Ohtsuka Electronics, DRM-1020) at 675 nm. The results of $\partial\rho/\partial c$ and $\partial n/\partial c$ were 0.200 and 0.200 cm^3/g, respectively.

Density and differential refractive index measurements were also made for the dialyzed solution of Fr-1-1 dissolved in DMSO containing Nap and Nap·HCl as mentioned above. The results of $(\partial\rho/\partial c)_\mu$ and $(\partial n/\partial c)_\mu$ at constant chemical potentials of diffusible components were 0.331 and 0.346 cm^3/g, respectively. For the mixed solvent system, sedimentation equilibrium data were analyzed using these $(\partial\rho/\partial c)_\mu$ and $(\partial n/\partial c)_\mu$ values.[12]

Viscometry. Viscosities of DMSO solutions of PCPA samples with or without Nap and Nap·HCl were measured by using conventional Ubbelohde-type capillary viscometers at 25 °C. The Huggins and Mead−Fuoss plots were used to determine the intrinsic viscosity $[\eta]$ and the Huggins coefficient k'.

Results and Discussion

Molecular Weights and Second Virial Coefficients. Figure 1 shows the plot of M_{app}^{-1} vs $\bar{c}$ for dilute DMSO solutions of seven PCPA fractions at 25 °C, where M_{app} is the apparent molecular weight and $\bar{c}$ is the average concentration of the solution under the centrifugal field. For Fr-1-1, Fr-1-2, Fr-2-1, and Fr-1-5, the data points almost obey straight lines with positive slopes. From the intercepts and slopes of the lines, we have determined the weight-average molecular weight M_w and the second virial coefficient A_2 for those fractions. Values of A_2 of PCPA in DMSO are comparable

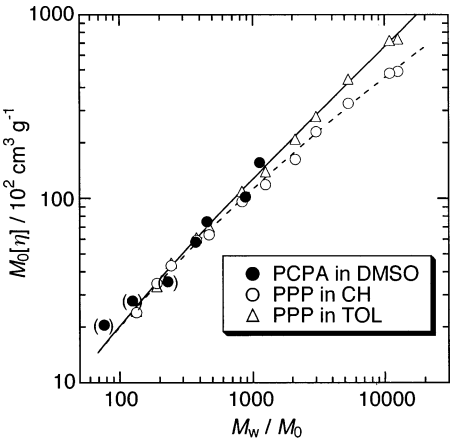

Figure 2. Double logarithmic plot of $[\eta]M_0$ against M_w/M_0 for PCPA in 25 °C DMSO (●) and also for PPP[13] in 25 °C toluene (△) and 34.5 °C cyclohexane (○). Key: filled circles in parentheses, data of PCPA fractions with negative A_2; solid and dashed curves, theoretical values calculated by the theory of Yoshizaki, Nitta, and Yamakawa[17] for the perturbed and unperturbed touched-bead wormlike chain model, respectively, with $M_L = 490$ nm^{-1}, $q = 3.9$ nm, $d_B = 1.1$ nm, $B = 0.6$ nm, $\Phi_\infty = 2.35 \times 10^{23}$ mol^{-1} (in toluene) and $M_L = 480$ nm^{-1}, $q = 3.8$ nm, $d_B = 1.2$ nm, $B = 0$, $\Phi_\infty = 2.17 \times 10^{23}$ mol^{-1} (in cyclohexane).

to those of a polyacetylene derivative with a similar chemical structure, poly(1-phenyl-1-propyne) (PPP), in toluene (a good solvent) studied by Hirao et al.,[13] indicating that DMSO is a good solvent for PCPA.

In Figure 1, the data points of Fr-1-6, Fr-2-4, and Fr-2-6 follow curves with negative initial slopes, indicating negative A_2 for those lower molecular weight fractions. The values of M_w and A_2 for the fractions were estimated from the intercepts and initial slopes of curves shown in Figure 1.[14] For fractions Fr-1-6 and Fr-2-6, their structures are not completely cis−transoidal, but the *cis*−*trans* isomerization may take place for those low molecular weight fractions during the fractionation process based on the NMR spectra. The negative A_2 implies that the isomerization reduces the solubility of PCPA in DMSO.

Intrinsic Viscosity in DMSO. Figure 2 compares the intrinsic viscosities $[\eta]$ of the seven PCPA fractions in DMSO with those of poly(1-phenyl-1-propyne) (PPP) in toluene at 25 °C and in cyclohexane at 34.5 °C, reported by Hirao et al.[13] To take into account the difference in the monomer molecular weight M_0 between the two polyacetylene derivatives, $[\eta]$ multiplied by M_0 is plotted against the degree of polymerization M_w/M_0 in Figure 2 ($M_0 = 146$ and 116 for PCPA and PPP, respectively). Although the data points for PCPA in DMSO are slightly scattered, they seem to follow the curve for PPP in toluene. Even the data points in the parentheses for the low molecular weight PCPA fractions with negative A_2, except for the lowest molecular weight PCPA fraction, do not deviate much from the curve for PPP in toluene.

In the previous study, Hirao et al.[13] analyzed $[\eta]$ and also the radius of gyration $\langle S^2\rangle^{1/2}$ data for PPP in toluene and cyclohexane using the wormlike chain (cylinder) model to estimate the molar mass M_L per unit contour length and the persistence length q. They found that to fit both $[\eta]$ and $\langle S^2\rangle^{1/2}$ data with the same M_L and q, the Flory−Fox constant Φ_∞ must be smaller than the theoretical one ($=2.87 \times 10^{23}$).[15,16] The solid and dotted curves in Figure 2 indicate the theoretical values of $[\eta]M_0$ calculated by the theory of Yoshizaki, Nitta, and Yamakawa[16,17] for the wormlike touched-beads model using M_L, q, and Φ_∞ they estimated;[13] the intramolecular excluded-volume effect in toluene was incorporated using the quasi two-parameter theory of Yamakawa, Stockmayer, and Shimada.[16,18−20] Agreements between the theoretical and experimental values are good for PPP both in toluene and cyclohexane.

From the M_L estimated, we can calculate the contour length h ($=M_0/M_L$) per monomer unit of PPP to be 0.24 nm, which is closer to the pitch per monomer unit of *trans*-polyacetylene in the crystalline state[21] or that calculated using an ab initio quantum-mechanical calculation.[22] Although the stereoregularity of the PPP samples studied was unknown, this h value implies that the PPP samples assume mainly the trans−transoidal structure, but the identical $[\eta]M_0$ vs M_w/M_0 relation of PCPA and PPP shown in Figure 2 seems inconsistent with the fact that our PCPA fractions assume the cis−transoidal structure except for the low molecular weight fractions. However, we can demonstrate that the solid curve in Figure 2 is reproduced by using the h (=0.22 nm) expected for the cis−transoidal structure,[23,24] if we choose slightly larger values for q (4.2 nm), the bead diameter d_B (1.3 nm), and the excluded-volume strength B (0.7 nm), choosing Φ_∞ to be 2.35×10^{23}. The PCPA chain may be thicker than the PPP chain due to the cis−transoidal structure and also the carboxyl group attached onto the phenyl ring, which may increase d_B and B.

Yashima et al.[4b] performed molecular mechanics (MM) calculations for PCPA and obtained a 7_3 helical conformation as the most energetically stable conformation for PCPA. The pitch of the 7_3 helix is 0.215 nm, which is not much different from that for the planar conformation of *cis*-polyacetylene and is consistent with the above value of h for PCPA.

The chain stiffness of the two polyacetylene derivatives, $q = 3.9$ nm for PPP in toluene and 4.2 nm for PCPA in DMSO, is not as high as that of typical stiff polymers, e.g., poly(alkyl isocyanate)s and aromatic polyamides ($q \approx 20-50$ nm) or α-helical polypeptides ($q \approx 150$ nm).[25] Recently, Sato et al.[26] formulated q of helical polymers in terms of the degree of fluctuation in the internal rotation and also the kink angle and its population due to the helix reversal. If the latter contribution is neglected, the q of helical polyacetylene derivatives is written as

$$q = \frac{1}{h}\left\{ {b_S}^2\left(\frac{1}{2} + \left[\frac{\mathbf{T}_S\mathbf{T}_D}{\mathbf{E} - \mathbf{T}_S\mathbf{T}_D}\right]_{33}\right) + {b_D}^2\left(\frac{1}{2} + \left[\frac{\mathbf{T}_D\mathbf{T}_S}{\mathbf{E} - \mathbf{T}_D\mathbf{T}_S}\right]_{33}\right) + b_S b_D\left(\left[\frac{\mathbf{T}_S}{\mathbf{E} - \mathbf{T}_S\mathbf{T}_D}\right]_{33} + \left[\frac{\mathbf{T}_D}{\mathbf{E} - \mathbf{T}_D\mathbf{T}_S}\right]_{33}\right)\right\} \quad (1)$$

where b_S and b_D are the lengths of the single and double bonds, respectively, $\mathbf{E}$ is the unit matrix, and $\mathbf{T}_i$ (i = S and D) are the transformation matrices defined by

$$\mathbf{T}_i = \begin{pmatrix} \langle\cos\tilde{\phi}_i\rangle\cos\theta_i & \langle\sin\tilde{\phi}_i\rangle & \langle\cos\tilde{\phi}_i\rangle\sin\theta_i \\ \langle\sin\tilde{\phi}_i\rangle\cos\theta_i & -\langle\cos\tilde{\phi}_i\rangle & \langle\sin\tilde{\phi}_i\rangle\sin\theta_i \\ \sin\theta_i & 0 & -\cos\theta_i \end{pmatrix} \quad (i = S, D) \quad (2)$$

with the bond angle θ_i and internal rotation angle $\tilde{\phi}_i$.[27]

In eq 2, $\langle\cdots\rangle$ means the average over the torsional fluctuation of $\tilde{\phi}_i$. Assuming Gaussian statistics for the fluctuation, we write

$$\langle\cos\tilde{\phi}_i\rangle = \cos\tilde{\phi}_{i,0}\exp(-\delta\tilde{\phi}_i^2/2),\ \langle\sin\tilde{\phi}_i\rangle = \sin\tilde{\phi}_{i,0}\exp(-\delta\tilde{\phi}_i^2/2) \quad (3)$$

with $\tilde{\phi}_{i,0}$ and $\delta\tilde{\phi}_i$ being the average ($=\langle\tilde{\phi}_i\rangle$) and the standard deviation ($=\langle(\tilde{\phi}_i - \tilde{\phi}_{i,0})^2\rangle^{1/2}$) of $\tilde{\phi}_i$, respectively. When both $\delta\tilde{\phi}_S$ and $\delta\tilde{\phi}_D$ are chosen to be 21° along with using the molecular parameters for PCPA, eqs 1−3 provide q experimentally determined for PCPA (4.2 nm).[28]

Actually the kink due to the helix reversal may also contribute to the chain flexibility. In a previous study, Morino et al.[29] have studied the helical conformation of chiral-achiral random copolymers of phenylacetylene derivatives by CD to estimate the helix reversal free energy ΔG_r to be 10−15 kJ/mol for poly(phenylacetylene) derivatives. In addition, we may calculate the kink angle at the helix reversal of the PCPA chain to be ca. 20° from the geometric consideration on the assumption that repeating units along the PCPA chain directly transform from one sense to the opposite sense of helical conformation at the helix reversal, without passing through any intermediate conformations (the *two-state approximation*).[26] Using these results, we can show that the contribution of the helix reversal to the chain flexibility is less than 2% of the contribution of the torsional fluctuation.

Clough et al.[24] made molecular dynamics (MD) calculations for polyacetylene and its derivatives and determined $\delta\tilde{\phi}_S$ and $\delta\tilde{\phi}_D$ at 300 K to be 13.4 and 10.0°, respectively, for cis−transoidal polypropyne (PPY). Similar MD calculations were performed for cis−transoidal poly(phenylacetylene) (*cis*-PPA, 40-mer) at 300 K with the same software used previously.[4b,30] The results of $\delta\tilde{\phi}_S$ and $\delta\tilde{\phi}_D$ averaged over interior bonds were 11.1 and 10.2°, respectively, comparable with the results of Clough et al. for PPY. This indicates that the main chain of cis−transoidal PPA favors a coplanar conformation. Inserting these results into eqs 1−3, we obtained q = 16 nm. Although the q value of *cis*-PPA has not yet been determined, this q value seems to be too large compared with 4.2 nm of the bulkier *cis*-PCPA, indicating that the force field used (the Dreiding force field, version 2.11) considerably underestimates the degree of the torsional fluctuation in the PPA chain. The solvent DMSO may affect the force field, which was not explicitly considered in the above MD calculations.[31]

Effect of Complexation with an Optically Active Amine. When Nap was added to DMSO solutions of a PCPA sample (S-3), the solution viscosity exhibited a unique polymer concentration dependence, as indicated by the squares in Figure 3. This dependence indicates that the PCPA chain behaves as a polyelectrolyte[32,33] after complexation with Nap in DMSO; i.e., the acid−base complex of the carboxyl group of PCPA and the amino group of Nap are at least partly dissociated into carboxylate and ammonium ions. To reduce the degree of the dissociation as well as to increase the ionic strength in DMSO, we added the hydrochloric salt of Nap (Nap·HCl) to the solution. At the salt molar concentration C_S = 0.02 M, the polymer concentration dependence of the solution viscosity became normal, as shown by filled circles in Figure 3, and we determined $[\eta]$ by the extrapolation to zero c.

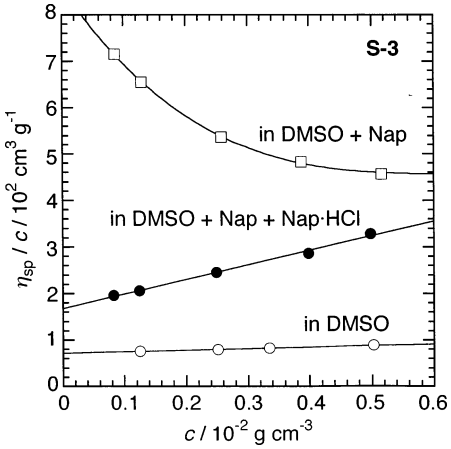

Figure 3. Concentration dependence of η_{sp}/c (η_{sp}: the specific viscosity) of sample S-3 in pure DMSO (○), DMSO + Nap (0.34 M, □), and DMSO + Nap (0.34 M) + Nap·HCl (0.02 M, ●).

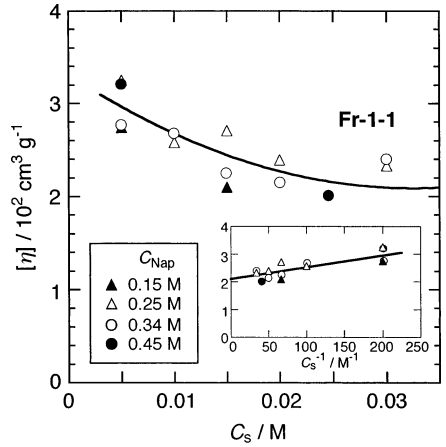

Figure 4. Added salt concentration dependence of $[\eta]$ for fraction Fr-1-1 at different C_{Nap}.

Figure 4 shows the added salt concentration dependence of $[\eta]$ for fraction Fr-1-1 at different Nap concentrations (C_{Nap}). Although the data points are rather scattered, $[\eta]$ seems to decrease with increasing C_S but is almost independent of C_{Nap} in the range of C_{Nap} examined. The C_S dependence indicates the reduction of the intramolecular electrostatic repulsion.[34] On the other hand, the C_{Nap} independence implies that the complexation of the carboxyl groups of PCPA with Nap is almost saturated in the range of C_{Nap} examined.[34] At higher C_S, we observed gelation in DMSO solutions of PCPA and Nap, so that we could not measure $[\eta]$ at such C_S.

We measured the second virial coefficient A_2 for fraction Fr-1-1 in DMSO containing Nap and Nap·HCl (C_{Nap} = 0.34 M and C_S = 0.02 M) at 25 °C by sedimentation equilibrium. The result is 8.0×10^{-4} cm^3 mol^{-1} g^{-2}, which is considerably larger than that (1.93×10^{-4} cm^3 mol^{-1} g^{-2}) of the same fraction in pure DMSO and is comparable with those of various polyelectrolytes in aqueous salt solutions[35−37] with the same Debye−Hückel screening length (at $C_S \sim 0.035$ M at 25 °C). This indicates that the intermolecular electrostatic interaction of the PCPA chain is still appreciable in DMSO at C_S = 0.02 M. On the other hand, the C_S dependence of $[\eta]$ shown in Figure 4 is not remarkable, and $[\eta]$ at C_S = 0.02 M (or C_S^{-1} = 50 M^{-1} in the insert of Figure 4) almost approaches one at the infinite C_S (or the zero C_S^{-1}). This means that the intramolecular

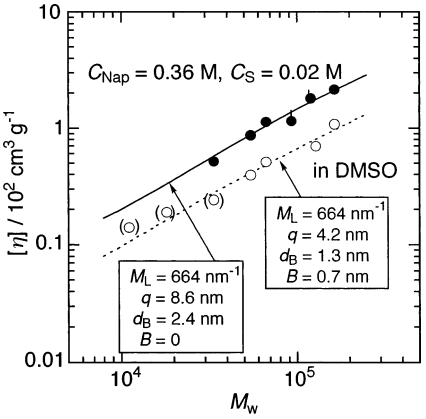

Figure 5. Molecular weight dependence of $[\eta]$ for PCPA in pure DMSO (○) and in DMSO containing Nap (C_{Nap} = 0.36 M) and Nap·HCl (C_S = 0.02 M) (●): filled circles with pip, $[\eta]$ for unfractionated samples at C_{Nap} = 0.34 M and C_S = 0.02 M plotted against the viscosity average molecular weight; curves, theoretical values calculated by the theory of Yoshizaki, Nitta, and Yamakawa[17] for wormlike touched-beads model ($\Phi_\infty = 2.35 \times 10^{23}$ mol^{-1}).

electrostatic interaction does not affect $[\eta]$ at C_S = 0.02 M, which may be due to the stiffness of the PCPA chain.[38]

Figure 5 compares $[\eta]$ of PCPA at C_{Nap} = 0.36 M and C_S = 0.02 M at 25 °C with that in pure DMSO. The figure includes two data points (filled circles with pip) for the unfractionated PCPA samples (S-3 and S-4) at almost the same solvent condition, where the molecular weights of the two samples were determined from $[\eta]$ in pure DMSO using the $[\eta] - M_w$ relation for fractions Fr-1-1 to Fr-1-5. Complexation with Nap considerably increases the $[\eta]$ of PCPA. Because the intramolecular electrostatic interaction in the PCPA−Nap complex is not important as mentioned above, the increase in $[\eta]$ indicates that the complexation with Nap stiffens and/or thickens the PCPA chains. From the chemical structure of Nap, the increment in the diameter of the helix by complexation may be estimated to be 1.1 ± 0.5 nm. By fitting the $[\eta]$ data for the complex according to the theory of Yoshizaki, Nitta, and Yamakawa[17] for the wormlike touched-beads model with M_L and d_B fixed to 664 nm^{-1} (= M_0/0.22 nm) and 2.4 nm (= 1.3 + 1.1 nm), we obtain q = 8.6 nm. The possible variance in d_B leads to uncertainty in the q of ±1.4 nm. Because of the increasing stiffness of the complex, the intramolecular excluded-volume effect does not contribute to the theoretical results in Figure 5.

We can estimate the torsional fluctuation $\delta\tilde{\phi}$ to be 15° from q of 8.6 nm using eqs 1−3 and assuming $\delta\tilde{\phi}_S = \delta\tilde{\phi}_D$, which is significantly smaller than $\delta\tilde{\phi}$ of 21° for the complexation-free PCPA chains. This is an important conclusion obtained by viscometry, indicating that the steric hindrance among Nap complexed with PCPA side chains creates a steeper internal-rotation energy well for the PCPA main chain. This is qualitatively consistent with the previous results of Yashima et al. for the MD calculation demonstrating that cis−transoidal poly(phenylacetylenes) with bulky side chains assume more regular helical conformations than poly(phenylacetylene) itself, whose helical structure is altered rather easily.[30]

The q value of the PCPA−Nap complex, however, does not attain values for typical stiff polymers (larger than ca. 20 nm). Thus, the helical conformation of the complex is still imperfect despite the intense CD induction. The conformational change in PCPA upon complexation is not as drastic as the coil to helix transition of polypeptides, where the persistence length remarkably increases from a few nanometers to a hundred nm.[25] On the other hand, the complexation alters remarkably the population of the right- and left-handed helices to induce intense CD. The remarkable alteration may result from difficulty of the helix reversal in a PCPA chain. As mentioned above, the helix reversal hardly affects the persistence length or the intrinsic viscosity due to the large torsional fluctuation. Thus, unfortunately we cannot extract the information on the difficulty of the helix reversal from the present viscometric results.

Recently, Yashima et al. found that the helical chirality induced by optically active amines is "memorized" even after replacement of the amines by achiral amines.[39] Because the induced CD disappears on adding an acid to the PCPA solution, PCPA itself is a dynamic helical polymer of which right- and left-handed helical conformations are rapidly interconvertible. Thus, the memory effect indicates that complexation with achiral amines makes PCPA a stable (or static) helical polymer; i.e., the internal rotational energy barrier between the right- and left-handed helical conformations becomes remarkably higher due to the complexation. Along with the viscometric results, we can conclude that the acid−base complexation with amines or amino alcohols can alter the internal rotation energy of the PCPA backbone.

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Supporting Information Available: Figure showing ^{1}H NMR spectra of PCPA fractions and molecular characteristics of PCPA samples used (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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