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Titration Behavior and Spectral Transitions of Water-Soluble Polythiophene Carboxylic Acids

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ABSTRACT: Water-soluble poly(3-thiophene acetic acid) (P3TAA) and its copolymers with 3-*n*-methylthiophene or with 3-*n*-octadecylthiophene were synthesized. The solution properties of these water-soluble polythiophene carboxylic acids were studied by potentiometric titration, viscosity measurements, and UV−visible spectroscopy. We have found that the Henderson−Hasselbach plot of the titration curve showed an inflection of the slope around pH = 5−6. The reduced viscosity and electronic spectra of the P3TAA aqueous solution also showed an abrupt change at this pH region. These results are quite different from that of a common flexible polyelectrolyte, such as poly(acrylic acid) (PAA) and strongly suggest that the pH-induced abrupt conformational changes occurred from the aggregated state to the extended state of the polymer main chain. The observed results are explained in terms of the rigid hydrophobic main chain and the nature of the conjugated polymer.

Introduction

Various types of soluble poly(3-alkylthiophene)s with a long alkyl side chain at the 3-position of a thiophene ring have been extensively studied in the past decades.[1−5] These neutral polythiophenes, bearing properly designed side chains, can undergo striking conformational changes when exposed to heat, light, electric fields or various chemical moieties giving rise to reversible thermochromism, photochromism, electrochromism, or ionochromism. These optical changes are believed to be related to a reversible planar-to-nonplanar conformational transition of the conjugated main chain.[6−7]

The incorporation of relatively long and flexible side chains have led the polymers with a stiff backbone to solubilize in organic solvents, and this has also been applied to water-soluble polythiophenes by substituting hydrophilic groups. For example, Heeger et al.[8,9] reported the synthesis and characterization of the sodium salts and corresponding acids of poly(thiophene ethanesulfonate) and poly(thiophene butanesulfonate). Masuda et al.[10] also reported the water-soluble conducting polymer using sodium salt of poly(thiophene-3-carboxylate). McCullough et al.[11,12] have recently shown that the regioregular water-soluble polythiophenes with a propionic acid at the 3-position of a thiophene ring can switch from purple to yellow phases by increasing the amount of NH_4OH in aqueous solution; in addition, they reported the cation size-dependent chromaticity due to a sterically induced disruption of the aggregated phase.

Solutions of these conjugated polymers as rigid polyelectrolytes are expected to show unique properties which are different from those of a common flexible polyelectrolyte, such as poly(acrylic acid) (PAA), but only a few studies have been reported.[6,12]

In this paper, water-soluble polythiophenes were synthesized by introducing pH-responsive carboxylic acid groups at the 3-position of thiophene ring, and the solution and spectral properties were studied. It was found that poly(3-thiophene acetic acid) (P3TAA) and its copolymer with 3-*n*-octadecylthiophene (3ODT) undergo an abrupt conformational change at pH = 6 which can be associated with the rigid conjugated structure of the main chain, and the roles of the hydrophobicity of the main chain were discussed.

Experimental Section

Materials. 3-thiopheneacetic acid (3TAA), 3-*n*-octadecylthiophene (Tokyo Kasei Kogyo Co. Ltd., Tokyo, Japan), anhydrous ferric chloride ($FeCl_3$) (Wako Pure Chemical Industries Ltd., Tokyo, Japan) were all used as received. Chloroform ($CHCl_3$) and methanol (CH_3OH) were dried over CaH_2 for 24 h under the nitrogen atmosphere and distilled, respectively.

Oxidative-coupling polymerization. 3-Thiophene methyl acetate (3TMA) was prepared by refluxing 3-thiopheneacetic acid (10.0 g) in dry methanol (50 mL) with 1 drop of concentrated H_2SO_4 for 24 h, to protect the oxidative decomposition of the carboxylic acid moiety of the monomer during the oxidative-coupling polymerization. The methanol was evaporated, and the residue was extracted with fresh diethyl ether. The extract was washed with deionized water, dried with anhydrous $MgSO_4$, and filtered. The 3TMA was recovered after evaporation of the diethyl ether.

The protected monomer, 3TMA, was polymerized by chemical oxidative coupling in dry chloroform using anhydrous ferric chloride and a procedure similar to that of Sugimoto et al.[13,14] In a 100 mL three-necked flask, 40 mmol of ferric chloride was dissolved in 30 mL of dry chloroform under nitrogen to which a solution of 10 mmol of monomer in 20 mL of chloroform was added dropwise. The molar ratio of the oxidant to monomer was 4:1 in all cases. The mixture was stirred for about 24 h at 0 °C under nitrogen. The blue-black doped polymers were poured into a large excess of methanol (1 L) to precipitate the poly(3-thiophene methyl acetate) (P3TMA), which turned brown-red, and the precipitate was purified by repeated washing with fresh methanol and deionized water to remove the residual oxidant and the oligomers and collected by filtration to give a yield of about 75%. The copolymer with 3TMA−3ODT composition $F = 0.06$ (The mole fraction of 3ODT in the monomer mixture) was also prepared by the same oxidative-coupling polymerization as the P3TMA. The obtained polymers were soluble in common organic solvents (chloroform, toluene, benzene, THF, etc.).

Hydrolysis. P3TMA and poly(3TMA-*co*-3ODT) were hydrolyzed as follows: the methyl groups on the side chain of these polymers were removed by heating the polymer (0.5 g) in 50 mL of 2.0 M NaOH solution for 24 h at 100 °C (deprotecting reaction). Especially for poly(3TMA-*co*-3ODT), the alkaline hydrolysis was performed for 3 days because the

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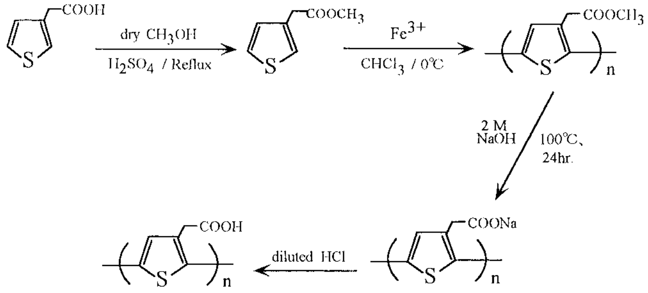
Scheme 1. Synthesis of P3TAA



copolymer is poorly wetted by water because of the hydrophobic long alkyl side chains. After the deprotecting reaction, the mixtures were filtered to remove the insoluble part. The water-soluble part was neutralized and precipitated by dilute HCl solution, carefully washed repeatedly with deionized water, and vacuum-dried for 2 days (40−60% yield). The hydrolysis for all polymers was nearly complete, as evidenced by ^{1}H NMR spectroscopy (the characteristic signal of the carboxylic acid of the P3TAA at 12.6 ppm appears after alkaline hydrolysis; therefore, the degree of hydrolysis can be calculated by the ratio of the peak integrals of 12.6−7.6 ppm, supposing the characteristic signal of the 4-position proton of a thiophene ring at 7.6 ppm is not changed after alkaline hydrolysis). After alkaline hydrolysis, these polymers became dark-brown and had a metallic luster. The reaction mechanism is shown in Scheme 1.

We obtained the P3TAA and the copolymer $F = 0.06$ which are soluble in dimethyl sulfoxide (DMSO), dimethylforamide (DMF), and weak alkaline solution. For example, the DMSO and DMF solutions of P3TAA have absorption peaks at 407 and 404 nm at room temperature, respectively. The P3TAA and copolymer of $F = 0.06$ (as calculated by ^{1}H NMR spectroscopy) were characterized by various analytical methods (^{1}H NMR, FT-IR, UV−visible spectroscopy, gel-permeation chromatography, etc.).

Characterizations. UV−visible absorption spectra were obtained with a Hitachi UV−visible spectrophotometer (model U-3000) under various conditions. A 10^{-4} base molarity polymer solution containing 1 M NaCl was used in all cases to maintain a constant ionic strength. The pH was varied from 3 to 12, and the temperature was varied from 20 to 100 °C.

The weight-average molecular weight (M_w) was estimated by gel-permeation chromatography (column: TOSOH TSK-gel, G3000H$_{XL}$, G4000H$_{XL}$, G5000H$_{XL}$, 7.5 × 600 mm^2 × 3) with standard polystyrene (Shodex Standard SM-105) as a reference using THF as an eluent at 40 °C. M_w and polydispersity were found as 1.6×10^4 (repeating unit = 35) and 2.81 for the P3TAA and 2.9×10^4 (repeating unit = 59) and 3.25 for the copolymer $F = 0.06$, respectively. The P3TAA and copolymer $F = 0.06$ were noncrystalline with an amorphous halo in the wide-angle X-ray diffraction region (40kV, 200mA; RINT-2000, Rigaku Co. Ltd., Tokyo, Japan). The differential scanning calorimetry measurement (DSC22C, Seiko Instruments, Tokyo, Japan) of the P3TAA and copolymer $F = 0.06$ exhibited no endothermic peak or glass transition up to 200 °C.

The structures of 3TAA, 3TMA, P3TMA, and P3TAA were determined by ^{1}H NMR (JEOL JNM-400, 400 MHz). ^{1}H NMR spectra of these polymers were in agreement with their expected structures: 3TAA (Figure 1a), ($CDCl_3$) δ 11.02 ppm (s, $-COOH$, 1H), 7.29−7.03 ppm (m, thiophene ring protons, 3H), 3.68 ppm (s, thiophene ring $-CH_2-$, 2H); 3TMA (Figure 1b), ($CDCl_3$) δ 7.28−7.03 ppm (m, thiophene ring protons, 3H), 3.70 ppm (s, thiophene ring $-CH_2-$, 2H), 3.66 ppm (s, $-CH_3$, 3H); P3TMA (Figure 1c), ($CDCl_3$) δ 7.26−7.03 ppm (m, thiophene ring proton, 1H), 3.68 ppm (s, thiophene ring $-CH_2-$, 2H), 3.64 ppm (s, $-CH_3$, 3H); P3TAA (Figure 1d), (DMSO) δ 12.60 ppm (s, $-COOH$, 1H), 7.55−7.28 ppm (m, thiophene ring proton, 1H), 3.80−3.37 ppm (m, thiophene ring $-CH_2-$, 2H). As shown in Figure 1b, the esterification was confirmed by the disappearance of the proton signal characteristic of the carboxylic acid at the 3-position of a thiophene ring. After the oxidative-coupling polymerization, the characteristic peaks for all polymers were broader than those of the monomer, as expected. One should note that as shown in Figure 1c the thiophene ring $-CH_2-$ and $-CH_3$ peaks are overlapped, and the small shoulder in the overlapped peaks is the $-CH_3$ peak. The structure of the P3TAA hydrolyzed by alkaline solution was also confirmed by the appearance of the proton signal characteristic of the carboxylic acid (Figure 1d). In addition, it is well-documented that in the ^{1}H NMR spectra of poly(3-alkylthiophenes) the proton signals associated with the α-methylenes are split because polymerization results in diads which are either head-to-tail (HT) or head-to-head (HH).[15,16] Similar splitting patterns were observed for the thiophene ring $-CH_2-$ peak of P3TAA. These complex features can be attributed to the combination of the conformational changes of the ring-to-ring bonds and the flipping of thiophene rings. In addition, the regioregularity of poly(3-alkylthiophenes) has been investigated by analysis of the spectral region 6.9−7.1 ppm corresponding to β-protons, indicating the configurational and regiochemical information of the polymer. As a result, we have found that the P3TAA used in this work has a nonregioregular structure with less than 40% HT−HT couplings, as evidenced by ^{1}H NMR spectroscopy.

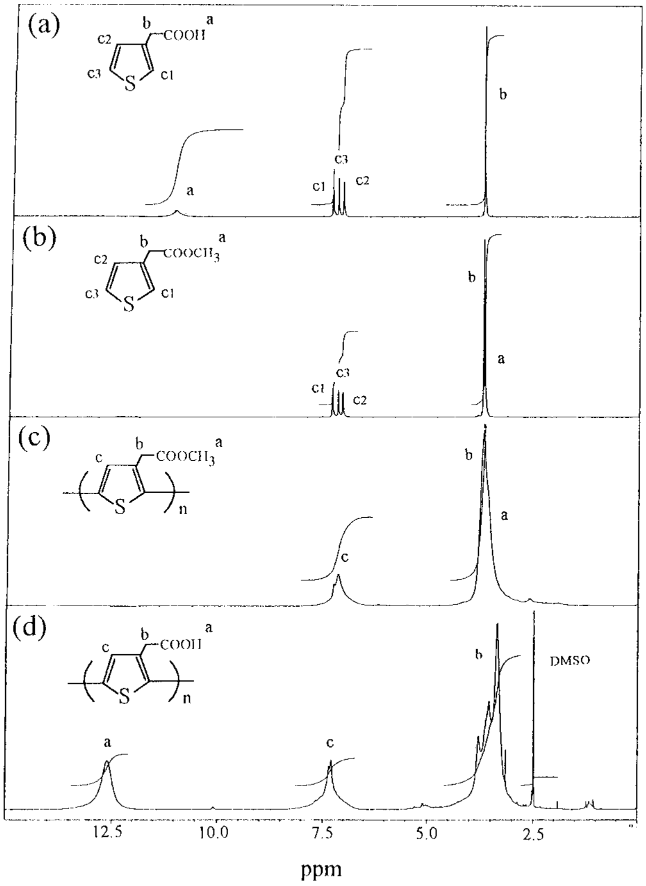


Figure 1. 400 MHz ^{1}H NMR spectra of (a) 3TAA, (b) 3TMA, (c) P3TMA, and (d) P3TAA.

FT-IR spectrum was recorded on a Japan Spectroscopic Co. MFT-2000 infrared spectrophotometer. Figure 2 shows the FT-IR spectrum of the neutral polymer powder (P3TAA). The spectrum shows the absorption band at 3200−3000 cm^{-1} assignable to the stretching vibration of the C−H bond on the thiophene ring; at 3000−2800 cm^{-1}, the aliphatic C−H bonds; at 1700 cm^{-1}, the C=O stretching vibration; at 1410 cm^{-1}, the thiophene ring-stretching vibration; and at 1300−1200 cm^{-1}, the C−O stretching vibration. The most characteristic feature in this spectrum is the extremely broad O−H absorption occurring in the region from 3400 to 2400 cm^{-1}, which is attributed to the strong hydrogen bonding of the dimer. This absorption often obscures the C−H stretching vibrations that occur in the same region. Moreover, because this broad

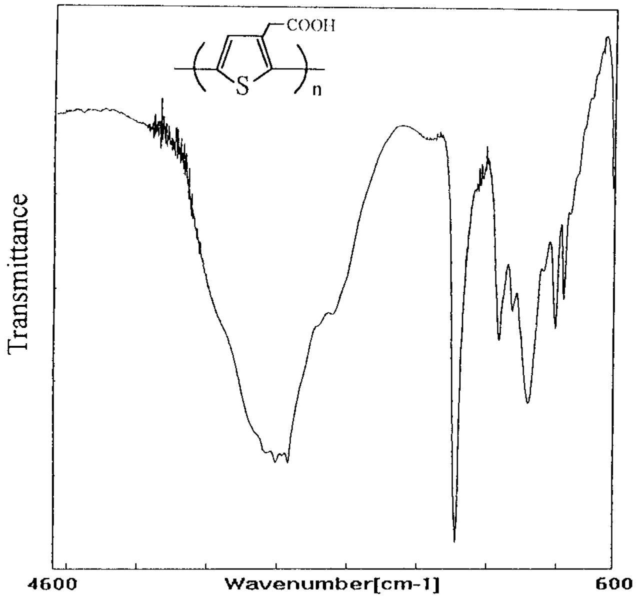


Figure 2. FT-IR absorption spectrum of the neutral powder (P3TAA) at 25 °C.

absorption due to the hydrogen bonding is observed together with the C=O absorption band, a carboxylic acid is certainly indicated. Therefore, it is obvious from the absorption at 1700 cm^{-1} that the ester groups were not deteriorated during the oxidative polymerization.[10]

The potentiometric titration was performed with a glass/reference electrode, calibrated with buffer solutions of pH 4, 7, and 9. The titration was performed from alkaline region, starting from a polymer solution of 10^{-2} base molarity, 0.02 M NaOH and 1.0 M NaCl, by adding the 0.01 M standard HCl solution with a microburet to the polymer solutions under the nitrogen at 25.0 ± 0.1 °C. As the equilibrium is found to be established rather slowly, the titration was performed until the pH remained constant for each step. The initial volume of the polymer solution was 20 mL. The potentiometric titration data of a conventional atactic sample of poly(acrylic acid) (M_w = 200 000) (ARON A-10H, DONGA Synthesis Ltd., Tokyo, Japan) is shown for reference.

Viscosities of the polymer solutions were measured with a conventional Ubbelohde capillary viscometer (SIBATA SU-98309) changing the temperature from 20 to 80 °C. A polymer solution of 10^{-2} base molarity was used in all cases. The pH value of the polymer solutions was varied from 4.0 to 12.0.

Results and Discussion

Dissociation Behavior. We have carried out the potentiometric titration to investigate the dissociation behavior and the local conformational change of P3TAA as the pH changes.

The potentiometric titration was carried out using 10^{-2} base molarity polymer solution containing 0.2 or 1.0 M NaCl, and the result is shown in Figure 3. The titration curve of P3TAA shows, to some extent, dissociation behavior similar to that of PAA below pH = 5.5, whereas the ionization of P3TAA is suppressed in the higher pH region. When the ionic strength is changed from 1.0 to 0.2 M, the dissociation of P3TAA is suppressed, presumably because of strong electrostatic repulsion between dissociated groups.

According to Katchalsky and Spitnik[17] and Leyte and Mandel,[18] the titration behavior of many polyelectrolytes is well-expressed by the extended Henderson–Hasselbach equation over a wide dissociation range:

$$\mathrm{pH} = \mathrm{p}K_a + n\log[\alpha/(1-\alpha)]$$

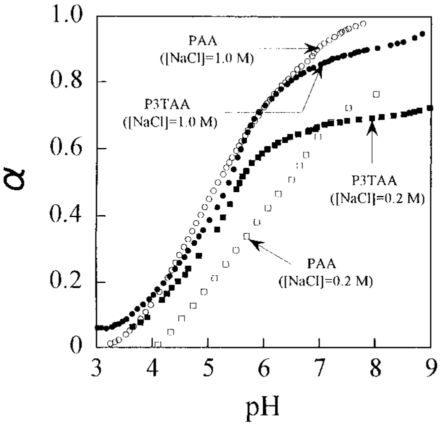


Figure 3. Potentiometric titrations at 25 °C. [polyanion] = 10^{-2} base molarity). ○ = poly(acrylic acid) (PAA); [NaCl] = 1.0 M, □ = PAA; [NaCl] = 0.2 M, ● = P3TAA; [NaCl] = 1.0 M, ■ = P3TAA; [NaCl] = 0.2 M.

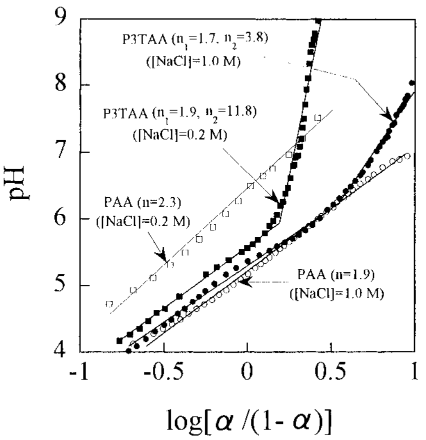


Figure 4. Extended Henderson–Hasselbach plots of Figure 3: [polyanion] = 10^{-2} base molarity, ○ = poly(acrylic acid) (PAA); [NaCl] = 1.0 M, □ = PAA; [NaCl] = 0.2 M, ● = P3TAA; [NaCl] = 1.0 M, ■ = P3TAA; [NaCl] = 0.2 M.

Here pK_a is the intrinsic dissociation constant, and α is the degree of dissociation. The n parameter reflects the extent of interaction between the next neighboring ionized groups of the polyelectrolytes. When the main chain is not very hydrophobic, it corresponds to the electrostatic repulsion between charged groups.

Figure 4 shows the extended Henderson–Hasselbach plots for P3TAA and PAA. As shown in Figure 4, the PAA is well-expressed by one slope with $n = 1.9$ in the presence of 1.0 M NaCl, whereas the P3TAA samples have two slopes with a transition at around pH = 6 with the slopes of n_1 (1.7) and n_2 (3.8). The n_1 value of P3TAA has dissociation nature approximately similar to that of PAA. However, as the pH increases above pH = 6, n_2 increases to 3.8, indicating an increased difficulty of the further dissociation on the rigid main chain of thiophene ring. Moreover, if the NaCl concentration decreases from 1.0 to 0.2 M, the n_2 value of P3TAA increases up to 11.8. The obtained n_2 value is extraordinary large and should not be associated simply by the electrostatic repulsion. At present, we cannot explain this phenomenon; however, this might be associated with the presence of a rigid thiophene ring which may strongly suppresses the further ionization at a pH range higher than 6. The strong suppression at α = 0.6 due to the rigid coplanar structure of the main chain might stabilize the ionized carboxylate and un-ionized carboxylic acid, for example,

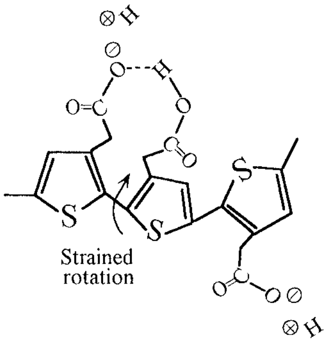


Figure 5. Stable bridge-structure scheme proposed for P3TAA at pH = 6 or higher at 25 °C. [NaCl] = 0.2 M.

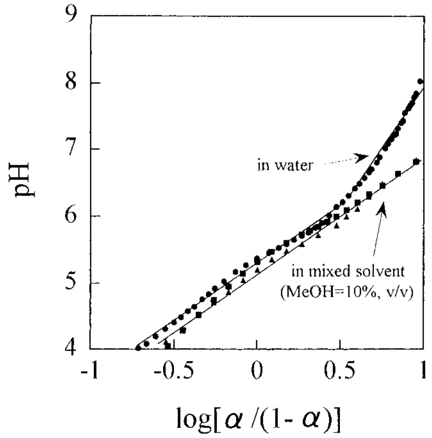


Figure 6. Extended Henderson−Hasselbach plots of P3TAA in water (●: [NaCl] = 1.0 M) and mixed solvent (MeOH = 10%, v/v) (■: [NaCl] = 0.2 M; ▲: [NaCl] = 1.0 M) at 25 °C. [P3TAA] = 10^{-2} base molarity.

with a structure as shown in Figure 5. If the main chain is flexible as it is in PAA, the formation of stable bridge structure illustrated in Figure 5 might not be formed because of an extensive rotation of the chain. To prove this experimentally, IR spectra of carboxylic and carboxylate groups were taken at various pH and compared with those of PAA. However, we failed to observe any new peaks as a evidence of the formation of the stable bridge structures for P3TAA.

To obtain further experimental information about this conformational transition, potentiometric titration was also carried out in mixed solvent (MeOH = 10%, v/v). As shown in Figure 6, the Henderson−Hasselbach curve of P3TAA in mixed solvent containing 0.2 or 1.0 M NaCl show a behavior rather similar to that of PAA in water without any conformational transition. This can be explained in terms of the breakdown of the hydrophobic interactions between thiophene rings[19] by MeOH. Addition of MeOH preferentially induces the solvation of the skeleton of the main chain and induces the enhanced main chain rotation; as a result, this brings about a dissociation similar to that in the case of PAA.

Viscosity. The change of the chain conformation upon dissociation was also investigated by viscosity measurements. Figure 7 shows the relationship between reduced viscosity (η_{SP}/C) and the pH. It is seen that the reduced viscosity of the P3TAA solution above pH = 6 is almost constant, whereas it abruptly decreased at around pH = 5.05. It should be noted that although the viscosity abruptly decreased, the solution is still transparent at pH = 5.05, as shown by the transmittance measurement in Figure 7. The solution became hazy only when pH became 4.93, and the polymer precipitated below pH = 4.

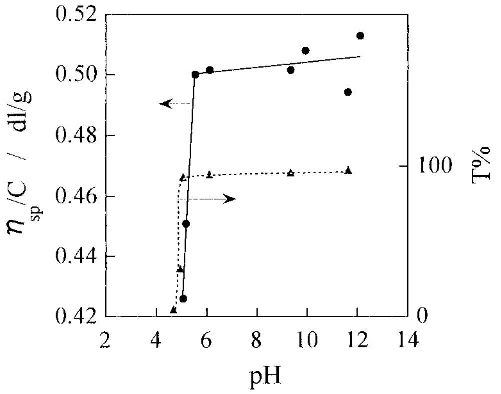


Figure 7. pH dependence of the reduced viscosity (●) and transmittance (▲) of P3TAA in water at 20 °C. [P3TAA] = 10^{-2} base molarity, [NaCl] = 1.0 M.

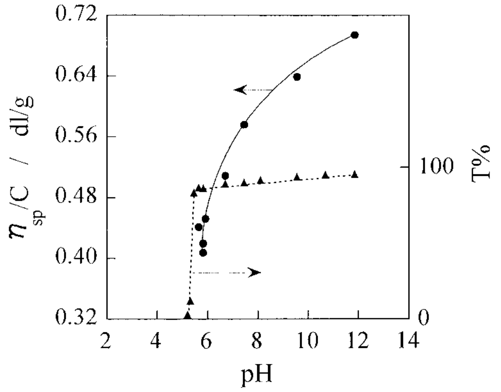


Figure 8. pH dependence of the reduced viscosity (●) and transmittance (▲) of P3TAA in mixed solvent (MeOH = 10%, v/v) at 20 °C. [P3TAA] = 10^{-2} base molarity, [NaCl] = 1.0 M.

The dramatic change of the reduced viscosity is due to a cooperative backbone conformational change from the aggregate state to the extended state and the unique feature of the polythiophene as a new class of a rigid-type polyelectrolyte. In contrast, the viscosity of PAA aqueous solution undergoes a well-known[20] gradual increase with an increase of the pH without any abruptly change.

Figure 8 shows the effect of MeOH on the viscosity of P3TAA. When a 10% MeOH is added, an abrupt conformational transition could no longer be observed, and only a monotonic increase of the reduced viscosity with an increase of the pH was found. These results suggest that by adding MeOH the rigid and aggregated structures of the main chain formed by the hydrophobic interaction between thiophene rings have been broken and the main chain became flexible by the addition of MeOH. These results are consistent with the results of dissociation behaviors of P3TAA solution in mixed solvent, which showed the PAA-like ionization without any conformational transition.

Electronic Spectral. The pH dependence of the UV−visible absorption spectra of the P3TAA solution of 10^{-4} base molarity was investigated in 0.2 and 1.0 M NaCl solutions. Figure 9 shows the pH dependence of λ_{max} at a range of pH ≥ 5. When the pH varies from 5 to 6, a dramatic increase in λ_{max} is observed, which became almost constant above pH = 6. These spectral transitions of the P3TAA aqueous solutions were observed to be reversibe by changing the pH of the solution.

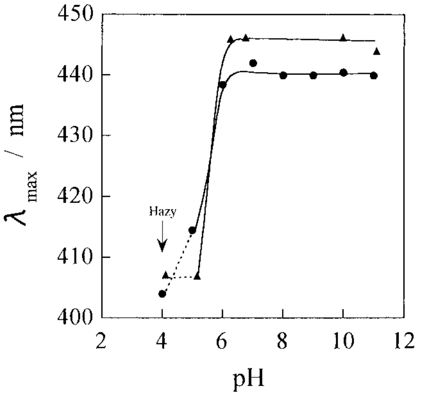


Figure 9. pH dependence of the UV−visible absorption spectra of P3TAA aqueous solution with various salt concentrations at 25 °C: [P3TAA] = 10^{-4} base molarity, ●: [NaCl] = 0.2 M, ▲ [NaCl] = 1.0 M.

We could not observe any isosbestic point[21] in the UV−visible spectra; thus, the presence of two phases related to the interchain aggregation could be excluded. Besides, there was no concentration dependence in λ_{max} of P3TAA aqueous solution at the constant pH, which implies that the spectral change is essentially a single-chain phenomenon and that the aggregation of the P3TAA polymer chain may occur only after the single-chain conformational change has occurred at pH below 4.93 when the solution became hazy. Therefore, an abrupt transition in λ_{max} could be attributed to the change in the effective electronic conjugation length, because of the pH-induced conformational changes from the aggregated state to the extended state of the polymer main chain by the electrostatic repulsion of the dissociated carboxylic acid in the side chain.[6]

Possible schemes for these spectral changes have been studied by the many researchers.[3−7] Heeger et al.[3] has suggested that the spectral change is due to the intrachain (side-group disorder, backbone conformational changes, etc.) or interchain (crystallization, microcrystallization, aggregation, gelation, induced rigidity, etc.) interactions. For a specific system, therefore, it is necessary to determine whether an intrachain or an interchain mechanism is involved. We have also found that as the ionic strength increases in the alkaline region, the λ_{max} increased a little, whereas λ_{max} decreases in the acidic region. This result also suggests that the increase of the ionic strength enhanced the dissociation of the carboxylic group in the alkaline region because of the effective screening of electrostatic repulsion between dissociated groups. As a result, the polymer backbone had a more extended state, giving rise to an increased effective conjugation length.

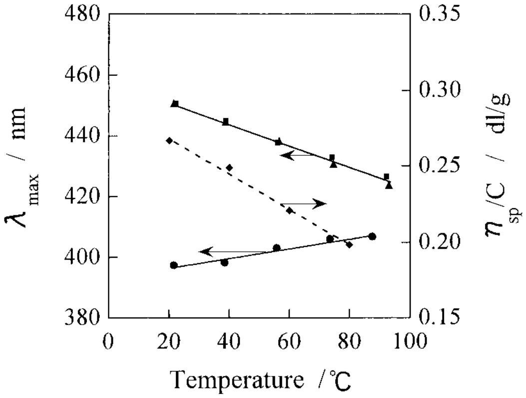


Figure 10. Temperature dependence of the UV−visible absorption spectra ([P3TAA] = 10^{-4} base molarity; ●: pH = 5.2, ▲: pH = 11.1, ■: pH = 6.3) and viscosity ([P3TAA] = 10^{-2} base molarity; ◆ pH = 10) of P3TAA aqueous solution at different pH. [NaCl] = 1.0 M.

Figure 10 shows the temperature dependence of λ_{max} of the P3TAA solution before (pH = 5.2) and after (pH = 6.3 and 11.1) the spectral transition. The λ_{max} of the polymer solution after transition decreases with the increase in temperature, whereas that before transition increases slightly with increasing temperature. These results suggest that the polymer solution in which P3TAA is considered to have a conjugated coplanar state (extended state) due to the strong electrostatic repulsion between charged groups transfers to more disordered state as temperature increases. The optical changes of the polythiophene solution responding to the temperature change have been well observed, where conformational change from a disordered coillike phase to a ordered rodlike phase occurs via rotational transitions and aggregation as the temperature is changed.[3,12,22] The temperature-induced transition of soluble polydiacetylene−4BCMU [where R = 4BCMU = $-(CH_2)_4$-$OCONHCH_2COOC_4H_9$] has also been demonstrated to be from extended rod to coil.[23−24] In the present case, thermal agitation of the side-chain segment may cause internal rotation about the coplanar polythiophenes and may induces a skeletal disordering of the coplanar polythiophene chain. The torsional mode due to the internal rotation about the ring-to-ring bonds breaks up the long $\pi-\pi$ conjugation system of the coplanar polythiophene rings, and leads to a blue shift in λ_{max}. This thermal agitation effect on the polymer conformation at high pH is also confirmed by the viscosity measurement which shows a decreased viscosity upon heating (Figure 10). On the other hand, at pH = 5.2 in which the polymer is coiled with the less conjugated aggregated state due to intramolecular hydrogen bonds

Table 1. n_1 and n_2 Values, pH at the Inflection Point in the Henderson−Hasselbach Plot, $\Delta\lambda_{max}$, and pH at the λ_{max} Transition Point

sample	[NaCl] (M)	n_1[a]	n_2[a]	pH at $n_1 - n_2$ inflection point	$\Delta\lambda_{max}$ (nm)	pH at λ_{max}[b] transition point
PAA	0.2	2.3				
	1.0	1.9				
P3TAA (DH[c] = 100%)	0.2	1.9	11.8	5.9	40	5−6
	0.2	1.7[d]				
	1.0	1.7	3.8	6.2	35	5−6
	1.0	1.7[d]				
P3TAA (DH[c] = 78%)	0.2	3.8	13.1	6.6	30	5−6
copolymer F = 0.06	0.2	1.9	4.6	6.7	20	5−6

[a] n_1 and n_2 are the slopes of the two lines in the extended Henderson−Hasselbach plot. [b] pH at the half $\Delta\lambda_{max}$ width. [c] DH = degree of hydrolysis. [d] In mixed solvent (MeOH = 10%, v/v).

of the carboxylic acid as well as intramolecular hydrophobic interaction, bonds can be broken when the temperature increases and the λ_{max} increases because of a more extended and less aggregated state.

Effect of Hydrophobic Modification. The hydrophobic side groups of water-soluble copolymers may play an important role in the dissociation behavior and conformational change. Therefore, we have also studied the behavior of a copolymer, poly(3TAA-*co*-3ODT) with 0.06 molar fraction of 3ODT ($F = 0.06$), and a partially hydrolyzed P3TAA sample (degree of hydrolysis = 78%) to clarify the effect of the steric hindrance of octadecyl groups and the hydrophobicity of methyl groups, respectively.

The potentiometric titrations of the hydrophobically modified P3TAAs were also carried out. The concentration of the polymer solutions is 10^{-2} base molarity, and that of the NaCl is 0.2 M. The 78% hydrolyzed P3TAA is more dissociated at low pH and less so at high pH in comparison with completely hydrolyzed P3TAA. Interestingly, the titration curve of copolymer $F = 0.06$ shows more dissociation than that of the P3TAAs at high pH, behaving similarly to that of PAA. This result suggests that the introduction of a small amount of long alkyl side chains enhances carboxyl dissociation. As shown in Table 1, similarly to the P3TAA, the hydrophobically modified derivatives showed two n values (n_1 and n_2), indicating the transition in its conformation.

The pH dependence of the UV−visible absorption spectra of various hydrophobically modified P3TAAs was investigated. The change in the λ_{max} ($\Delta\lambda_{max}$) as well as the λ_{max} value in the alkaline region depended largely on the chemical nature of the polymers. For example, as shown in Table 1, the $\Delta\lambda_{max}$ of P3TAA with a 78% degree of hydrolysis was lower than for complete hydrolysis in the alkaline region, because of the lower charge density and the hydrophobicity of the methyl groups. On the other hand, the $\Delta\lambda_{max}$ of copolymer $F = 0.06$ having a long alkyl side group was much smaller than that of other polymers, presumably because of the steric hindrance to the internal rotation about the ring-to-ring bonds.

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