Macromolecules
COMMUNICATION TO THE EDITOR

DOI: 10.1021/ma902453e

Redox-Induced Reversible Conformational Switching of Poly(aniline sulfonic acid) with Transition Metals in Aqueous Solution

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Received November 6, 2009
Revised Manuscript Received December 23, 2009

Introduction. Structural control of conductive polymers has drawn much attention due to their potential applications in materials chemistry and electrochemistry.[1] Polyanilines (PANIs, Figure 1a) are widely regarded as one of outstanding conductive polymers because of their availability and practical applicability.[2] Structure and/or conformation of PANIs strongly influence the properties. Some researches have been carried out to control the structures of PANIs via supramolecular interaction, such as rotaxane formation,[3] DNA and biomolecule directed assembly,[4] and complexation with metal ions.[5] The conductivity strongly depends on the polymer main-chain conformation of the emeraldine salt (ES)PANI when it is doped with acid.[2] The extended coil conformation of the polymer chain of (ES)PANI shows large conductivity although the compact coil conformation does not.[6] Furthermore, not only conductivity but also various studies concerning on the polymer main-chain conformations have been carried out since MacDiarmid and Epstein reported the conformational change during the secondary doping process in 1994.[7] Poly(aniline sulfonic acid) (PAS) was designed to allow self-doping to show high conductivity without an external dopant.[8] Another advantage of PAS is high solubility in water. Conformational change of PAS has been reported by Kane-Maguire, Wallace, and co-workers using poly(2-methoxyaniline-5-sulfonic acid)[9] (PMAS, Figure 1b),[10] where their results suggest that the conformational change is likely to be induced by the countercation of the sulfonate moiety[10a,b] and/or the redox of the polymer chain.[10c] In this context, we expected that use of "transition metals" can induce and control the conformational change (Figure 1b). On the other hand, to the best of our knowledge, there is no report for the conformational switching of not only (ES)PMAS but also (ES)PANIs despite a lot of reports for the conformational change. Development of the method for the reversible conformational switching remains a worthwhile goal for the dynamic controllable conductive polymers.

So far, we have investigated the construction of the multiredox systems based on d,π-conjugation of PANIs with various metal ions (i.e., Pd^{II}, Cu^{II}, and V^{III})[5,11−13] or metal nanoparticles.[14] The present study was conducted to investigate the interaction between (ES)PMAS and various transition metals in order to control the conformational change of (ES)PMAS, and we report here some novel and valuable findings on (1) the redox-induced conformational change, (2) the remarkable sensitivity to Cu^{II} compared to other transition metal salts, where 0.01 equiv of Cu^{II} (0.06 ppm) could induce the structural arrangement from the extended coil to the compact coil, (3) the reverse conformational change between the compact coil and the extended coil by metal capture and addition of a reductant under air, and (4) the several time conformational switching (Figure 1c).

Results and Discussion. (ES)PMAS was deionized through cation-exchange resins before use. The redox interaction was mainly studied by UV−vis−NIR spectrometry in pH 8.8. The conformation was determined by the corresponding diagnostic peak to each conformation. The sharp peak around 475 nm attributed to the polaron band was characteristic to the extended coil conformation.[10a] On the other hand, the broad peak around 750 nm attributed to the localized polaron band was characteristic to the compact coil conformation.[10a] One equiv of various transition metals ($FeSO_4$, $Co(OAc)_2$, $Ni(OAc)_2$, $Cu(OAc)_2$, $Zn(acac)_2$, $RuCl_3$, $PdCl_2$, $AgNO_3$, $SnCl_2$, $PtCl_2$, and $HgCl_2$) based on the aniline monomer unit was added to the stirred aqueous solution of (ES)PMAS with the extended coil conformation (1.0×10^{-4} M based on the aniline monomer unit) at room temperature under air. The reaction was followed by UV−vis−NIR spectrometry. Increase of the peak at 750 nm for the compact coil conformation was observed in the case of $Cu(OAc)_2$, $RuCl_3$, $AgNO_3$, and $HgCl_2$, where the color of the solution changed from yellow/green to blue. On the other hand, such conformational change to the compact conformation was not observed in the case of $FeSO_4$, $Co(OAc)_2$, $Ni(OAc)_2$, $Zn(acac)_2$, $PdCl_2$, $SnCl_2$, and $PtCl_2$.

Further study was carried out in the case of $Cu(OAc)_2$, which induced the most remarkable change. Figure 2 shows the spectral change of (ES)PMAS in pH 8.8 buffer solution with 1 equiv of $Cu(OAc)_2$ under air at 25 °C. In the spectra, the polaron band at 471 nm decreased gradually, and completely disappeared after 2 h. Concomitantly a broad peak around 650 nm appeared and grew gradually with red-shifting. The color changed from yellow/green to green within 1 min, then blue within 10 min. After stirring for 24 h, a weak, broad shoulder appeared at 540 nm, probably consistent with the oxidation to the pernigraniline state.[10c] Next, the dynamic behavior was followed with changing the amount of $Cu(OAc)_2$ from 3 to 0.005 equiv based on the aniline monomer unit. The spectra are shown in Figure S1. A catalytic amount of $Cu(OAc)_2$ was found to be enough to generate the conformational change from the extended coil to the compact one. Surprisingly, only 0.01 equiv of $Cu(OAc)_2$, which corresponded to 1 μM (0.06 ppm) under these conditions, were able to induce the conformational change to a certain extent after 24 h.

Using 1 μM of various transition metal salts (Figure 3, parts a−r), the conformational change in PMAS was investigated for comparison. As shown in Figure 3, $Cu(OAc)_2$ remarkably changed the color from yellow to green based on the conformational change in pH 8.8 buffer solution under air at 25 °C after 18 h although almost no or little change was observed in the case of other transition metal salts.

To investigate the mechanism, the reaction was carried out under argon. The conformational change proceeded very slowly, and at least 0.1 equiv of $Cu(OAc)_2$ were needed (based on the aniline monomer unit). These results suggest that the reoxidation of Cu^{I} with O_2 is involved for the conformational change. The partial scission of π-conjugation of

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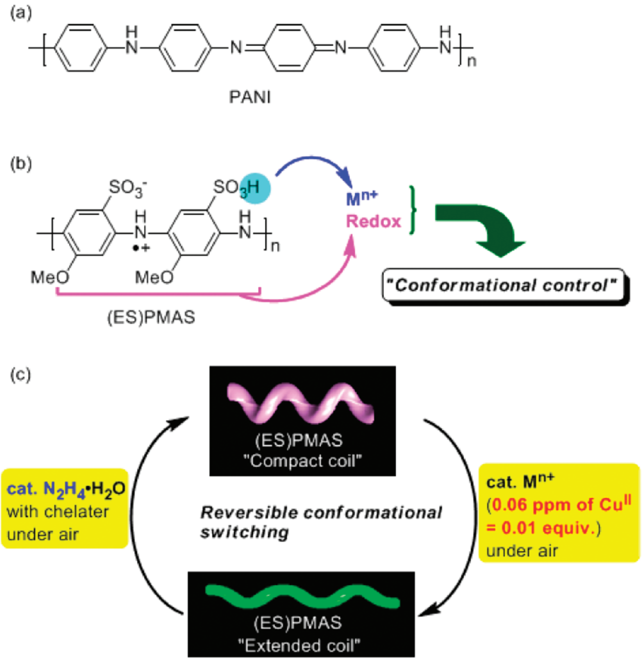


Figure 1. Structures of (a) PANI and (b) (ES)PMAS. (c) Schematic representation of the reversible conformational switching.

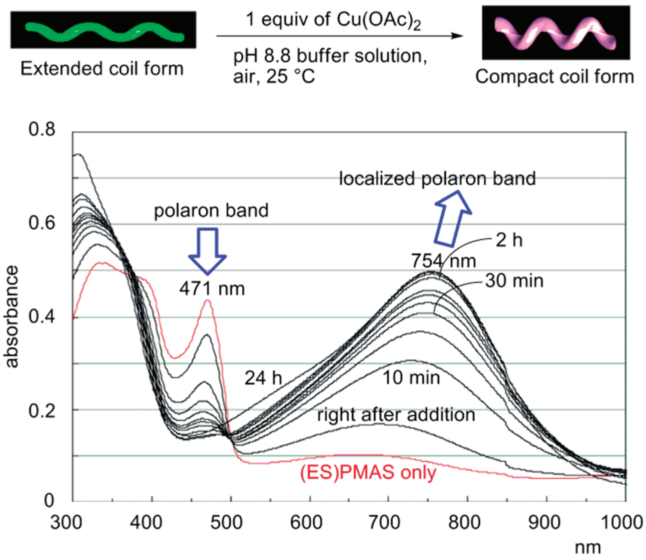


Figure 2. Time-dependent UV−vis−NIR spectra of (ES)PMAS in pH 8.8 buffer solution with 1 equiv of $Cu(OAc)_2$ under air at 25 °C (1.0×10^{-4} M based on the aniline monomer unit; 0, 10, 20, 30, 40, and 50 min and 1, 2, 3, 4, and 24 h).

the main chain due to partial oxidation by Cu^{II} is likely to bring the conformational change from the extended coil to the compact one. To confirm such a mechanism, a catalytic amount of $KMnO_4$ was used as a strong oxidant for this experiment. The conformational change occurred as expected (Figure S2).

These results imply that the partial reduction could induce the reverse conformational change. Immediately after the addition of a reductant, $N_2H_4 \cdot H_2O$ (1 equiv), to the solution of the (ES)PMAS compact coil form, the (ES)PMAS extended coil form was observed, together with the reduced leucoemeraldine form. Then, the reduced form increased with decrease of the (ES)PMAS extended coil form. After 10 min, in turn, the compact coil appeared again due to the

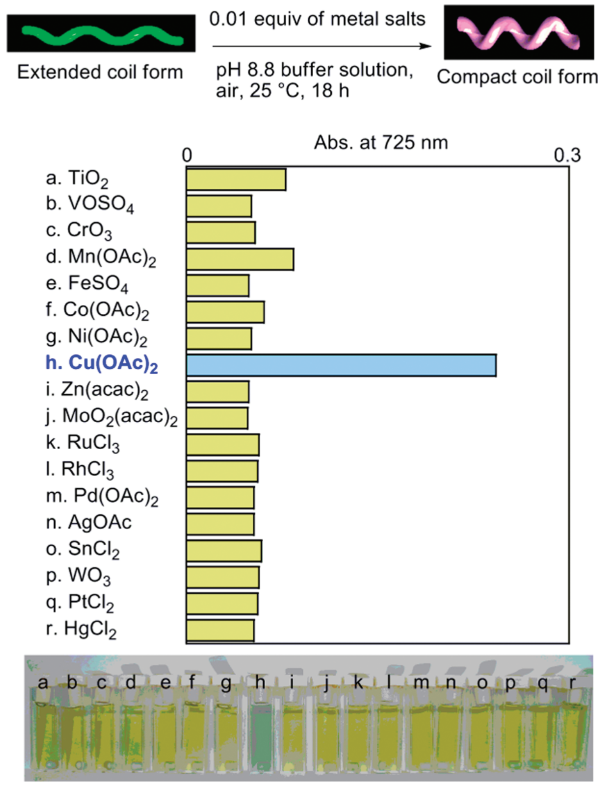
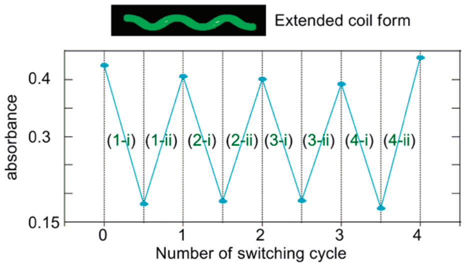
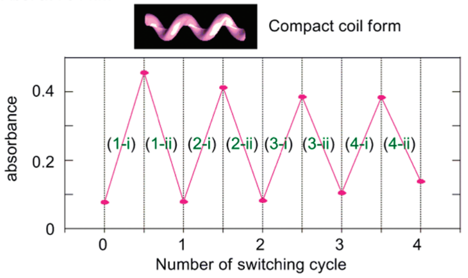


Figure 3. Optical density at 725 nm in the absorption spectra of (ES)PMAS in the presence of various metal salts (a−r) in pH 8.8 buffer solution under air at 25 °C after 18 h, and the picture of the corresponding solution in the cells.


(a) Abs. at 471 nm


(b) Abs. at 754 nm

cycle		equiv of the additives			reaction time (h)
		$Cu(OAc)_2$	EDTA	$N_2H_4 \cdot H_2O$	
1st	1-i	0.05	-	-	4
	1-ii	-	0.1	0.03	2
2nd	2-i	0.25	-	-	1
	2-ii	-	0.5	0.03	1
3rd	3-i	1.25	-	-	1
	3-ii	-	2.5	0.03	1
4th	4-i	5	-	-	1
	4-ii	-	10	0.03	2

Figure 4. Conformational switching of (ES)PMAS. Optical density at (a) 471 nm for the extended coil form and (b) 754 nm for the compact coil form in the absorption spectra under air, and equiv of the additives and reaction time.

copper-catalyzed aerobic oxidation (Figure S3). To avoid this, ethylenediaminetetraacetic acid disodium dihydrate (EDTA) was used to capture Cu ion, which was effective for the selective reverse conformational change (the compact coil to the extended one via the leucoemeraldine) (Figure S4).

The conformational switching was then investigated under air. Figure 4 shows the optical density at (a) 471 nm for the extended coil form and (b) 754 nm for the compact coil form in the absorption spectra. In the first cycle, the extended coil conformation was transformed to the compact one in the presence of 0.05 equiv of $Cu(OAc)_2$ (1-i), followed by the addition of 0.1 equiv of EDTA with 0.03 equiv of $N_2H_4 \cdot H_2O$ to get back to the extended coil conformation again (1-ii). A similar operation resulted in the second cycle, where higher concentrations of $Cu(OAc)_2$ and EDTA were used (0.25 and 0.5 equiv, respectively) (2-i and 2-ii). Finally, four cycles of the conformational switching were performed.

Conclusions. In conclusion, conformational change from "extended coil" to "compact coil" was induced by the addition of $Cu(OAc)_2$ to the aqueous (ES)PMAS solution. It should be noted that the addition of a small amount of $Cu(OAc)_2$ (up to 0.06 ppm) was able to induce such conformational change, which is substantially superior to other transition metals. This can be applied to a colorimetric transition metal sensor for water contamination. Reverse conformational change was also accomplished by the treatment of (ES)PMAS with EDTA and $N_2H_4 \cdot H_2O$ under air. This conformational switching was repeated several times. Present results provide a novel approach for dynamic functional materials.

Acknowledgment. D.S. expresses his special thanks to the Global Center of Excellence (GCOE) program "Global Education and Research Center for Bio-Environmental Chemistry" of Osaka University. This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas "Chemistry of Concerto Catalysis" from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. This work was also financially supported in part by Mitsubishi Rayon Co.

Supporting Information Available: Text giving the experimental procedure and figures showing UV−vis−NIR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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