Environmental Responses of Polythiophene Hydrogels

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ABSTRACT: A chemically cross-linked and water-swollen poly(3-thiopheneacetic acid) (P3TAA) gel was synthesized, and its swelling and spectral changes associated with its ionization were studied. The gel undergoes an abrupt red shift in the electronic spectra at a certain pH, suggesting that a conformational transition due to ionization occurred despite the chemical cross-linkage. By changing the solvent composition, during cross-linking, gels with an enhanced π conjugated structure were prepared. By doping of P3TAA gel with a $HClO_4$ solution, a satisfactorily high electrical conductivity was obtained.

Introduction

In the previous paper, we reported the synthesis and the solution properties of water-soluble poly(3-thiopheneacetic acid) (P3TAA), a semirigid polyelectrolyte.[1] The reduced viscosity of the P3TAA aqueous solution increased abruptly at pH 5−6. In parallel to this transition, an abrupt red shift in the absorption maximum (λ_{max}) from 407 to 446 nm and a change of the slope of the Henderson−Hasselbach plot of the titration curve were observed. Since the observed phenomena did not show any concentration dependence, they indicated a conformational transition of the polythiophene main chain from a nonplanar aggregated structure in the low-pH range to the planar extended structure in the high-pH region.

These results suggest that if P3TAA is chemically cross-linked, one can obtain an electroconductive hydrogel capable of changing its size and spectral properties simultaneously by changes in pH, temperature, and ionic strength. A polythiophene hydrogel would be interesting since both the electronic and ionic conductivities would respond to external stimuli.[2−6]

In this paper, we described the synthesis of water-swollen hydrogels of P3TAA. Its swelling and spectral behavior are explained in terms of the ionization process. The effect of the cross-linking is also studied and compared with that of the dissolved polythiophene.

Experimental Section

Materials. Adipoyl dihydrazide (ADH) (Wako Pure Chemical Industries, Ltd.) as a cross-linking agent, *N*,*N*′-dicyclohexylcarbodiimide (DCC) (Tokyo Kasei Kogyo Co., Ltd.) as a condensation agent, and perchloric acid (Junsei Chemical Co., Ltd.) as a dopant were all used as received. Dimethyl sulfoxide (DMSO) (Wako Pure Chemical Industries, Ltd.) was dried over CaH_2 for 24 h under the nitrogen atmosphere and distilled under vacuum before use.

Preparation of Gels. The poly(3-thiopheneacetic acid) (P3TAA) was synthesized by chemical oxidative coupling in dry chloroform using anhydrous ferric chloride as a catalyst according to the method previously reported.[1] A series of P3TAA gels with different cross-linking densities were prepared by condensation reaction of a 10 wt % solution of P3TAA polymer in the presence of a prescribed amount of ADH and DCC in DMSO at 25 °C for 2 days. The obtained gel was immersed in a large amount of DMSO for 1 week to remove unreacted substances and then in water until it reached its equilibrium state. The degree of swelling (q) of the gel was calculated as a weight ratio of the water-swollen gel to its dry state. The degree of cross-linkage (DCL) was defined as the molar ratio of cross-linking agent to polymer.

Measurements. Electronic spectra were obtained with a Hitachi UV−vis spectrophotometer (model U-3000). The 1.0 M NaCl solution was used in all cases in order to keep the ionic strength of all solutions constant. The pH was varied from 2 to 12, and the temperature was varied from 0 to 80 °C.

Absorption spectra were recorded on gel membranes (about 2 μm thick), prepared by spin-coating, with the DCL of 5, 7, and 10 mol %. Absorption spectra were recorded on gel membranes immersed in 1.0 M NaCl solution with different pH for 1 h at a given temperature.

The potentiometric titration of P3TAA gel was carried out by measuring pH of the immersing fluid using a glass/reference electrode. A piece of cubic gel (5 × 5 × 2 mm) was immersed in 20 mL of 0.02 M NaOH solution containing 1.0 M NaCl for 3 days, and a prescribed amount of 0.02 M HCl solution was added into the immersing fluid and was left for at least 1 week in order to establish equilibrium before the pH measurement.

The shear modulus of the water-swollen P3TAA gel was measured using a rheometer (3ARES-17A, Rheometric Scientific F. E. Ltd.) with a 100 g load cell. The gel was cut into disks with a 10 mm diameter and 3 mm thickness and glued between two surfaces of coaxial disk-shaped platens. The rotation velocity range was varied from 10^{-2} to 10 Hz.

The electrical conductivity of the polythiophene gel was measured by the ac two-terminal method at 20 °C using an LCZ meter in the frequency range from 50 to 100 Hz with an applied voltage of 1 V. The polythiophene gel was cut into a 5 × 5 × 2 mm rectangular shape and was sandwiched between a pair of platinized platinum electrodes. The accurate distance between two electrodes was determined using a microscope. A detailed description of the measurement was given previously.[7]

Results and Discussion

Swelling Properties. The chemically cross-linked P3TAA gel swelled in water and showed an equilibrated degree of swelling (q) of 8.4, 5.7, and 4.3 for the gels of the degree of cross-linkage (DCL) of 5, 7, and 10 mol %, respectively. These gels exhibited viscoelastic behavior like most of hydrogels, and the shear modulus of the water-swollen P3TAA gel with DCL = 7 mol % is shown in Figure 1. It is seen that G', G'', and tan δ change moderately with frequency, and G'' is much lower than G' in the measured frequency region, indicating that P3TAA gel undergoes little dispersion and energy

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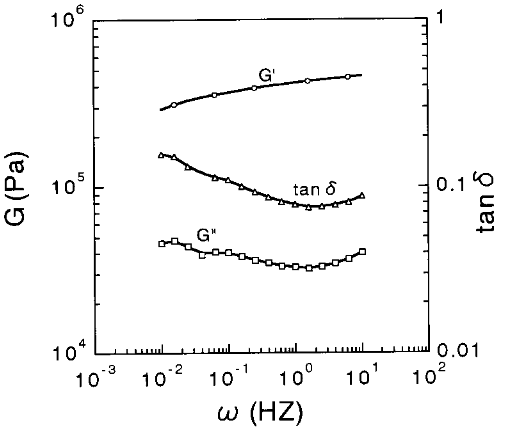

Figure 1. Storage modulus G' (○), loss modulus G'' (□), and tan δ (△) as a function of the frequency of P3TAA gel. DCL: 7 mol %.

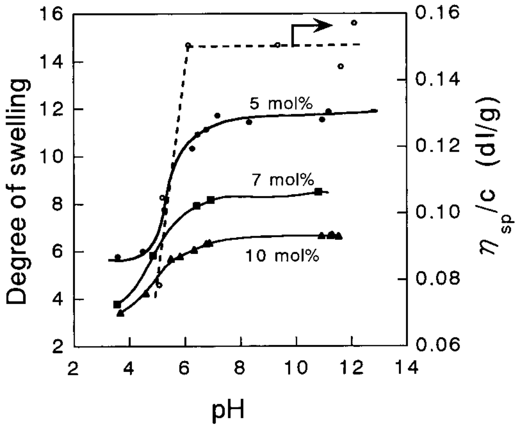

Figure 2. pH dependence of the degree of swelling (q) of the P3TAA gels with different DCL at 25 °C and the reduced viscosity (○) of its polymer solution at 20 °C. [P3TAA] = 10^{-2} M, [NaCl] = 1.0 M.

dissipation with a periodic deformation, as usually observed for common hydrogels. Considering the conformational transition of P3TAA solution occurring at around pH 5, pH dependencies of the swelling, dissociation, and spectral changes of the P3TAA gel with different cross-link densities have been studied.

Dissociation Behavior. As shown in Figure 2, the q abruptly increased in a pH region of 4−7 and then saturated, which agrees well with the increase in the viscosity of a P3TAA solution (Figure 2). As expected, the lower the cross-linking density, the higher the q and the sharper the transition. The pH-induced increase in the q is due to a backbone conformational transition from the aggregated state to an extended state in the network.

Since the change of q could be associated with the dissociation behavior of carboxylic groups of P3TAA, the potentiometric titration of the gels was studied. As shown in Figure 3, the dissociation of carboxylic groups of solubilized P3TAA starts at pH 3.5 and gradually increases, while that of the gel starts at around pH 5 and increases rapidly with an increasing pH, with 80% of the carboxylic groups dissociating at around pH 7 regardless of the DCL of the gel. This indicates that the dissociation of P3TAA gel is strongly suppressed presumably due to the cross-linkage in the low-pH region. Since the pH region where the dramatic increase in the dissociation occurred parallels the swelling of the gel, the increase of the swelling is due to the electrostatic repulsion among the dissociated carboxylic groups.

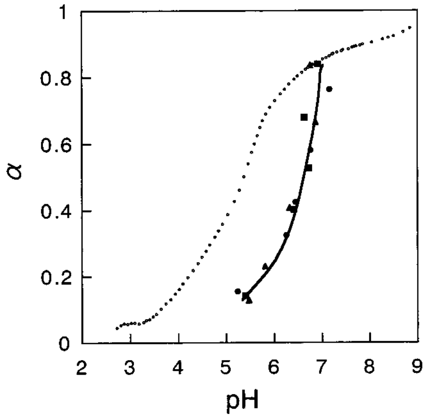

Figure 3. Potentiometric titrations of the P3TAA gels with different DCL and its polymer solution (○). DCL of gels: (●) 5 mol %, (■) 7 mol %, (▲) 10 mol %. [P3TAA] = 10^{-2} M, [NaCl] = 1.0 M. Temperature = 25 °C.

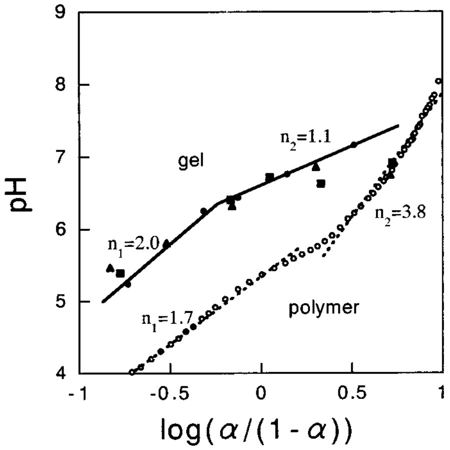

Figure 4. Extended Henderson−Hasselbach plots of Figure 3.

Figure 4 shows the extended Henderson−Hasselbach plots for the solvated and cross-linked P3TAA. The solvated P3TAA sample has two slopes with a transition at around pH = 6 with the slopes of n_1 = 1.7 and n_2 = 3.8.[1] As discussed in the previous paper, the increased n_2 value which reflects the difficulty of successive dissociations might be associated with the rigid coplanar structure of the main chain where the intramolecular hydrogen bonding between the ionized and unionized carboxylic groups suppresses further dissociation. In contrast to this, n_1 for the gel is 2.0 in the pH range of 5−6 and n_2 is 1.1 in the pH range of 6−7. The low value of n_2 indicates that there is practically no electrostatic hindrance for the ionization in this pH region and suggests that the cross-linkage stabilizes the coplanar conformation due to chemical bridging.

Spectral Changes. We found in our previous paper that there is an abrupt increase in λ_{max} of P3TAA solution when the pH varies from 5 to 6. If the intrinsic viscosity is calculated from the Kirkwood−Auer theory,[8] assuming that the polymer is rodlike with a molecular weight of 1.6 × 10^4, one gets the value 0.061 dL/g, which is in reasonable agreement with our experimental result 0.116 dL/g. Besides, there is no concentration dependence of λ_{max} at pH 7 over a wide concentration range from 10^{-5} to 10^{-2} mol/L, as shown in Figure 5. This implies that the spectral change is essentially a single

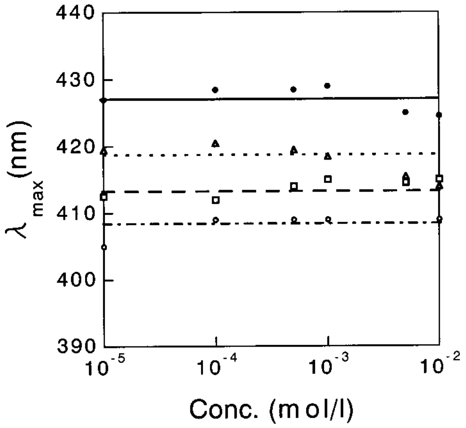

Figure 5. Concentration dependence of λ_{max} of the P3TAA in various solutions: (●) a phosphate buffer solution of pH 7, (○) DMSO, (△) DMSO containing 25% formamide, (□) DMSO containing 25% water.

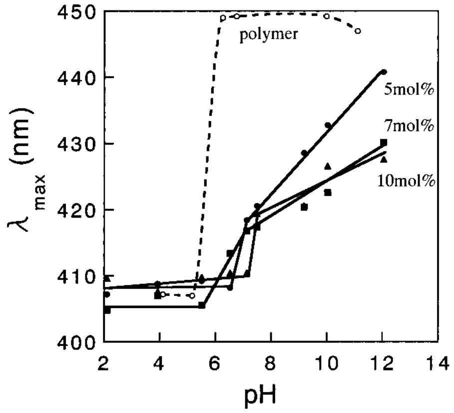

Figure 6. pH dependence of the λ_{max} of the P3TAA gels with different DCL and its linear polymer (○). DCL of gels: (●) 5 mol %, (■) 7 mol %, (▲) 10 mol %. [P3TAA] = 10^{-4} M, [NaCl] = 1.0 M. Temperature = 25 °C.

chain phenomenon. Thus, an abrupt increase in λ_{max} is attributed to an enhanced effective electronic conjugation length of the polymer main chain associated with the conformational change from aggregated state to extended state due to electrostatic repulsion of the ionized carboxylates. To examine such conformational transition of the gel, the spectral changes of P3TAA gels were measured in the various pH ranges. Figure 6 shows the pH dependence of λ_{max} of the P3TAA gels with various DCLs. A red shift of the absorption maximum is observed for every gel when pH increases, and it exhibits some interesting features. First, λ_{max} increases much less than in solution, and with decreasing DCL, the $\Delta\lambda_{max}$ increases. Second, the pH at which λ_{max} abruptly increases shifts from pH 5.2 for the linear polymer to pH $\sim$ 7 for gels, as if the conformational transition of polythiophene network had been locked due to the chemical cross-linkage. Third, as shown in Figure 2, the swelling of the gel (q) is almost complete below pH 6, and no increase in q is observed above pH 7, whereas Figure 6 shows no λ_{max} change below pH 6 but increases above pH 6 up to pH 12. These results suggest that the network changes from an aggregated state in low-pH region to more extended state in the high-pH region with an increased electronic conjugation length. Thus, the increase in λ_{max} of gels could be attributed to a conformational transition from an aggregated nonplanar state to an extended planar state of the polymer network, as in the dissolved polymer, although this conformational transition in the network is partly suppressed due to the cross-linkages.

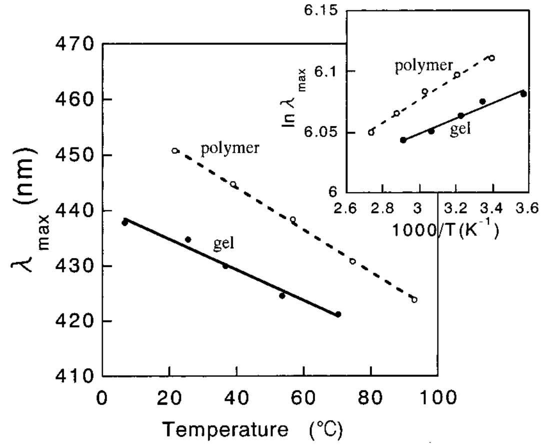

Figure 7. Temperature dependence of the λ_{max} of the P3TAA gel with 5 mol % DCL in pH 12 solution (●) and its linear polymer in pH = 11 (○). Inset is the Arrhenius plot of the λ_{max}.

Figure 7 shows the temperature dependence of the λ_{max} for the dissolved and the cross-linked (DCL = 5 mol %) P3TAA equilibrated at pH 12. In both cases λ_{max} decreases with increasing temperature, suggesting that the rotation of ring-to-ring bonds is thermally enhanced, disrupting the long $\pi-\pi$ conjugation system of coplanar polythiophene rings. The activation energies derived from a plot of ln λ_{max} against $1/T$ (Figure 7, inset) for the gel and the linear polymer solution are 513 and 777 J/mol, respectively. Since these values are associated with the difference in the potential energy ($\Delta\epsilon$) corresponding to the conformational change from nonplanar to planar structure, the smaller activation energy of the gel demonstrates again that the planar state of network of the gel is locked into a less stable structure due to the cross-linkages.

As described in the Experimental Section, the chemical cross-linking of P3TAA was performed in DMSO. To confirm the conformational state of P3TAA in DMSO, the λ_{max} of the polymer was measured in DMSO over a wide concentration range of $10^{-5}-10^{-2}$ mol/L. No concentration dependence of λ_{max} was found as shown in Figure 5. This suggests that the cross-linking reaction was performed in an extended state of P3TAA macromolecules although the extension is smaller than in alkaline solution because of the smaller λ_{max} value.

If the cross-linking reaction of P3TAA is performed under a condition where the conformation of the polymer is characterized by a long electronic conjugation, one can expect this longer electronic conjugation to be retained in the gel. We have found that the DMSO solution of P3TAA shows a significant color change if a small amount of water or formamide is added to it. Figure 8 shows the λ_{max} when water or formamide is added to DMSO solution of P3TAA. One can see that the λ_{max} increases with an increase in formamide or water concentration until the volume ratio formamide/DMSO is 2 or the water/DMSO ratio is 1. The observed spectral change parallels the viscosity change as shown in Figure 8, indicating that the λ_{max} change is due to the conformational change of P3TAA. The concentration dependence of the λ_{max} of P3TAA in DMSO solution containing 25% formamide or water was also measured. As shown in Figure 5, λ_{max} does not depend on the concentration of P3TAA, implying that the macromol-

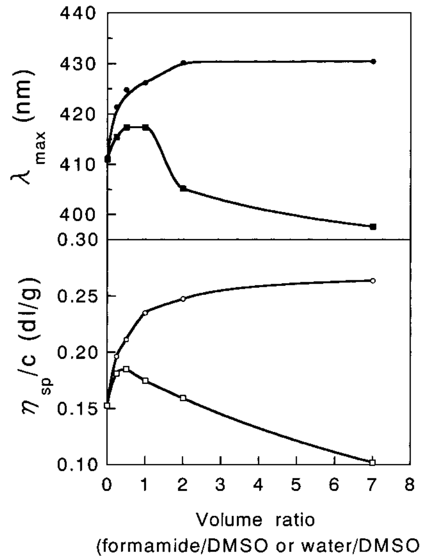

Figure 8. λ_{max} and the reduced viscosity of P3TAA solution as a function of the volume ratio formamide/DMSO (●, ○) and water/DMSO (■, □). Polymer concentrations are 10^{-4} and 10^{-2} M for λ_{max} measurement and viscosity measurement, respectively. Temperature = 25 °C.

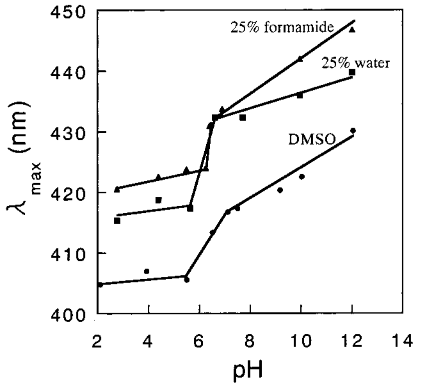

Figure 9. pH dependence of the λ_{max} of the P3TAA gels cross-linked in different solvents: (▲) in DMSO containing 25% formamide, (■) in DMSO containing 25% water, (●) in DMSO. The DCL of gels is 7 mol %. [NaCl] = 1.0 M. Temperature = 25 °C.

Table 1. λ_{max} (nm) of P3TAA Gels Prepared in Different Solvents

DCL (mol %)	DMSO	DMSO containing 25% water	DMSO containing 25% formamide
5	407	412	420
7	404	410	418
10	404		409

ecules of P3TAA are in the extended state in these mixed solvents.

On the basis of these results, the cross-linking reaction was carried out in DMSO containing 25% water or formamide. As summarized in Table 1, the gels prepared in these mixed solvents exhibit a higher λ_{max} compared with those prepared in DMSO, suggesting that P3TAA in these gels has a longer conjugated structure. These gels were immersed in various pH solutions, and changes in λ_{max} were measured at 25 °C. As shown in Figure 9, the gels prepared in the mixed solvents exhibit a higher λ_{max} than those prepared in DMSO at any pH, confirming that the increased electronic conjugation structure of P3TAA chains was retained during the chemical cross-linking. The λ_{max} of the gels prepared in the mixed solvents undergoes a conformational transition more sharply than those prepared in DMSO at around pH 6. We have no explanation why the mixed solvent increases the λ_{max}, but we assume that the increased dielectric constant (ϵ) due to addition of water (ϵ = 80.36) or formamide (ϵ = 109.5) increased the dissociation of carboxylic groups.

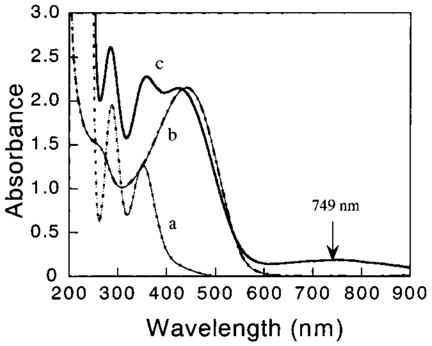

Figure 10. Electronic spectra of (a) 0.2 M KI solution containing 2 × 10^{-3} wt % I_2, (b) 5 × 10^{-4} M P3TAA in a phosphate buffer (pH = 7), and (c) P3TAA solution after I_2 doping. Temperature = 25 °C.

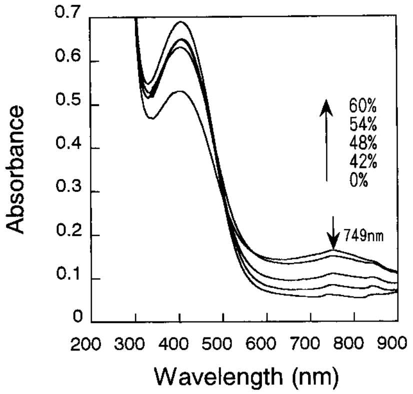

Figure 11. Electronic spectra of P3TAA gel (DCL = 7 mol %) after doping with $HClO_4$ solutions of various concentrations.

Doping of P3TAA Gel in Water. Doping of π-conjugated polymers is a common method to increase their conductivity. Doping is commonly performed from the vapor state or in organic solvents[9-11] and has rarely been studied in an aqueous solution.[12] We attempted the I_2-doping of P3TAA polymer and gel in phosphate buffer solution containing 0.2 M KI at pH = 7.0 under an argon atmosphere. No peak characteristic of the I_2 doping was observed for the gel, while the P3TAA solution changed from yellow to black, suggesting the presence of free carriers in the conducting state. A very broad peak around 749 nm was observed as shown in Figure 10. The absorption intensity at 749 nm increases up to 10^{-3} wt % I_2 and remains almost constant at higher I_2 concentrations.

We tried to dope a P3TAA solution by $HClO_4$. The solution turned black (oxidized state), and the polymer precipitates on addition of 60 wt % $HClO_4$ solution. When a P3TAA gel was immersed in a 60 wt % $HClO_4$ solution, the gel also turned black and shrank to some extent. The absorption spectrum measured under an argon atmosphere showed a new and broad peak with λ_{max} around 749 nm besides the absorption around 405 nm (Figure 11). The intensity of the broad peak increased remarkably with the $HClO_4$ concentration higher than 40 wt %. This might be the first successful doping of a water-swollen gel using $HClO_4$.

Table 2. Electrical Conductivity of the P3TAA Gel

P3TAA gel	water-swollen state	dry state
undoped (S/cm)	$(4.0-7.0) \times 10^{-4}$	7.0×10^{-8}
doped (S/cm)[a]	$4.0 \times 10^{-3}-2.0 \times 10^{-2}$	$3.0 \times 10^{-4}-1.0 \times 10^{-3}$

[a] Dopant: 60 wt % $HClO_4$ solution.

The electrical conductivities of P3TAA gels measured by the ac two-terminal method at 20 °C are shown in Table 2. The undoped water-swollen gel has an electrical conductivity of 7×10^{-4} S cm^{-1}, much higher than that in the dry state (7×10^{-8} S cm^{-1}). This is obviously due to ionic conduction. Interestingly, a swollen sample doped with $HClO_4$ showed the highest conductivity of 10^{-2} S cm^{-1}. The electrical conductivity of the doped and water-swollen P3TAA gels is lower than the 10^{-1} S cm^{-1} of electropolymerized poly(3-alkylthiophene)s doped by perchlorate counterions,[13,14] but the results demonstrate that the water-swollen ionizable P3TAA gel has a satisfactorily large conductivity on doping.

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