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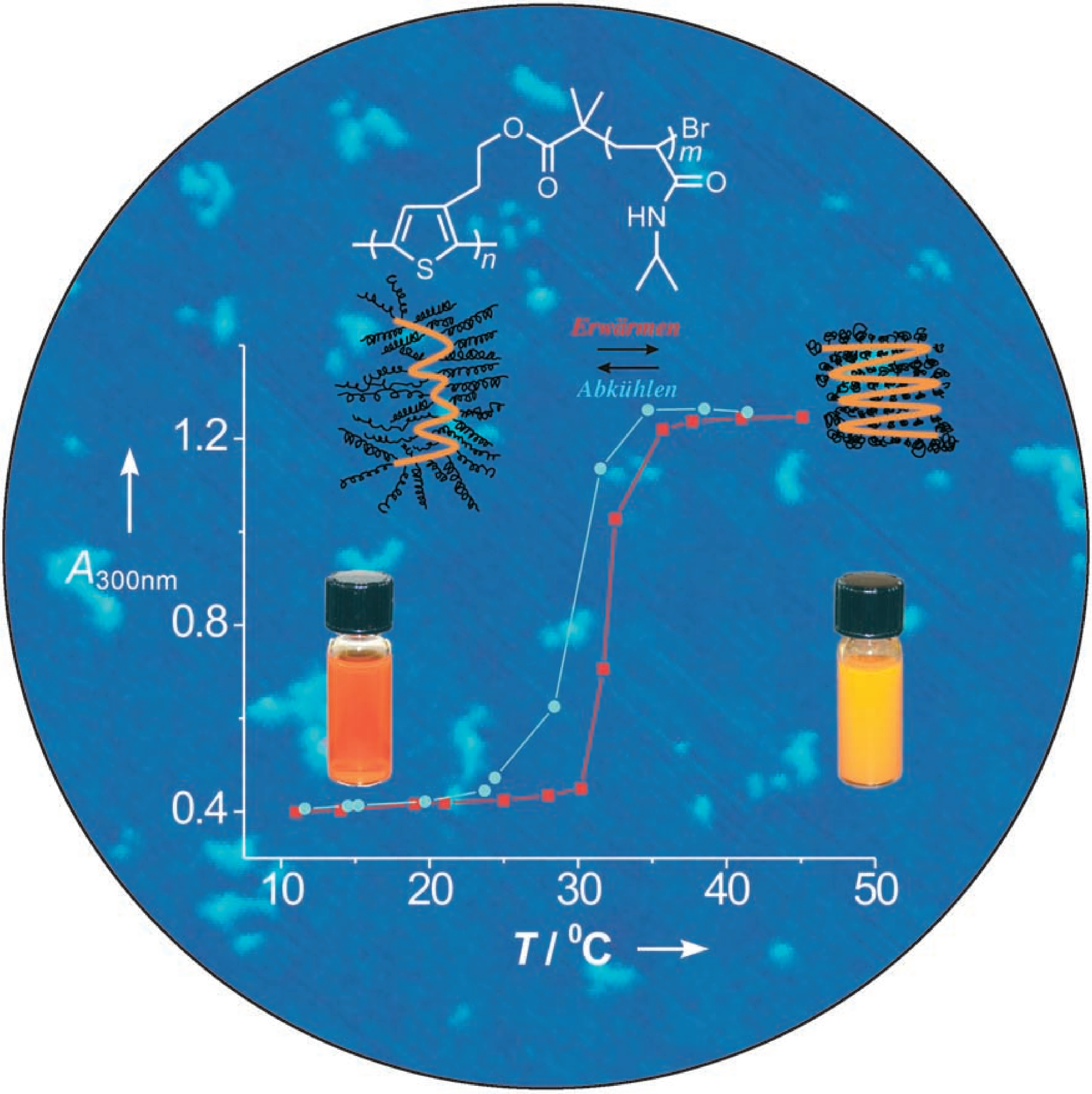

Ein molekulares Bürstencopolymer, das aus elektrooptisch aktivem Poly(3-substituiertem Thiophen) und thermisch beeinflussbarem Poly(*N*-isopropylacrylamid) besteht, ist außergewöhnlich wasserlöslich und zeigt ein einzigartiges thermochromes Verhalten. Weitere Einzelheiten finden Sie in der Zuschrift von R. L. McCarley et al. auf den folgenden Seiten.

Thermochromic Polymers

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Highly Water-Soluble Thermally Responsive Poly(thiophene)-Based Brushes**

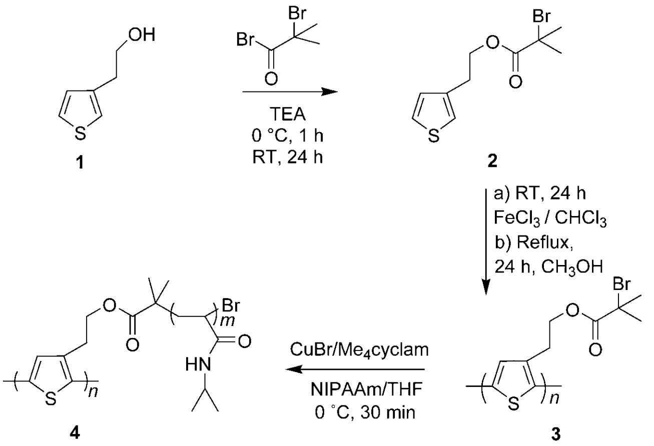
*Sreelatha S. Balamurugan, Grigor B. Bantchev, Yuming Yang, and Robin L. McCarley**

The need for highly water-soluble conducting polymers is great, particularly in applications that would benefit from environmentally friendly processing steps or those applications that center on use of conducting polymers in biological environments.[1] In addition, the chromic response of certain conducting polymers (due to changes in polymer conjugation length as a result of conformational changes of the polymer backbone)[2] should allow for development of sensing systems capable of detecting a multitude of analytes or stimuli, in a broad spectrum of environments, as long as conducting-polymer compatibility, solubility, and processability issues can be addressed. In particular, conducting polymers with a wide variety of solubilizing groups are needed, including those made soluble in aqueous media without the use of ionic solubilizing groups.

As the result of efforts to extend the unique optical and electrical properties of substituted poly(thiophene)s (PTs)[2–4] to aqueous media[5,6] and strategies for developing chromism-based PT materials that respond to biological analytes,[7–11] significant advances in the fabrication of water-soluble PTs have occurred. Water-soluble PTs possessing cationic side chains were recently used in the specific detection of DNA hybridization events,[10] nucleic acids,[12] and human thrombin.[11] Such aqueous-soluble PTs have been prepared by incorporating ionic groups into the side chains of the PT backbone[5,6,13–15] and by complexation of PT with cyclodextrins.[16] Recently, a low-molecular-weight oligo(thiophene) substituted with neutral oligo(ethylene oxide) groups at the 3-position ($M_n = 1400$) was shown to be water soluble to a level of approximately 1 $\mathrm{g\,L^{-1}}$.[17,18]

Poly(*N*-isopropylacrylamide) (PNIPAAm) is an environmentally responsive polymer that has kindled interest in many researchers for a long time due to its unique lower critical solution temperature (LCST, 30–32 °C[19]) and its relative ease of synthesis. At its LCST, PNIPAAm undergoes a rapid and reversible conformational change from an extended hydrated coil to a collapsed hydrophobic globule that is insoluble in water;[19,20] the driving forces for this conformational change are associated with temperature-dependent hydrogen bonding and hydrophobic interactions. Substitution of responsive PNIPAAm units on PT at the 3-position should lead to a highly water-soluble conducting polymer possessing unique optical and electronic properties as the result of the extension and collapse of the PNIPAAm brushes toward the PT backbone; this system and its characteristics are the topic of the study reported here.

In general, the tethering of PNIPAAm brushes on PT (Scheme 1) involved functionalization of a thiophene monomer with an atom-transfer radical polymerization (ATRP) initiator to yield **2**, followed by its oxidative polymerization to afford a macro initiator **3**, and then growth of PNIPAAm chains from the PT macro initiator by ATRP.[21,22] Specifically, commercially available 2-(3-thienyl)ethanol (**1**) was esterified with 2-bromoisobutyryl bromide to yield 3-[1-ethyl-2-(2-bromoisobutyrate)]thiophene (**2**). Formation of **2** was confirmed by FTIR, GC-MS, and ^{1}H NMR analyses.[23] Compound **2** was polymerized by oxidative coupling[24] using $FeCl_3$ in chloroform to yield 2,5-poly(3-[1-ethyl-2-(2-bromoisobutyrate)]thiophene) **3** (83 % yield). Because the initiator is anchored before polymerization, the presence of the grafting site at each repeat unit is ensured. The PT macroinitiator **3** is soluble in many organic solvents, such as tetrahydrofuran, dimethylformamide, chloroform, dichloromethane, and toluene, due to the presence of the bromoisobutyl initiator group at the 3-position. Formation of **3** was confirmed by ^{1}H NMR spectroscopy and gel permeation chromatography (GPC), the latter of which yielded $M_n = 1.09 \times 10^5$ and $M_w/M_n = 2.95$.[23] As expected owing to the $FeCl_3$-mediated polymerization, **3** was found to be regioirregular, as evident in its ^{1}H NMR spectrum; the protons on the 3-alkyl chain adjacent to the thiophene ring (65 % head-to-tail coupling) give rise to a two-component signal at 3.24 ppm and 3.00 ppm.



Scheme 1. Synthesis of poly(thiophene-g-NIPAAm) **4**. TEA = triethylamine.

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[*] Dr. S. S. Balamurugan, Dr. G. B. Bantchev, Y. Yang,
Prof. Dr. R. L. McCarley
Department of Chemistry and
the Center for Biomodular Multi-Scale Systems
Louisiana State University
Baton Rouge, LA 70803-1804 (USA)
Fax: (+1) 225-578-3458
E-mail: tunnel@LSU.edu

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PNIPAAm chains were grown from the PT macroinitiator **3** by the ATRP technique, using CuBr/1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane as the catalyst and THF as solvent (53 % yield). This ATRP catalyst system has been used in the high-yield synthesis of PNIPAAm brushes having a polydispersity of ca. 1.4.[25–27] Formation of PNIPAAm grafts on the PT macroinitiator **3** to yield **4** was confirmed from ^{1}H NMR data, as indicated by the presence of a broad NH peak at $\delta = 6.59$ ppm and CH peak at $\delta = 3.98$ ppm, both associated with the PNIPAAm brushes.[23] Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry evaluation of PNIPAAm chains cleaved from **4** (ester hydrolysis)[28] led to the routine observation of mass spectra characteristic of polymer molecules possessing the NIPAAm repeat unit and molecular weights between 1000 and 5000 amu. The molar mass of **4** was found by GPC to be roughly 2×10^6. It is interesting to note that the graft polymer is soluble in a wide spectrum of organic solvents, such as THF, acetone, chloroform, dichloromethane, and methanol. Importantly, poly(thiophene-*g*-PNIPAAm) **4** is soluble in room-temperature water up to 11 $\mathrm{g\,L^{-1}}$! To date, this is the highest reported water solubility for a PT possessing neutral substituents, and only the second such PT described in the literature.

The individual poly(thiophene-*g*-NIPAAm) molecules were readily observed by scanning force microscopy (SFM; Figure 1). Images such as that in Figure 1 were routinely obtained by imaging freshly cleaved mica that had a $\approx 1\ \mathrm{mg\,L^{-1}}$ solution of **4** (unfractionated) in acetone spin-coated on it. A broad distribution of random coiled structures for **4** on mica is noted in Figure 1, with lengths ranging from 30 to 260 nm and heights from 0.7 to 0.9 nm. This wide distribution in molecular size is in agreement with the GPC data for **4** and **3**, as well as that from MALDI-MS of the cleaved PNIPAAm.

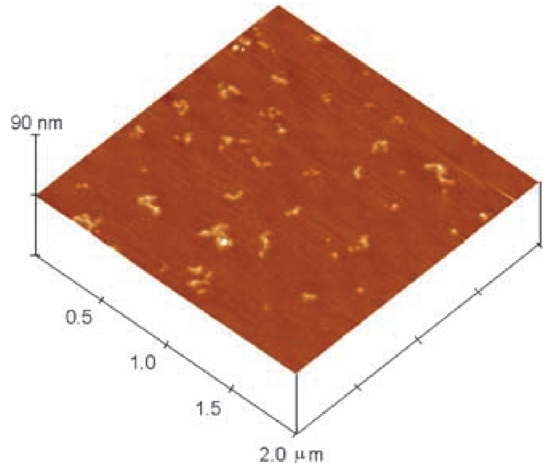

Figure 1. SFM image of poly(thiophene-*g*-NIPAAm) **4** on mica recorded in tapping mode.

The enthalpy of transition of the grafted polymer in water was monitored using differential scanning calorimetry (DSC) by repeatedly cycling the solution between 5 and 60 °C (four heating and three cooling cycles; Figure 2). Such temperature excursions led to observation of an endothermic transition at 31.8 ± 0.2 °C and an associated exothermic peak at 29.6 ± 0.4 °C; these are assigned to the enthalpy change associated with the breaking/making of hydrogen bonds between PNIPAAm grafts and water.[20] These results are in agreement with previous studies of PNIPAAm and confirm that the stimuli-responsive conformational change of the poly(thiophene-*g*-NIPAAm) brushes is reversible and very sensitive to temperature variation.[19]

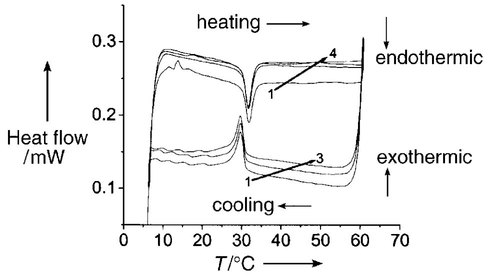

Figure 2. DSC data for 8.25 $\mathrm{g\,L^{-1}}$ poly(thiophene-*g*-NIPAAm) **4** in water; repeated cycles of heating (1–4) and cooling (1–3) between 5 and 60 °C.

In Figure 3 are displayed the electronic absorption spectra of the PT macro initiator **3** and poly(thiophene-*g*-NIPAAm) **4**. In chloroform solution, **3** and **4** exhibit identical $\lambda_{\max}$ values (423 nm, 2.95 eV) for the absorption band associated with the $\pi \rightarrow \pi^*$ transition of the PT backbone. This indicates that PT has a high degree of disorder in the main PT backbone. Thin films of **3** and **4** display bathochromic shifts of 21 nm and 8 nm, respectively, relative to their solution counterparts, indicating better structural ordering (increased conjugation length) of the PT backbone in the solid state.[28–30] The smaller increase in $\lambda_{\max}$ for the film of graft polymer **4** (8 nm) compared to that of the PT macroinitiator **3** (21 nm), versus the solution values, points to the fact that the PNIPAAm chains separate the PT backbones, preventing PT backbone–backbone interactions to some extent.[28] Aqueous solutions of the graft polymer **4** displayed a relatively low-energy $\lambda_{\max}$ at ca. 445 nm at room temperature (Figure 4) compared to that in chloroform solution ($\lambda_{\max} = 423$ nm); this likely results from the nature of the solvent, for as the solvent quality decreases (becoming more polar), it is known for soluble PTs that the backbone units tend to adopt a more planar structure.[17]

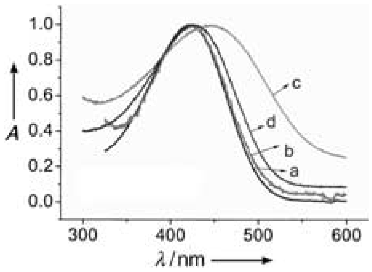

Figure 3. Electronic absorption spectra (normalized) of a) **3** and b) **4** in chloroform (0.01 $\mathrm{g\,L^{-1}}$); films of c) **3** and d) **4** on quartz.

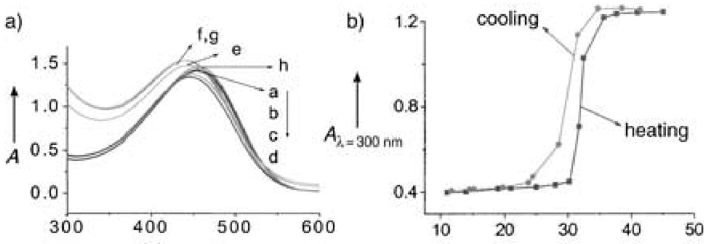

Figure 4. a) Electronic absorption spectra of 0.8 $\mathrm{g\,L^{-1}}$ poly(thiophene-*g*-NIPAAm) **4** in pure water at various temperatures: a) 11, b) 18, c) 28, d) 30, e) 32, f) 38, and g) 45 °C, all in the heating direction; h) at 11 °C after cooling from 45 to 11 °C. b) Absorbance intensity at 300 nm (heating and cooling).

Light-scattering studies of poly(thiophene-*g*-NIPAAm) **4** in water indicate that the polymer brush exhibits a change in molecular shape upon passing through the LCST of 32 °C.[23] Static light-scattering experiments of **4** in water demonstrate that at temperatures above the LCST, the scattering intensity is significantly greater than that below the LCST, and the radius of gyration of the poly(thiophene-*g*-NIPAAm) is approximately 50% of that at temperatures below 32 °C ($\approx$70 nm vs. $\approx$150 nm). Confirming this decrease in molecular size on transition from below the LCST to above the LCST, analysis of low-angle (30°) dynamic light-scattering data leads to the observation of a roughly threefold increase in the apparent diffusion coefficient when the temperature is increased above the LCST ($1.7\times10^{-8}\,\mathrm{cm^2\,s^{-1}}$ vs. $5.2\times10^{-8}\,\mathrm{cm^2\,s^{-1}}$). Preliminary evaluation of the light-scattering data excludes the possibility for intermolecular aggregation of individual poly(thiophene-*g*-NIPAAm) molecules when the temperature is increased above the LCST and suggests that the shape of the molecules changes from a random coil to collapsed sphere when the LCST is traversed.[23] Finally, the light-scattering data points to a second, more subtle transition in the 25–28 °C temperature range that is associated with precollapse of the PNIPAAm chains; this is in agreement with theory and recent experimental work for surface-grafted PNIPAAm materials.[25,31] This precollapse is also noted in the electronic absorption spectra of **4** in water (see below). Extensive studies to more fully understand the temperature-induced changes in conformation of the poly(thiophene-*g*-NIPAAm) materials are planned.

In Figure 4a are displayed the electronic absorption spectra of poly(thiophene-*g*-NIPAAm) **4** in water as a function of temperature. As the temperature was increased from 11 °C to 30 °C, there was a small decrease in the intensity of the absorption band and a small blue-shift (456 to 446 nm). Above 30 °C, the solution became cloudy, and a significant increase in the absorption intensity, along with a 6-nm (from 446 to 440 nm) blue-shift of $\lambda_{\max}$ and a broadening of the absorption band, was noted. The temperature dependence of the absorption intensity at 300 nm for poly(thiophene-*g*-PNIPAAm) **4** in water upon heating and cooling is shown in Figure 4b; a very sharp change between 30 and 35 °C is evident. The data in Figure 4b demonstrate that this steep transition is reversible with some hysteresis, the latter which is most likely associated with PNIPAAm intrachain and interchain associations formed during collapse that require a significant amount of time to disentangle. Such hysteresis is observed in dilute solutions of PNIPAAm[32] and when the polymer is grafted on surfaces.[25] All of these observations reveal that the PT backbone responds to the temperature-induced conformational changes of the grafted PNIPAAm chains.

We propose that the temperature-dependent spectral shift and intensity change of the $\pi\rightarrow\pi^*$ transition of the poly(thiophene-*g*-NIPAAm) **4** in water are the result of changes in the effective conjugation length of the PT backbone caused by steric interactions between the collapsed PNIPAAm moieties and the PT backbone, as well as changes in the hydrophobicity of the environment near the PT main chain.[33] Furthermore, we conclude that the observed behavior is associated with the folding of a single chain (molecule) of poly(thiophene-*g*-NIPAAm). The spectroscopic changes are not due to the well-known thermochromic effect found in substituted regioregular and regioirregular PTs in solution[34] or in the solid state,[35–37] as the sensitivity of the changes in $\lambda_{\max}$ for the $\pi\rightarrow\pi^*$ transition for the poly(thiophene-*g*-NIPAAm) with temperature (21 °C increase yields a 16-nm blue-shift) is much higher than that previously reported for regioirregular poly(3-hexylthiophene) solutions in THF (100 °C increase yields a 20-nm blue-shift[34]). Instead, we propose that the collapse of the PNIPAAm chains toward the PT backbone causes an increase in the steric interactions between the PNIPAAm groups and the main PT chain, as well as an increase in the hydrophobicity of the PT backbone environment, the latter which would mimic an increase in the quality of the solvent. It is well known that upon its collapse above the LCST, PNIPAAm becomes quite hydrophobic due to expulsion of water from the polymer, loss of hydrogen bonding between amide groups, and substantially increased hydrophobic interactions between the isopropyl groups. The larger steric and environmental effects with increased solution temperature would result in a more twisted PT backbone (a lower conjugation length) for the poly(thiophene-*g*-NIPAAm) **4** in water. Also, the 10-nm blue-shift that occurs between 11 and 28 °C supports our conclusion and deserves further comment. It has been shown from theoretical[31,38] and experimental[25,39,40] points of view that tethered PNIPAAm brushes exhibit what is referred to as a continuous collapse before the precipitous collapse event at the LCST transition. That is to say, as the LCST is approached from lower temperatures, the solvent is expelled from the interfacial region from which the chains are grafted, and the interfacial PNIPAAm chains undergo precollapse. In our case, the interface is a poly(thiophene) backbone, and slow collapse toward it over the 11 °C to 28 °C range induces strain on the PT backbone and leads to an increase in the hydrophobicity of the interfacial region, both of which result in observation of the spectral changes. Finally, we found no effect of the concentration of the graft polymer (0.8–0.2 $\mathrm{g\,L^{-1}}$) on the temperature-dependent spectral shift and intensity change for the $\pi\rightarrow\pi^*$ transition of the graft polymer in water, supporting a single-chain event for the temperature-dependent folding of poly(thiophene-*g*-NIPAAm) **4** in water.

On the basis of the results obtained from light-scattering experiments, SFM, DSC, and electronic absorption spectroscopy, a proposal for the conformational transition of poly(thiophene-g-NIPAAm) **4** is schematically depicted in Figure 5. The highly water-soluble graft polymer possesses a disordered backbone and adopts a roughly random-coiled structure at temperatures below the LCST. Once the solution temperature is above the LCST, **4** adopts a more globular structure, and the backbone is more ordered as a result of the combined steric interactions between the collapsed PNIPAAm and PT moieties and the hydrophobic environment afforded by the PNIPAAm.

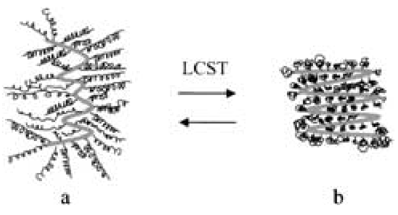

Figure 5. Conformational transition of poly(thiophene-*g*-NIPAAm) **4** at its LCST: a) extended random conformation of molecules that are soluble in water at $T <$ LCST, and b) collapsed sphere conformation of molecules that are insoluble in water at $T >$ LCST.

In conclusion, the highly water-soluble, thermally responsive poly(thiophene-*g*-NIPAAm) was synthesized and characterized. The DSC, UV, and light-scattering measurements clearly show that between 28 and 35 °C in water this polymer undergoes a reversible phase transition from a coiled structure to a collapsed globule. By analyzing the optical properties of PT substituted with responsive PNIPAAm chains, we were able to gain insight into the mechanism for changes that happen to the PT backbone when transition of the PNIPAAm chains takes place. The unique optical and electronic properties that result from combining the PT with the water-soluble and temperature-responsive PNIPAAm side-chain groups promise important applications of this polymer brush system in responsive soft nanodevices, LEDs, bioelectronics, biosensors, actuators, fluorescent thermometers, and supramolecular materials. In particular, the use of regioregular PT materials will augment the capabilities of such applications.

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