Morphology and Photophysical Properties of a Thermally Responsive Fluorescent Material Based on a Rod-Coil Tri-Block Copolymer

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ABSTRACT: A thermally responsive rod-coil poly[poly (N-isopropylacrylamide)-b-polyfluorene-b-poly(N-isopropylacrylamide)] triblock copolymer has been successfully synthesized by atom transfer radical polymerization from an end-functionalized macroinitiator. The thermochromic behavior and relevant morphology of this polymer were investigated by UV-vis spectra, DLS, and AFM, respectively, at various temperatures. A thermally responsive fluorescent material was achieved facilely by combining the optically active polyfluorene with temperature-responsive poly(N-isopropylacrylamide). All the measurements demonstrated that in the region of 25–45°C, the polymer underwent a phase transition and the corresponding change in optical properties in its water solution. However, the polymer did not show completely reversible behavior upon heating and cooling. On the basis of the comparison with two other thermally responsive conjugated polymers in literatures, a tentative mechanism has been proposed that π–π interaction induced rigid segments to remain chain conformation and packing styles as in collapsed state. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 18–22, 2008

Key words: fluorescent probe; polyfluorene; rod-coil; thermally responsive

INTRODUCTION

Stimuli responsive polymers can provide a variety of applications in many fields, such as drug delivery, biotechnology, and chromatography.[1–3] The interest in these polymers has exponentially increased due to their promising potentials. Among them, temperature-responsive polymers have been considerably investigated because thermal stimuli is relatively convenient and effective in many applications.[4,5] One of the unique properties of temperature-responsive polymers is the presence of a critical solution temperature. As a thermally responsive polymer, poly(N-isopropylacrylamide) (PNIPAAm) which has a lower critical solution temperature (LCST) is the most popular one for application.[6–8] At its LCST (~32°C), PNIPAAm undergoes a rapid and reversible conformational change from an extended hydrated coil to a collapsed hydrophobic globule that is insoluble in water,[9,10] and the collapse of individual polymer chains increases the scattering of light in solution (cloud point).[11]

Fluorescent conjugated polymers (FCPs) have emerged as a powerful class of sensory materials[12] and have enabled the formation of ultrasensitive sensors for metal ions and biomolecules.[13–16] The photoluminescence (PL) performance of FCPs is sensitive to their conformation changes and intermolecular interactions.[17–19] This allows for development of sensing systems capable of detecting a multitude of stimuli in a broad spectrum of environments. Polyfluorene (PF) and its derivatives are one of the best candidates for FCPs because of their unique optical and electrical properties and easy modification. As the result of efforts to apply PFs as fluorescent probes for the detection of strand-specific DNA and metal ions, water-soluble PFs possessing ionic side chains have been intensively investigated.[20–22] Incorporation of aqueous-soluble groups such as hydroxyl groups, cyclodextrin, mannose/glucose, into the side chains of the PFs backbone is also an important method to realize water-solubility.[23–25,13]

In this contribution, we are seeking to develop a new structural type of thermally responsive fluorescent copolymer based on triblock rod-coil poly (PNIPAAm-b-PF-b-PNIPAAm) (**P-I**) by tethering PNIPAAm blocks on PF rod segment. Successful atom transfer radical polymerization (ATRP) in N,N-dimethylformamide (DMF)/water/THF ternary solvents was applied to propagate PNIPAAm chains
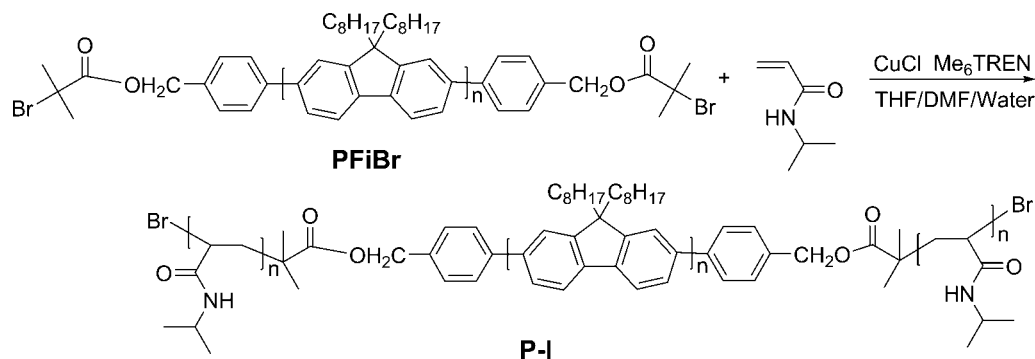
Scheme 1 The synthetic route of ATRP.

from a PF macroinitiator (**PFiBr**). The light-scattering studies of **P-I** in water indicated that the rod-coil copolymer formed a nano-scale core-shell structure in cold water and changed in conformation and solubility above its LCST. By depositing the water solution of **P-I** on single crystal silicon surface and after drying, the globular particles of **P-I** were revealed by atomic force microscope (AFM). The photophysical properties of **P-I** at various temperatures were investigated by UV–vis spectra and a plausible reason for the morphological variation of this rod-coil copolymer as temperature altering, was discussed based on these spectra. Moreover, the morphology, thermochromic, and relevant photophyical properties were compared with the previous findings on similar thermally responsive fluorescent polymers.[26,27] Also it is revealed that the stimuli responsive properties significantly lie on the polymer structures and consequently can be tuned and controlled by fine design of molecular structures.

EXPERIMENTAL

Materials

Tris(2-aminoethyl)amine (TREN), CuCl, ethyl 2-chloropropionate (ECP), DMF, and tetrahydrofuran (THF) were purchased from Aldrich and used as received. *N*-isopropylacrylamide (NIPAAm, Aldrich) was recrystallized from hexane and dried under vacuum prior to use. Me$_6$TREN was synthesized as described previously.[28]

Characterization

^{1}H-NMR (400 MHz) spectroscopy was performed on a Varian Mercury Plus 400 with tetramethylsilane as the internal standard. UV–Vis spectra were collected on a Shimadzu UV-3150 spectrophotometer. Fluorescence measurement was carried out on a Shimadzu RF-5300PC spectrophotometer. Number-average molecule weight (M_n) and weight-average molecule weight (M_w) were determined by Shimadzu GPC LC10A in

THF using calibration based on polystyrene standards. Atomic force microscopy (AFM) and dynamic light scattering (DLS) were performed on a Nanoscope IIIa microscope (Digital Instruments, Santa barbara, CA) operating in a tapping-mode and Malvern Autosizer 4700 light-scattering apparatus, respectively.

PF macroinitiators (PFiBr)

PFiBr was prepared according to the literature procedures via Yamamoto reaction and further modification of end-caps.[29] The polydispersity and M_n of this PF rod homopolymer are 1.37 and 4100, respectively.

PF-*b*-P(Nipaam) triblock copolymer (P-I)

A Schlenk tube was charged with 10.0 mg of CuCl, 0.1 g **PFiBr** and 0.14 g NIPAAm before it was sealed with a rubber septum. The tube was degassed by three cycles of vacuum and back-filling with argon, and 0.9 mL DMF, 1.8 mL THF, and 0.6 mL deionized water were added with syringes. The mixture was performed freeze-pump-thaw cycles for three times to remove the oxygen. Then the tube was placed in the preheated oil bath at 40°C for 10 min and when 28.0 μL of the ligand Me$_6$TREN was added into, the solution became green. After 24 h, the tube was removed from the oil bath and the reaction mixture was frozen with liquid nitrogen and diluted 1:2 with THF. The solution filtered through an Al$_2$O$_3$ column to remove the metal salts. The mixture was concentrated again and precipitated in ethyl ether. The light yellow polymer (146 mg, 61%) was collected after drying under vacuum. Formation of **P-I** (Scheme 1) was confirmed by ^{1}HNMR data, as indicated by the presence of two broad PF aryl peaks in the region of 7.84–7.66 ppm and a typical PNIPAMm peak (—NH—C*H*—) at 3.98 ppm.

RESULTS AND DISCUSSION

The successful ATRP of NIPAAM using DMF/water mixed solvents at room temperature and ethyl 2-
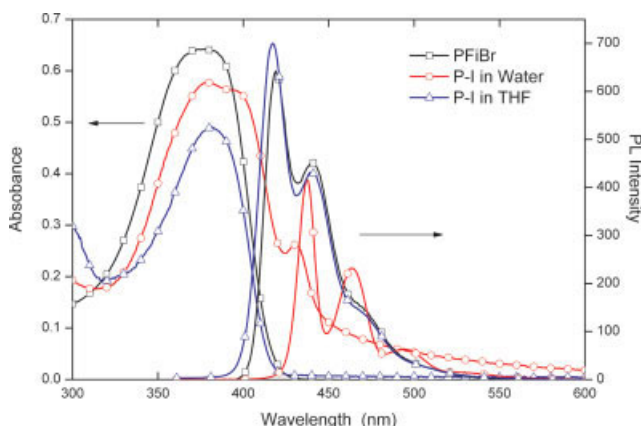
Figure 1 UV-vis and PL spectra of **PFiBr** in THF and **P-I** in THF and water (at 25°C). [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

chloropropionate (ECP)/CuCl/Me6TREN as an initiator/catalyst system has been reported.[30] But in our system, a large amount of precipitates appeared as soon as dropping DMF solution of **PFiBr** into water. To improve the solubility of macroinitiator in the reaction mixture, ternary solvents (DMF/Water/THF) were successfully applied in ATRP. The addition of THF significantly increased the solubility of macroinitiator in the reaction and did not show much influence on ATRP results. The molar mass of **P-I** was found by gel permeation chromatography (GPC), yielding $M_n = 9.1 \times 10^3$ and $M_w/M_n = 1.58$. And the number average molecular weight – M_n (8.7 $\times 10^3$) was also estimated from ^{1}H-NMR spectra which is a little less than the value obtained by GPC. This is a common feature for conjugated polymer because of their relatively rigid backbone. The polydispersity of molecular weight was larger than general ATRP which was due to the following two reasons: (i) the polydispersity of the middle block-PF segments is not low and after ATRP the polydispersity of **P-I** just increased by 1.15-fold, which convinces us that the addition of the two arms is well controlled. (ii) the existence of macroinitiators with only one end-cap.

In Figure 1, were depicted the absorption and PL spectra of **P-I** at 25°C. In THF, the sample concentration was 1×10^{-4} g/L; and in water, 5 μL **P-I** THF solution (1 mg/mL) was diluted by 50 mL deionized water. In THF, **P-I** exhibited absorption and emitting peaks around 380 nm and 417 nm (439 nm as a shoulder peak) respectively, identical with its precursor-**PFiBr**. This indicated that the PF segment remained a high degree of disorder in the main backbone. However, **P-I** showed a much broader absorption peak (overlapped by peaks at 378 and 395 nm) and a little shoulder peak round about 430 nm appeared in water. And the emitting peaks

of **P-I** red-shifted (437, 463, and 494 nm) and decreased in intensity. All demonstrated that the triblock copolymer formed a new conformation in water, which was due to the hydrophobicity of PF rod block and the hydrophilicity of PNIPAMm coil blocks in water. So that PF segments packed closely each other to be a core and PNIPAMm chains formed shells peripherally and this aggregation of PF led to red-shifts, broader peaks and lower quantum efficiency.[31,32]

For better confirmation of core-shell structure shaped in water, dynamic light-scattering was employed to study the conformation of **P-I** in different concentrations, as listed in Table I. These experiments indicated that the particle sizes and polydispersity indexes (DI) of rod-coil copolymers in water were in the vicinity of 200 nm and 0.2, respectively. The size increased with the higher polymer concentration, which corresponds to an increase in the aggregation number of the micellar aggregates. In high concentrations, more micelles existed in solutions and they agglomerated to be larger particles. Especially, when **P-I** solution was dropped into hot water (60°C) directly, the particle size became much larger (457 nm) and the relevant DI was 0.7, which exhibited a sharp change in polymer solubility upon passing through the LCST. At this temperature, the copolymers showed poor solubility in water, resulting in more remarkable intermolecular aggregation and larger particle size, even though hydrophobic molecular collapse occurred. This interesting feature is different with the result of analogical thermally responsive polymer brushes reported by McCarley and coworkers.[26] This may be due to that weak polymer solubility in hot water led to interchain aggregation and precipitates, hence, large size particles appeared in DLS. On the contrary, the brush structure in the literature intensively excluded the possibility of the aggregation;[33] however, our molecule was a linear polymer, possessing of much less steric hindrance.

TABLE I
Dynamic Light-Scattering Data of P-I in Water

Sample	D_h (nm)[a]	DI[b]	Water[c] (mL)	P-I (1 g/L in THF) (μL)
1	178	0.190	5	10
2	182	0.238	5	15
3	217	0.210	5	50
4	222	0.208	5	100
5	457	0.705	5[d]	50

[a] Hydrodynamic diameter.
[b] Polydispersity index.
[c] P-I solution was added dropwise into deionized water by micro-syringe.
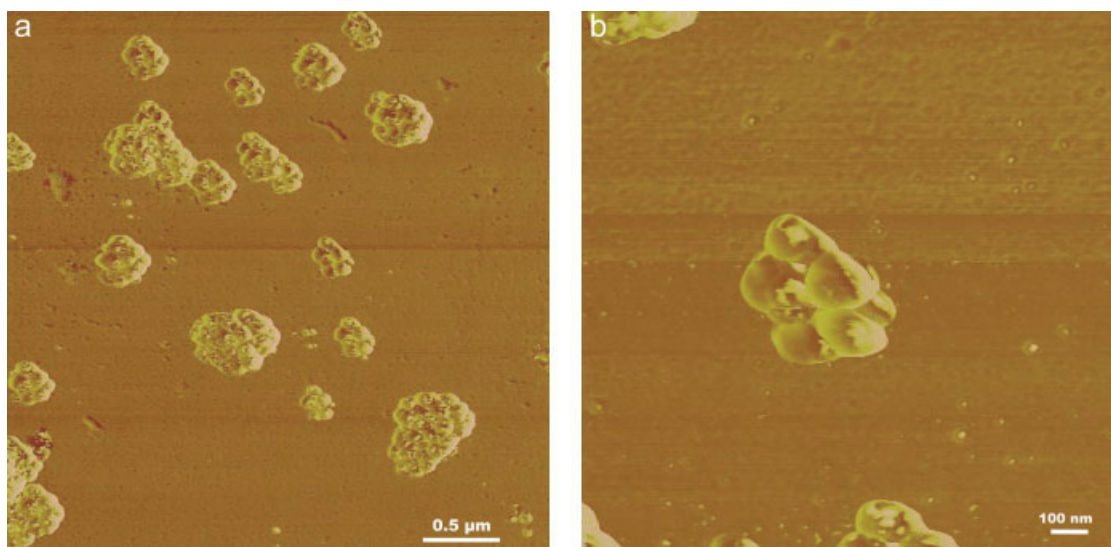[d] The temperature of this water solution was 60°C.

Figure 2 Atomic force microscopy image of **P-I** on silicon surface recorded in tapping mode. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

A drop of sample three for DLS was cast on a silicon surface. After drying, it was observed by AFM, as shown in Figure 2. The morphology of **P-I** thin film on surface consisted of many spherical aggregates diameter around 200 nm. And the enlarged picture (the right one) clearly showed that one aggregate was assembled by some round particles, which may be induced by the further aggregation of the smaller micelles during the evaporation of the solvent. The process was similar with it in concentrated solutions. All of the above further demonstrated that the shape of polymer **P-I** in its water solution was spherical micelle like a coil.

The absorption spectra of **P-I** in water as a function of temperature are displayed in Figure 3(a). All these experiments were carried out at the equilibration state. At 25°C, **P-I** showed two main peaks at 400 and 433 nm respectively, and a shoulder one at 382 nm. As the temperature was escalated to 35 and 45°C, there were stepwise decreases in the intensity of the absorption band and small red-shift (from 400 at 25°C to 413 nm at 45°C). Moreover, the absorption intensity of the peak at 400 nm decreased more than the peak at 433 nm and the absorption intensity above 500 nm became remarkable when the water temperature was higher than 35°C. When decreasing the solution temperature step by step, the whole UV–Vis spectra did not have distinct changes in shape but exhibited lower intensities. This feature was possibly attributed to the following reasons. As polymer coils changed to collapses, PF blocks tended to pack closely with each other and assembled in partially ordered structure to lower the system energy.[17] Even below the LCST, hence, hydrophobic PF segments inclined to remain chain conformation and packing styles as in collapsed state, because of
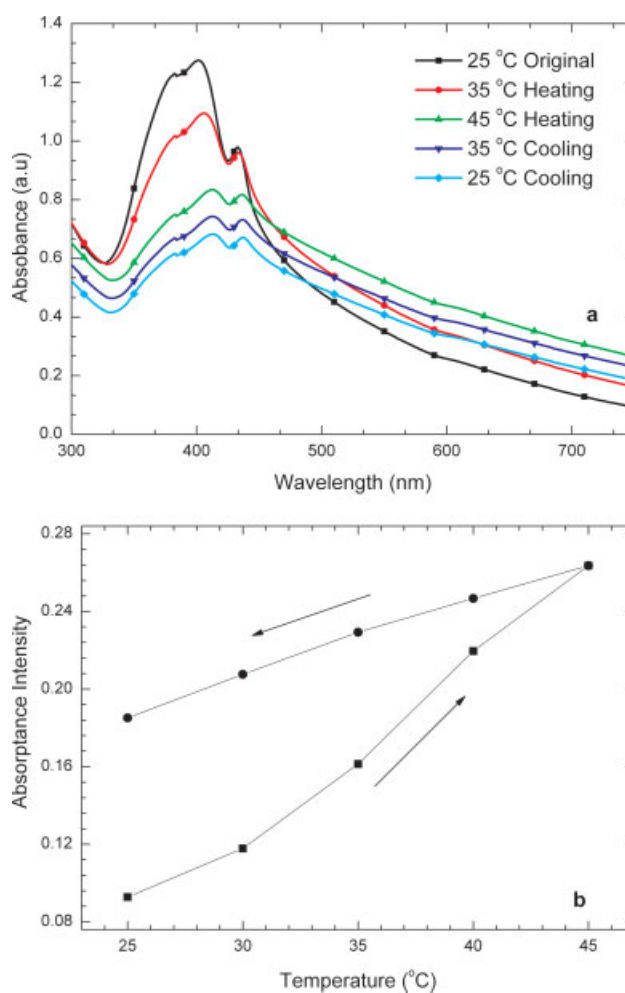

Figure 3 (a) UV-Vis spectra of 2×10^{-3} g/L P-I in deionized water at various temperatures. (b) Absorbance intensity at 750 nm (heating and cooling). [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

π–π interaction between rigid PF chains and system energy optimum. It is not easy and simultaneous for these PF chains to disperse in water again so that the spectra of aggregates were preserved despite of the extension of PNIPAMm chains and the increase in the copolymer solubility. The similar tendency of π-conjugated system to keep the ordered state and the relative suppression of the disordered effect, have also been reported.[34,35] Above 30°C, the polymer solution became cloudy, and a significant increase in the absorption intensity was depicted in Figure 3(b). The cooling curve did not reverse back to the original state, which was in accord with the results of UV spectra. Compared with another temperature-responsive copolymer consisting of fluorene dimmers as side groups,[27] which exhibited thermochromic behavior in water only at a basic condition; and the other thermally responsive analogue with brush structure as aforementioned; it was concluded that the polymer structure played a dramatic role in its stimuli responsive fluorescence. This provides us many alternatives to control and develop multifunctional sensors for various application demands via designing and tuning polymer structures.

CONCLUSIONS

A thermally responsive fluorescent polymer was achieved by combining the optical properties of PF with the simuli responsive capabilities of PNIPAMm. This triblock copolymer was synthesized from end-functionalized macro-initiator and further ATRP. This water-soluble target polymer was characterized by UV, PL, DLS, and AFM. All the measurements demonstrated that in the region of 25–45°C, the polymer underwent a phase transition and the corresponding change in optical properties in its water solution. Furthermore, we investigated the morphology and photophyical properties of this polymer and also found the relatively lower reversibility of this linear triblock copolymer compared with its two analogues with different structures, because of less steric hinderence and more facility to intermolecular aggregation and stacking.

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