PAPER

Reversible isomerization of a zwitterionic polysquaraine induced by a metal surface

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The variation of visible and IR absorption spectra and of small-angle X-ray scattering of poly(3-octylpyrrole)squaraine in trichloromethane solution indicates that, for this zwitterionic conducting polymer (CP), a reversible change of conformation is induced by contact of the solution with the surface of an active metal. The structure of the target polymer might switch from being linear to being folded. For a copper surface, the activation energy of isomerization between the two forms, whatever their nature, is 18.9 ± 0.7 kJ mol^{-1}, whereas for the reverse process the activation energy is 38 ± 6 kJ mol^{-1}. In a folding transformation, formation of intramolecular hydrogen bonds might play a key role. This observation of a reversible conformation for a zwitterionic polymer induced by a metallic surface provides an impetus to investigate both such a structural modification of other CP and applications of this phenomenon.

Introduction

Polymers with extended π-electron conjugation that have unique intrinsic conductivity are classified as conjugated polymers or conducting polymers (CP)s;[1–3] these compounds exhibit novel electrical, optical and magnetic phenomena that can lead to optoelectronic,[4–7] solar cell,[8–10] sensor[11–13] and biomedical applications.[14–16] The polymeric nature of a CP enables great structural flexibility; CPs thus attract attention and remain at the forefront of many areas of development. One of the most significant interests in developing a CP is that its optical, physical and electronic properties are affected strongly by a variation in the polymer conformation.[17–20] Development of a CP requires an understanding of its detailed structure and its variation under various manipulations. This topic has hence become a focus of research from both scientific and practical points of view.

Polysquaraines are π-conjugated polymers based on organic squaraine dyes in various forms;[21] these CPs provide great sensitivity and optimal performance in such applications as communication and biosensors, *etc.*[22–25] To optimize the performance, controlling the conformation is a critical issue for applications based on these materials. Preceding authors have investigated the variation of the structural conformation for squaraine-based materials through external stimuli by solvent concentration,[26–28] solvent polarity,[26,29,30] temperature,[26,31] metal ions[32–34] and other conditions.

A condensation of squaric acid with electron-donating aromatic compounds produces squaraines.[35–37] In one such reaction, squaric acid reacts with a pyrrole derivative to form poly(pyrrolyl)squaraines,[38] having either covalent or zwitterionic backbones, so differing in the chain of the polymer. The intrinsic molecular structure of polysquaraine is expected to influence strongly its stability and optoelectronic properties; for instance, as the positive moiety containing an N atom in the zwitterionic polysquaraine can bind to either a H atom or an alkyl group (R), this subtle local variation of molecular structure is likely to affect its chemical and physical properties.

Here we demonstrate that, besides induction by metal ions, the structure of poly(3-octylpyrrole)squaraine having a zwitterionic repeating unit is variable when its solution in trichloromethane makes contact with the surface of an active metal. A possible structural alteration of this CP is thus a reversible isomerization from a linear conformer to a folded one induced by an active metal surface. This observation has no precedent; our findings provide an impetus for further investigation of the structural modification of similar CPs and the structural dynamics of their polymer chains in solution.

Experimental

Preparation

To synthesize, poly(octylpyrrole-*co*-squaric acid), 1-octylpyrrole or 3-octylpyrrole (1.1224 g, 6.26 mmol) and squaric acid (0.714 g, 6.26 mmol) in equimolar proportions were refluxed in a mixture of 1-butanol (60 mL) and benzene (30 mL) under continuously flowing N$_2$ for 24 h.[35,36,39–41] After the obtained solutions were filtered, the filtrates were concentrated through vacuum

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distillation and poured into diethyl ether. The crude products were collected on filtration and washed with diethyl ether, before being redissolved in trichloromethane to yield solutions that were filtered again; the filtrates were evaporated to dryness in an open fume cupboard to eliminate HCCl₃. The precipitates were finally washed again with diethyl ether and dried in a vacuum chamber near 295 K for two days. According to our syntheses, the end products poly(1-octylpyrrole-*co*-squaric acid) and poly(3-octyl-pyrrole-*co*-squaric acid) are named poly(1-octylpyrrolyl)squaraine, denoted **P1**, and poly(3-octylpyrrolyl)squaraine, denoted **P2**, respectively.

Characterization

P1 and **P2** were characterized by elemental analysis, thermogravimetric analysis, gel-permeation chromatography, and ¹H NMR, ¹³C NMR, UV/visible absorption, infrared absorption and photoluminescence spectroscopy. By these means, we deduced that product **P1** from reagent 1-octylpyrrole possesses a backbone ratio of 1 : 2 of covalent repeating units to zwitterionic ones, whereas polymer **P2** from reagent 3-octylpyrrole was produced with mostly zwitterionic repeating units (>97%). The detailed characterization of **P1** and **P2** can be found in a previous report.[39] The molecular masses according to M_n are 23 kDa for **P1** and 21 kDa for **P2**, and according to M_w are 45 kDa for **P1** and 38 kDa for **P2**.

Measurements

Visible absorption spectra were recorded with a UV-visible spectrophotometer (Ocean Optics). IR absorption spectra were recorded with an interferometric spectrometer (Nicolet Magna 860 FTIR) attached to the IR beamline at National Synchrotron Radiation Research Center (NSRRC); a HgCdTe detector rendered the mid IR range 500–4000 cm⁻¹ or a DTGS detector for 400–4000 cm⁻¹. Small-angle X-ray scattering (SAXS) curves were recorded with the 15 keV beam (*ca.* 0.2 × 0.2 mm) from beam line 23A at NSRRC;[42] the target polymers were dissolved in trichloromethane then injected into a stainless-steel or copper cell (diameter 5 mm, thickness 2.2 mm) with Kapton windows for incident X-rays. The resistance of the polymer solution was measured by the AC impedance method using electrochemical workstations (PARATAT 2263).

Materials

Reagents 1-octylpyrrole (97.3%), 3-octylpyrrole (99.5%) and squaric acid (99.0%) (all from T.C.I.), copper perchlorate hexahydrate (98%) (Acros), solvents 1-butanol (99.9%), diethyl ether (99%), benzene (99.8%), and trichloromethane (99.4%) (all from Merck) were obtained from the indicated suppliers. Plates of iron (0.1 mm, 99.994%), aluminium (0.25 mm, 99.997%), silver (0.1 mm, 99.998%), cobalt (0.1 mm, 99.995%), nickel (0.5 mm, 99.994%), tin (1.0 mm, 99.9985%), lead (1.0 mm, 99.9995%), zinc (2.0 mm, 99.999%), gold (0.1 mm, 99.9975%), rhenium (0.025 mm, 99.97%), tantalum (0.127 mm, 99.95%) and molybdenum (0.5 mm, 99.0+ %) (all from Alfa Aesar), and of copper (0.5 mm, 99.98%), rhodium (0.025 mm, 99.9%), tungsten (0.127 mm, 99.9+ %), platinum (0.127 mm, 99.99%) and palladium (0.25 mm,

99.98%) (all from Sigma-Aldrich), were obtained from the indicated suppliers.

Results and discussion

The target polysquaraines were synthesized from squaric acid with 1-octylpyrrole and 3-octylpyrrole under condensation conditions.[39] The general condensations of squaric acid with 1-octylpyrrole and 3-octylpyrrole are expressed in Scheme 1.

The end products of poly(pyrrolyl)squaraines for poly-(1-octylpyrrole-*co*-squaric acid) and poly(3-octylpyrrole-*co*-squaric acid) are denoted with formulae **I** and **II**, respectively.

Polysquaraines are described as having π-conjugated structures that typically possess intense absorption in the visible range. Fig. 1 displays the visible spectra of poly(1-pyrrolyl)squaraines in trichloromethane; poly(1-octylpyrrolyl)squaraine (**P1**) and poly(3-octylpyrrolyl)squaraine (**P2**) exhibit distinct features in their visible spectra. The visible absorption of zwitterionic **P2** in trichloromethane exhibited a single and narrow absorption band centred at 543.6 nm, producing a magenta color in solution, whereas **P1** has a line with a maximum absorption at 547.9 nm and a broad shoulder near 600 nm, appearing navy blue in solution. As reported previously,[39] because **P2** as synthesized possesses mostly zwitterionic repeating units in its structure, the backbones tend to be identical, resulting in only one narrow band within its visible absorption, whereas **P1** contains backbones of two types in its polymer chain, resulting in a more complicated absorption spectrum. Through comparison with the narrow absorption for zwitterionic **P2**, we deduce the corresponding narrow band of **P1** to imply its zwitterionic moiety; the shoulder is due to its covalent part.

The strengths and shapes of the visible absorption features of **P1** and **P2** in a silica cell remained constant for over seven days; these polymers hence appear to be stable in trichloromethane solution. With a polymer solution as a blank for comparison, we inserted metal plates or gauzes into the silica cells and monitored the visible absorption of the polymer solutions as a function of time. For polymer **P1** in the silica cell, the strength and shape of the absorption spectra remained constant regardless of the metal inserted in the solution; we conclude that the solution of polymer **P1** is insensitive to contact with metals.

When metal plates were inserted into solutions of polymer **P2**, the absorption spectra of solutions varied depending on the metal. For metals Al, Co, Ni, Mo, Pd, Sn, Ta, W, Re, Au and
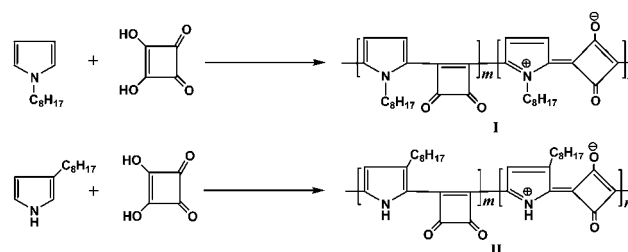
Scheme 1 In the general condensation of squaric acid with 1-octylpyrrole and 3-octylpyrrole, the product poly(pyrrolyl)squaraines containing *m* repeating units of a covalent backbone and *n* repeating units of a zwitterionic backbone are represented with formulae **I** and **II**, respectively.
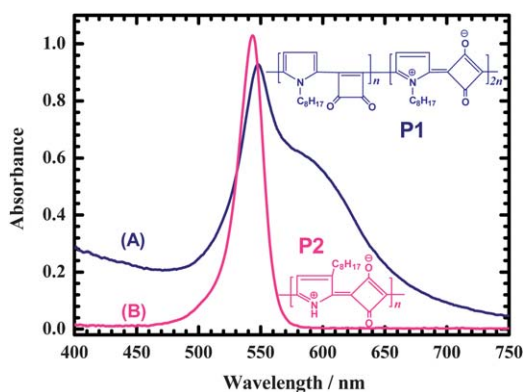
Fig. 1 Visible absorption spectra of poly(pyrrolyl)squaraines in trichloromethane solution (concentration 3.5 mg L^{-1}) and a silica cell (length 1 cm of optical path) at 295 K: (A) poly(1-octylpyrrolyl)squaraine (**P1**); (B) poly(3-octylpyrrolyl)squaraine (**P2**). The insets show the molecular structures of **P1** and **P2**; **P1** consists of repeating units of covalent and zwitterionic structural backbone in a 1 : 2 ratio, whereas **P2** possesses mostly zwitterionic repeating units (>97%).

stainless steel, we observed no change in the visible absorption spectra for solutions of polymer **P2**. These results thus resembled those for polymer **P1**; zwitterionic polysquaraine **P2** in trichloromethane is hence unaffected on contact with those metals. In contrast, when metal plates of Ag, Cu, Fe, Zn, Rh, Pt and Pb were inserted into solutions of polymer **P2** in trichloromethane, the visible absorption spectra of the solutions altered markedly. Polymer **P2** in trichloromethane solution is hence unstable to contact with those metals, but the rates and extents of the alterations of the visible absorption of the solution varied, depending on the particular metal used. For metals Ag, Zn, Pt and Pb, the visible spectra altered slightly over a protracted period. For the solution of polymer **P2** at 295 K in contact with a Rh plate (surface area 372 mm^2) in a silica cell, the absorption altered more markedly, as shown in Fig. 2; the stature of the line at 543.6 nm decreased by about 15% after 77 h and the intensity near 500 nm increased discernibly.
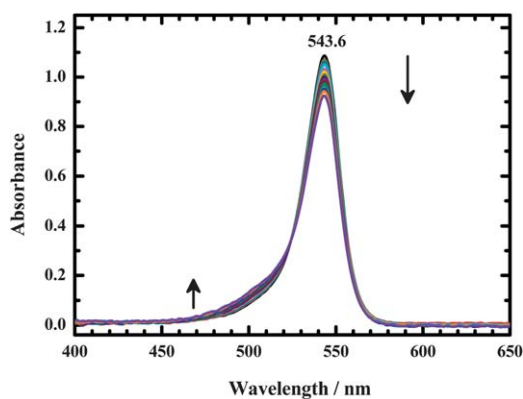
When we inserted a Cu or Fe plate into a solution of poly-(3-octylpyrrole)squaraine, the visible absorption spectra of these polymer solutions altered profoundly. Fig. 3 illustrates the temporal variation of the visible absorption spectra when using a Cu plate (surface area 382 mm^2) at 295 K; over 40 h the original spectral feature with a maximum absorption at 543.6 nm gradually decreased, and became replaced with another broad feature with a maximum at 513.8 nm. All spectra retained an isosbestic point at 525.8 nm. The inset photograph in Fig. 3 displays the distinct color change from pale magenta before insertion of the copper plate to pale orange afterwards.

For these active metals, the relative rates of variation of the spectra of poly(3-octylpyrrole)squaraine solution are derived from the decrease of absorbance at 543.6 nm during the same periods. The corresponding rates relative to that for copper are listed in Table 1. Among these active metals, copper is the most active, and iron the second most: the rate for iron is about 0.37 times that for copper. Relative to the rate for copper, the rates for other metals are Rh 0.21, Ag 0.09, Pt 0.08, Zn 0.06, and Pb 0.03. Although copper and iron are metals commonly used in electronic devices, nobody expects that these two metals would cause a color change of this kind for a CP.

The rates of decreasing intensity at 543.6 nm and increasing intensity at 513.8 nm for **P2** polymer solutions depend on the area of the metal surface, with rates increasing with increasing area. For copper plates with surface areas 860, 1720 and 1960 mm^2, the color changes were completed in 11, 6 and 4 h, respectively. Fig. 4 depicts the decrease of absorbance at 543.6 nm in 1 h *vs.* the area of the copper surface at 295 K: the relation is linear. The rate of color modification for this zwitterionic polysquaraine **P2** induced by a copper surface thus increases with its increasing area.

Fig. 3 demonstrates the existence of an isosbestic point in the temporal variation of the absorption spectra of the solution of polymer **P2** into which was inserted a copper plate. This effect implies that two species are present in the varying system; one species is characterized with its absorption at 543.6 nm and the
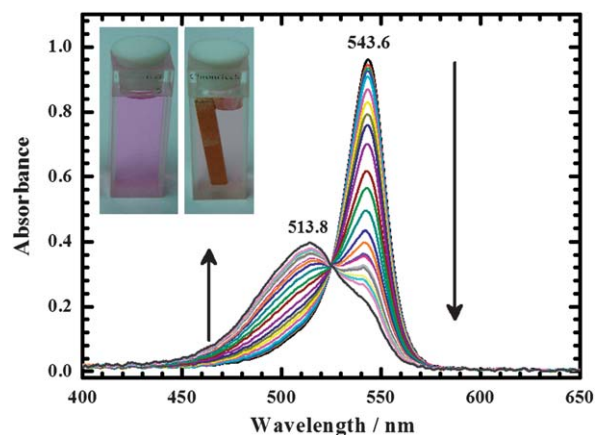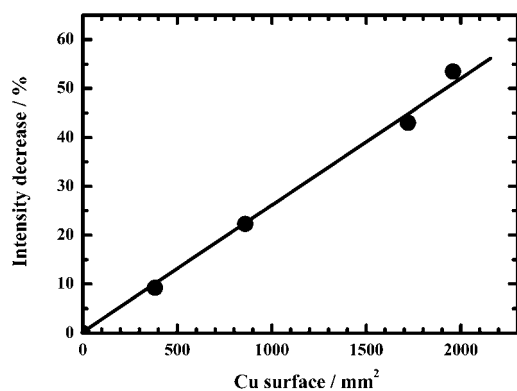

Fig. 2 Temporal variation over 77 h of visible absorption spectra of poly(3-octylpyrrole)squaraine (3.5 mg L^{-1}) in trichloromethane solution (3.0 mL) in a silica cell (optical path 1 cm) into which was inserted a Rh plate (surface area 372 mm^2) at 295 K.

Fig. 3 Temporal variation over 40 h of absorption spectra of poly-(3-octylpyrrole)squaraine (3.5 mg L^{-1}) in trichloromethane solution (3.0 mL) in a silica cell (optical path 1 cm) into which a copper plate was inserted (surface area 382 mm^2). Inset photograph: visible color change of poly(3-octylpyrrole)squaraine in trichloromethane solution: (left side) no metal plate, (right side) after 40 h with a Cu plate.

Table 1 Relative rates of isomerization caused by the active metals based on the decrease of absorption at 543.6 nm during 1 h

Metal	Area/mm^2	Decrease (%)	Relative rate[a]
Cu	860	22.3	1
Fe	593.2	5.66	0.37
Rh	371.6	2.05	0.21
Ag	907	2.0	0.09
Pt	545.7	1.1	0.08
Zn	430.6	0.57	0.06
Pb	381	0.3	0.03

[a] Relative rate is derived from the decrease of absorption and normalized with surface area.

Fig. 5 Absorbance decrease at 543.6 nm in 0.5 h *vs.* temperature; copper plates (surface area 1720 mm^2) were inserted into trichloromethane solutions of poly(3-octylpyrrole)squaraine.

Fig. 4 For poly(3-octylpyrrole)squaraine in trichloromethane solution, the decrease of absorbance at 543.6 nm in 1 h *vs.* area of copper surface at 295 K.

other at 513.8 nm. As no obvious driving force is present to induce a chemical reaction in this system, and consistent with the reversibility of transformation, two distinct chemical species are unlikely to exist there. An alternative possibility is that the same chemical species exists in two structures, or isomers, in that solution; in that case the color change would reflect a conformational isomerization of this polysquaraine induced by a copper surface.

For an active metal in contact with the polymer solution, the rate of decreasing absorbance at 543.6 nm and increasing absorbance at 513.8 nm depended also on the temperature, with the rate increasing with increasing temperature. Fig. 5 depicts how the absorbance decreased at 543.6 nm for 0.5 h *vs.* temperature after copper plates (surface area 1720 mm^2) were inserted into solutions of **P2**. The plot of ln k *vs.* T^{-1} in range 283–323 K is linear, consistent with a barrier of activation for the process accompanying the absorption line shifting from 543.6 nm to 513.8 nm. The activation energy, denoted E_a and derived from the Arrhenius equation, ln $k = $ ln $A - E_a/RT$ (R = gas constant) for the assumed isomerization of polymer **P2** in trichloromethane solution induced by copper is thus 18.9 ± 0.7 kJ mol^{-1}.

A notable feature of the transformation of visible absorption of this zwitterionic polymer with metals is its reversibility. After the absorption at 543.6 nm became replaced with the feature at 513.8 nm induced by the metals, the reverse shift from 513.8 nm to 543.6 nm occurred on removal of the metals from the solution. Fig. 6 shows this phenomenon; on removal of the copper plates
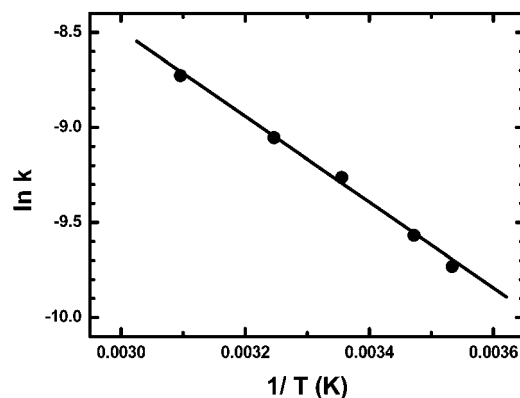
from the solution after insertion for 11 h, the absorption at 513.8 nm of the polymer solution with the Cu plates became replaced with the band at 543.6 nm. The temporal variation of these spectra preserves the same isosbestic point at 525.8 nm. This reversibility of absorption behavior implies that the polymer, without the metal in contact with its solution, reverted to its original conformation.

The rate of the reverse transformation of **P2** on removal of a metal from the solution depends also on temperature, with the rate increasing with increasing temperature. The completion of the reverse transformation required 24 h at 323 K but more than 102 h at 295 K. Fig. 7 depicts the dependence of absorbance at 513.8 nm for 1 h on temperature after the inserted copper plates were removed from the **P2** solutions. The linear relationship in terms of ln k *vs.* T^{-1} in the range 303–328 K implies an activation energy of 38 ± 6 kJ mol^{-1} of the reverse isomerization.

This observation of a reversible optical effect of the zwitterionic polysquaraine induced by the metal plates is unprecedented. How can one explain this phenomenon for a carrier induced only by its solution in contact with a metal surface? To account for this phenomenon accompanying a structural isomerization, we propose the transformation for the zwitterionic
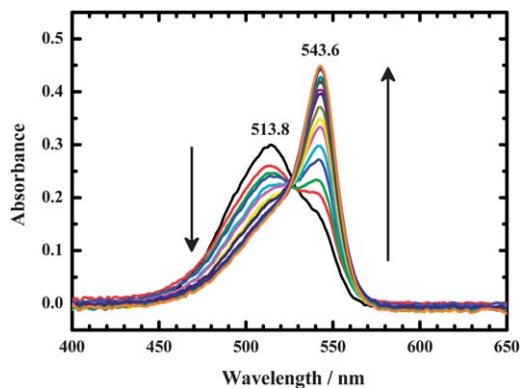
Fig. 6 Temporal variation of absorption spectra of poly(3-octylpyrrole)squaraine in trichloromethane at 323 K after removal of the copper plate following its insertion for 11 h: scans were made at hourly intervals from 0 to 12 h, then at 15, 19 and 22 h.
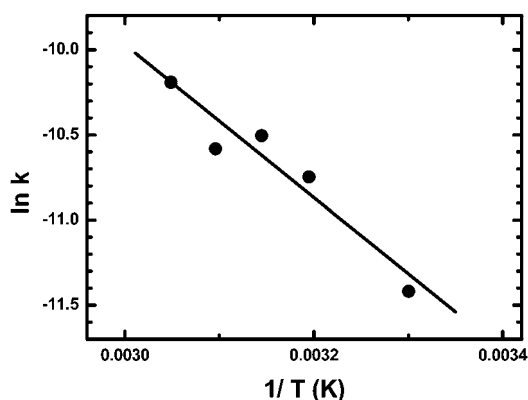
Fig. 7 Absorbance decrease at 513.8 nm in 1 h *vs.* temperature after removal of inserted copper plates from **P2** solutions.

polymer in solution to occur in three sequential steps: diffusion to and adsorption on a metal surface, folding of the structure, and desorption and diffusion from the metal, as schematically displayed in Fig. 8.

According to this mechanism, the backbone structure of this free zwitterionic polymer in solution is originally present in a linear form. When a metal plate is inserted into the solution, the polymer molecule diffuses to the metal surface and becomes adsorbed, process (a). As the zwitterionic moieties of the polymer affix to the metal surface, the molecule becomes strongly anchored on the surface through the interaction of its charged regions with the metal. Although anchored on the metal surface at some points, other portions of the polymer chain are free to move in the solution and to swing back and forth in motion until the polymer folds, process (b). This closure decreases the force of the anchor attachment to the metal surface; as a result, the folded polymer desorbs from the metal surface, process (c). The folded polymer retains its modified conformation in solution and thus exhibits its altered optical property on removal of the metal plate. In absence of the interaction with a metal surface, the free folded polymer eventually acquires energy on collisions and reverses its closure by becoming linear again.
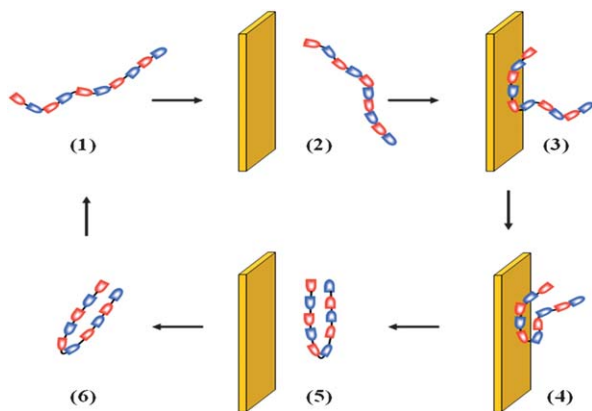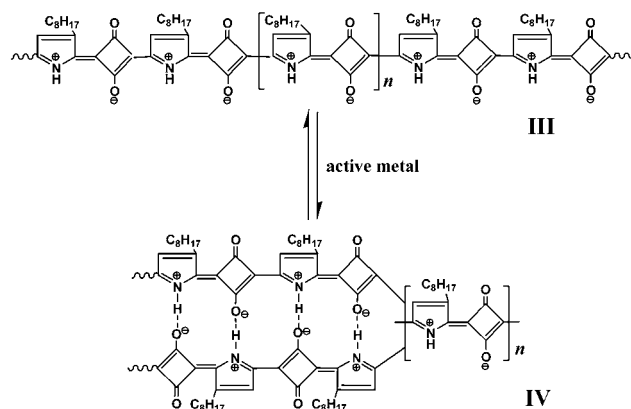
Although not definitive, this mechanism of isomerization explains the observation of the optical reversible phenomena for the zwitterionic polysquaraine on interaction with a metal. From a thermodynamic point of view, the free zwitterionic polymer in solution tends to maximize its entropy and thus exists in an almost linear form.[31,43–45] When the zwitterionic polymer makes contact with the surface of the active metal, the zwitterionic moiety attaches to the metallic surface to resemble becoming anchored on the metal surface. If the adsorption on the metallic surface occurs in this step, the rate of transformation should depend on the extent of the metal surface. Fig. 4 shows that the rate of transformation for **P2** induced by copper is proportional to the area of the copper surface; also, the fitting line of the relationship intercepts at the point of the origin. That the structural modification of the polymer is directly associated with the area of the metal surface supports adsorption as the first step.

The adsorbed polymer might desorb from the surface from random movements or collisions and maintain its linear conformation in solution, but, while the zwitterionic polymer is anchored at one end on the metal surface, the other terminus of the polymer chain remains free to move in the solution. The polymer chain would swing back and forth and might fold its structure. If an energy term for the folded conformation compensates the entropy term, this conformation might be stable and exist in solution for a protracted period. The zwitterionic poly(3-octylpyrrole)squaraine has alternately negatively charged $-O^-$ and positively charged $-NH^+$ moieties that might interact in the folded conformation. The closure might cause the $-O^-$ and the $-NH^+$ moieties to attract each other and to bind together through hydrogen bonds. Scheme 2 illustrates the proposed molecular structures of the reversible isomerization of poly(3-octylpyrrole)squaraine induced by an active metal; the internal hydrogen bonds are schematically depicted in the folded conformation.

According to Scheme 2, we perceive that internal hydrogen bonds might be formed in the folded structure of poly(3-octyl-pyrrole)squaraine. Such a formation of hydrogen bonds might play a key role in this closure. Information about the structure of this polysquaraine in solution might be derived from infrared

Fig. 8 Schematic illustration of the isomerization of a zwitterionic polymer induced with a plate of an active metal; the colored segments represent separate charged moieties of the polymer.

Scheme 2 Reversible structural transformation of poly(3-octylpyrro-le)squaraine induced by an active metal depicted in molecular structures; formulae **III** and **IV** represent the linear and folded conformers, respectively.

spectra. Although trichloromethane absorbs strongly in the mid IR region, so interfering with measurements of dissolved samples, it is still possible to obtain useful IR absorption spectra of liquid samples by careful subtraction of the absorption by the solvent. Fig. 9 presents the IR net absorbance of poly(3-octyl-pyrrole)squaraine between solutions without, Fig. 9 (A), or with, Fig. 9 (B), contact with a Cu plate, relative to the solvent.

Apart from artefacts produced by imperfect subtraction of trichloromethane in both spectra, the significant feature located at 1602 cm^{-1} belongs to the functional group of the zwitterionic carbonyl of this polysquaraine sample.[38,46–48] A notable difference between these two spectra is a line at 3364 cm^{-1} that appears only in Fig. 9 (B), and that is assigned to an OH stretching mode of a intra-hydrogen bond.[49] As discussed above, the carrier sample of poly(3-octylpyrrole)squaraine in trichloromethane is postulated to exist as a linear form (formula III) that contains no OH functional groups, consistent with its absence from Fig. 9 (A), whereas in the presence of the copper plate this poly-squaraine sample has a folded structure (formula IV); the negatively charged –O$^-$ then binds to a positively charged –NH$^+$ to form an internal hydrogen bond, revealed through its OH stretching mode at 3364 cm^{-1} in Fig. 9 (B). The evidence from the IR spectra is thus consistent with a folded conformation of this polysquaraine sample induced by active metal surfaces, as demonstrated in Scheme 2.

To retain its maximum entropy in solution, the free zwitterionic polymer is thus configured as a flexible linear chain. For the zwitterionic polymer to convert to a folded conformation, energy must be released to compensate for the entropy term. In this folding, poly(3-octylpyrrole)squaraine possesses –NH$^+$ groups that can bind to its –O$^-$ ends. In this way internal hydrogen bonds O—H form in the folded conformation and stabilize the folded structure for this polymer. If the structure has no contribution from such an energy factor, the polymer would not fold its chain. To clarify this point, we compared the behaviors of poly(1-octylpyrrole)squaraine in the same experimental conditions. The similar structure of poly(1-octylpyrrole)squaraine possesses its octyl group bound to –N (position 1) instead of –C

(position 3); with such an alkyl location, it contains charged –$^+$NC$_8$H$_{17}$ groups, not –NH$^+$ groups, as shown in the formula I. No intra-hydrogen bonds can form even when the charged –$^+$NC$_8$H$_{17}$ group is able to approach the charged –O$^-$ group. In this case, no hydrogen bonds can form to stabilize the closure of the structure; poly(1-octylpyrrole)squaraine can thus not adopt a folded structure. As the visible absorption of poly(1-octylpyrrole)squaraine solution in contact with a metal remained constant under our experimental conditions, poly(1-octylpyrrole)squaraine preserves its linear conformation in solution. This constancy of the poly(1-octylpyrrole)squaraine in solution is consistent with the folded model.

Experiments of small-angle X-ray scattering provide further evidence supporting the isomerization of the target polymer in solution induced on contact with an active metal. For SAXS measurements of poly(3-octylpyrrole)squaraine in trichloromethane solution, we used stainless-steel and copper cells. As the SAXS curve remained constant for this cell, stainless steel is an inactive metal for the isomerization of this polymer in solution. In contrast, the SAXS profiles of solution for poly(3-octylpyrrole)squaraine in a copper cell varied with time, as shown in Fig. 10. The SAXS curve of the polymer solution in the copper cell at the initial stage, displayed as a solid line, was similar to that in the stainless steel cell; it gradually altered and eventually became the dotted curve in Fig. 10. The radius of gyration (R_g) of the polymer is determined from the plot of ln $I(q)$ vs. q^2 in the range of small q; the value of R_g thus extracted from the slope ($-R_g^2/3$) of this plot,[50,51] as shown in the inset of Fig. 10, was 21 $\pm$ 2 nm and 16 $\pm$ 2 nm in the copper cell at the initial and final stages, respectively. The result is consistent with two conformers existing in solution and with our folded model.

Summarizing the above, we observed reversible changes in visible absorption, IR absorption and SAXS spectra of poly-(3-octylpyrrole)squaraine in solution in contact with particular metals; we postulate that the effects reflect conformational isomerization of this conducting polymer induced by metals. Is there another possible mechanism to cause the changes in these spectra of poly(3-octylpyrrole)squaraine on exposure to metal
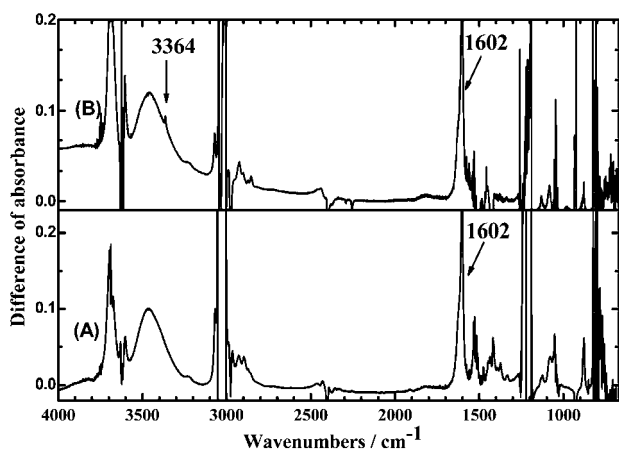

Fig. 9 The difference of IR absorbance in trichloromethane solution with an optical path of 1 mm relative to pure solvent: (A) poly(3-octyl-pyrrole)squaraine in trichloromethane solution, (B) the same solution into which a Cu plate is inserted.
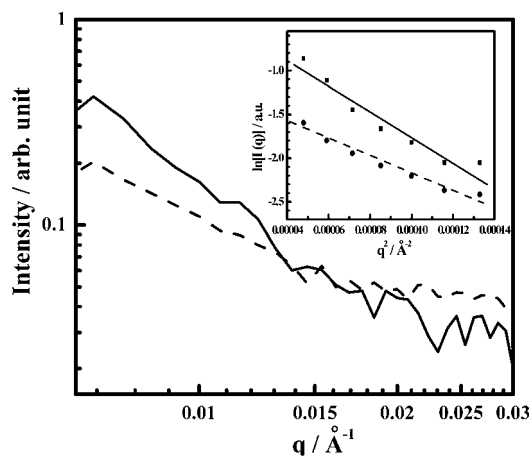

Fig. 10 SAXS profiles of poly(3-octylpyrrole)squaraine in trichloro-methane solution in a copper cell at initial (solid line) and final (dotted line) stages. The inset depicts relations of ln $I(q)$ vs. q^2 for small q at initial (solid line) and final (dotted line) stages.

plates in solution? One mechanism that might explain these spectral changes is the chemical oxidation of the polymer chains by either dissolved metal ions or oxidation of the polymer chains by dissolved oxygen at the metal surfaces.

Zwitterionic organic dyes act as ligands and react with metal ions to form stable complexes producing altered optical properties. This phenomenon of a color change for the zwitterionic organic dyes induced by metal ions has a prospective practical technical application as a sensor.[52–54] To test the role of metal ions, we added cations to similar polymer solutions. Fig. 11 displays the variation of visible absorption spectra of poly(3-octylpyrrole)squaraine in trichloromethane to which we added a saturated solution of Cu^{2+} in trichloromethane; the absorption maximum shifted with time from 543.6 nm to 523.9 nm, and the intensity of the former band correspondingly decreased, as shown in Fig. 11. The curves of these spectra intersect at 531.2 nm, the isosbestic point.

Scrutiny of Fig. 3 and 11 indicates that, although the spectral changes are similar, they are not the same. The wavelength of the line caused by the copper ion is 523.9 nm, whereas that influenced by the copper plate is 513.8 nm; the difference is about 10 nm. Moreover, the isosbestic point on adding the copper ion is at 531.2 nm, but that on inserting the copper plate is at 525.8 nm; the difference is about 5.4 nm. These discrepancies suffice to indicate that the copper ion is not the factor driving the transformation of this zwitterionic polymer solution induced by metallic surfaces. Copper is unlikely to dissolve into ions from the copper sheet in trichloromethane. Moreover, after the dissolved cations cause a structural modification of this CP, it is difficult to remove those cations from the solution; for this reason the transformation is irreversible so that the altered structure does not revert to the original conformation. In contrast, with the metal plates, simply withdrawing the plate from the solution of the polymer suffices to initiate reversion of the polymer to its original form. These two structural transformations of this zwitterionic polymer differ intrinsically: with the metal plate in heterogeneous contact with the solution of the polymer, the phenomenon involving the structure of the polymer
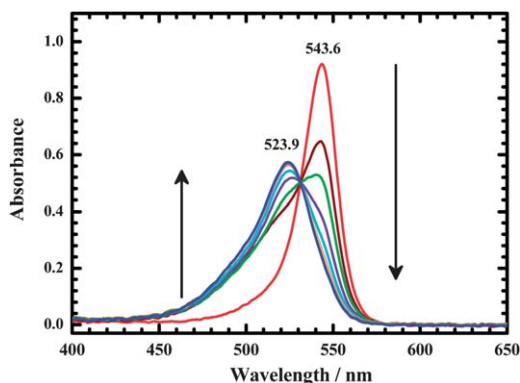
is reversible, whereas with metal ions homogeneously present in the solution phase the change is irreversible. According to this test, we exclude the possibility of a conformational change of this CP induced by metal ions dissolved from the metal.

In addition, although this polysquaraine solution exhibited a similar variation of the conformation induced by both cations and some active metal plates, this zwitterionic polymer folds its structure in two distinct ways. While the polysquaraine reacts with a cation and folds its structure, the negative charge of $-O^-$ binds to the cation; in this case, no OH groups are formed in the complex. The difference IR absorption spectrum of poly-(3-octylpyrrole)squaraine with added Cu^{2+} cations in trichloromethane is shown in Fig. 12; compared to Fig. 9 (B), this IR absorption spectrum possessed no such OH band. The evidence from the IR spectra thus further confirms the distinct conformational changes of this polysquaraine sample induced by cations and by the surfaces of active metals.

An analogous argument of reversible and irreversible processes applies also to the oxidation of the polymer from oxygen dissolved at the metal surfaces: a conformational change caused by such oxidation would be irreversible. Without adding a reductant, the oxidation product would not be reduced to its original form. The intrinsic irreversibility of an oxidation mechanism is inconsistent with the reversible observation and must be excluded.

As mentioned within the Introduction, the linear conformation of the target polymer is stable in solution; without perturbation; it does not transform spontaneously to the folded structure. The barrier for transformation from the linear zwitterionic polysquaraine to the folded conformer is large in the free solution. Induced by active metals, this CP performs the folding isomerization in solution, in which an active metal behaves as a catalyst for the conformational transformation. With the copper catalyst, the activation energy of the structural change from the linear to the folded conformer for poly(3-octylpyrrole)squaraine is decreased to 18.9 ± 0.7 kJ mol^{-1}; the value is sufficiently small that isomerization proceeds near 295 K, but the folded conformer of poly(3-octylpyrrole)squaraine is unstable in the free solution and eventually opens its conformation; the activation energy of this structural opening for poly(3-octylpyrrole)squaraine is 38 ± 6 kJ mol^{-1}. According to our proposed

Fig. 11 Temporal variation of visible absorption spectra of poly-(3-octylpyrrole)squaraine in trichloromethane (3 mL) in a quartz cell (length 1 cm of optical path) to which was added a saturated solution (20 μL) of Cu^{2+} in trichloromethane: before addition (red curve), and after 0.5, 2, 5, 10, 30, 60, 120, 180 (blue curve) min. For this reaction we prepared a saturated solution of Cu^{2+} in trichloromethane over $Cu(ClO_4)_2 \cdot 6H_2O$.
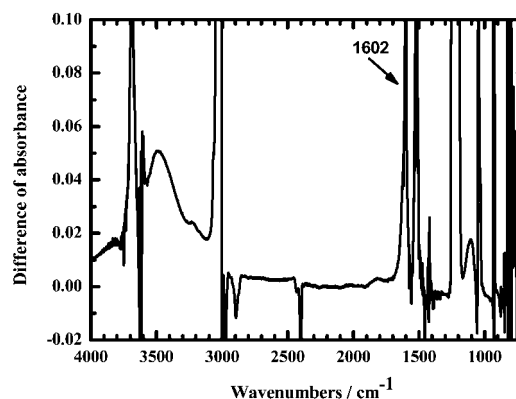

Fig. 12 Difference IR absorption spectrum of poly(3-octylpyrrole)squaraine in trichloromethane (optical path 1 mm) to which Cu^{2+} was added in solution.

model, these activation energies are associated with intramolecular hydrogen bonds N—H⋯O. The typical bond strength of an intra-hydrogen bond N–H⋯O is about 8 kJ mol^{-1}.[55–58] By comparison with the activation energy of the unfolding, it is possible that five hydrogen bonds N–H⋯O are formed in the folded conformer.

The observation of this reversible structural modification accompanying the optical alterations for the zwitterionic polysquaraine induced by active metal surfaces is unprecedented; it represents a new chemical and physical process. The duration of forward and reverse reactions for this isomerization might be subject to manipulation. For the forward transformation, increasing the surface area of the metal and the temperature, decreases the duration of reaction. For example, with Cu gauze (100 mesh, diameter 0.11 mm and mass 2.133 g) in a cell of liquid volume 3 mL and optical path of length 1.0 cm, the change was completed in less than 20 min at 323 K. For the reverse transformation in the free solution, increasing the temperature decreases the duration of unfolding. Ultrasonic agitation to perturb the folded polymer solution also decreases the duration profoundly: we found that only 20 min was required to accomplish the reversal with ultrasonic agitation. The response periods of the transformations might be further decreased with an improved technique. This reversible behavior which accompanies color changes endows materials of this type with a great prospective capability for display applications or information storage, and might lead to the development of other significant applications. For example, by means of this mechanism, an optical switch might be achievable in the liquid state.

The optical, physical and electronic properties affected by a variation of the polymer conformation are quite interesting for applications. For example, the conductivities of altered conformational structures for target polymer in solution might be different. Fig. 13 displays the impedance plots of linear and folded conformers of this CP. The conductivity (σ) of the polymer in solution was calculated from the measured resistance (R_p), the area ($S = 1.227$ cm^2) and the length ($L = 0.44$ cm) of the liquid cell using the equation $\sigma = L/SR_p$; in which, the R_p of the polymer solution was determined from the intercept of the line of the impedance curve at the high frequency end. By this means,
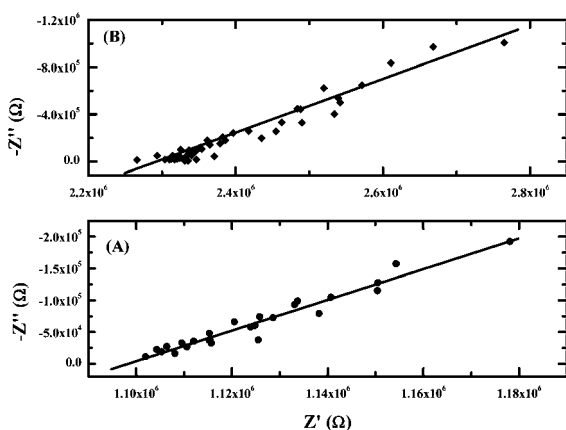
the conductivities of the linear and folded conformers were obtained to be 3.27×10^{-7} and 1.56×10^{-7} S cm^{-1}, respectively; the value of the linear conformer is twice to that of the folded one.

This reversible phenomenon encourages the discovery of further knowledge about the interactions of polymers with metallic surfaces, and about the dynamics and energetics of conformational changes of polymers. We expect our findings to motivate the investigation of conformational modifications of other CPs and applications of this phenomenon. Applying these polymer solutions onto substrates might enable these CPs to retain their specific structures in the solid after removal of solvent. The properties and applications of these switchable films or materials remain uncharted territory. These CPs might be developed as shape-memory polymers;[59–61] further work is required.

Conclusions

Visible and infrared absorption spectra and small-angle X-ray scattering curves of poly(3-octylpyrrole)squaraine, having a zwitterionic repeating unit, in trichloromethane solution altered on contact of the solution with the surface of an active metal. These observed spectral variations are deduced to indicate that the conformation of this CP becomes modified on contact with an active metallic surface. Spectral evidence unambiguously confirms the reversible isomerization of poly(3-octylpyrrole)squaraine induced by an active metallic surface; the structure of this polysquaraine might be switchable from a linear conformer to a folded one back and forth depending on the presence or absence of an active metal. Induced by the copper surface, the activation energy of the forward isomerization is 18.9 ± 0.7 kJ mol^{-1}, whereas the activation energy of the reverse process to regenerate the linear conformer is 38 ± 6 kJ mol^{-1}; this result might indicate that approximately five intramolecular hydrogen bonds form in the folded conformer of poly(3-octylpyrrole)squaraine. Observation of the reversibility of the postulated change of conformation associated with a metallic surface for this zwitterionic polymer provides an impetus to investigate both this structural modification of other CPs and applications of this phenomenon.

Acknowledgements

Fig. 13 Impedance plots of poly(3-octylpyrrole)squaraine (3.5 mg L^{-1}) in solution: (A) the linear conformer and (B) the folded conformer.

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