Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 46 (2005) 10672–10677

polymer

www.elsevier.com/locate/polymer

Ruthenium-centered thermosensitive polymers

Guangchang Zhou, Issifu I. Harruna*, Conrad W. Ingram

Department of Chemistry, Clark Atlanta University, 223 James P. Brawley Drive SW, Atlanta, GA 30314, USA

Received 19 July 2005; received in revised form 2 September 2005; accepted 7 September 2005
Available online 3 October 2005

Abstract

Bipyridine-centered poly(*N*-isopropylacrylamide) polymers with controlled molecular weight and low polydispersity were synthesized by RAFT polymerization using a novel bipyridine-functionalized dithioester as a RAFT agent, and were further complexed with ruthenium ion to produce ruthenium-centered thermosensitive polymers with well-defined structure. Results from UV–vis, fluorescence and DSC characterizations of the thermosensitive polymeric ruthenium complexes indicated that tris(2,2′-bipyridine)ruthenium(II) ion was successfully grafted onto the center of polymer chains.

Keywords: Tris(2,2′-bipyridine)ruthenium(II) complex; Reversible addition-fragmentation chain transfer (RAFT) polymerization; Thermosensitive polymers

1. Introduction

Stimuli-responsive polymers are polymers that show dramatic property changes in response to an environmental stimulus [1]. Poly(*N*-isopropylacrylamide) (PNIPAM) is one of the most studied stimuli-responsive polymers, exhibiting a lower critical solution temperature (LCST) in water at 32 °C [2]. At temperatures below the LCST, PNIPAM chains are hydrated and adopt flexible and expanded random-coil conformations in water. Above the LCST, PNIPAM chains become dehydrated and collapse into tightly packed globular conformation. Recently, PNIPAM has been extensively altered through the introduction of functional groups for multiresponse to external stimuli such as temperature, pH, solvent composition, salt concentration, light, mechanical stress, and magnetic field [3]. Many potential applications such as biotechnological devices, tissue engineering, immobilization of enzymes, and drug-delivery systems stem from the properties of PNIPAM described above [3].

Ruthenium complexes offer a number of desirable features in electrochemistry and light emitting materials [4,5]. Moreover, ruthenium complexes in a polymer matrix offer several advantages over discrete complexes such as better processability and control over morphology [6,7]. Interestingly, the introduction of metal complexes into polymers can lead to the response of the materials to photo-stimuli [4,5]. Recently, tris(2,2′-bipyridine)ruthenium(II) [$\mathrm{Ru(bpy)_3^{2+}}$, bpy = bipyridine] complexes have been incorporated into a variety of (co)polymers such as polystyrene [8], poly(methyl methacrylate) [9], poly(ε-caprolactone) [10], poly(ethylene glycol) [11] as well as conjugated polymers [12]. Also, $\mathrm{Ru(bpy)_3^{2+}}$ moiety was introduced into PNIPAM chains via radical random copolymerization with a ruthenium(II)-containing comonomer [13,14]. However, the metal complex set on PNIPAM chains, molecular weight and architecture of PNIPAM, which have a large effect on the properties of the final metallopolymers, cannot be well-controlled by conventional radical polymerization. Recently, we reported the synthesis of a novel terpyridine-functionalized RAFT agent and its use in RAFT polymerization of NIPAM for preparation of terpyridine-endfunctionalized polymers [15]. However, in addition to terpyridine-endfunctionalized polymers, bipyridine-centered polymers are also useful precursors for preparation of metallopolymers. For this purpose, we first explored the preparation of $\mathrm{Ru(bpy)_3^{2+}}$-centered poly(*N*-isopropylacrylamide) metallopolymers with well-defined structure via reversible addition-fragmentation chain transfer (RAFT) living polymerization.

2. Experimental

2.1. Materials

2,2′-Azobis(isobutyronitrile) (AIBN, 97%, Aldrich) was purified by recrystallization from methanol.

---

* Corresponding author. Tel.: +1 404 880 6883; fax: +1 404 880 6890.
E-mail address: iharruna@cau.edu (I.I. Harruna).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.09.032

N-Isopropylacrylamide (NIPAM, 97%, Aldrich) was purified by recrystallization from a mixture (60/40, v/v %) of toluene and hexane. Dichlorobis(2,2′-bipyridine)ruthenium(II) hydrate [$Ru(bpy)_2Cl_2 \cdot xH_2O$, 99%] and silver hexafluorophosphate ($AgPF_6$, 99.99%) were purchased from Aldrich and used as received. All other reagents and solvents were used as received unless indicated otherwise. The chain transfer agent **1** was synthesized starting from 5,5′-dimethyl-2,2′-bipyridine [16].

2.2. Measurements

^1H NMR spectra were recorded on a Bruker ARX400 spectrometer at 400 MHz. UV–vis spectra were recorded using a Beckman DU640 spectrophotometer. Fluorescence spectra were recorded on a Photon Technology International (PTI) spectrofluorimeter. SEC was carried out on a Viscotek SEC assembly consisting of a model P1000 pump, a model T60 viscometer-light scattering dual detector, a model LR40 laser refractometer as refractive index detector and three mixed bed columns (bead size: 10 μm, the molecular weight range for those columns is 1000–5,000,000) from American Polymer Standards Corporation using THF as an eluent with a flow rate of 0.7 mL/min at ambient temperature. Polymer solutions for SEC experiments were prepared in a concentration of about 3.0 mg/mL. The SEC system was calibrated using a narrow polystyrene standard ($M_n = 9870$, $M_w = 10,300$, $M_p = 10,300$, $M_w/M_n = 1.04$) from American Polymer Standards Corporation. Differential scanning calorimetry (DSC) measurements were performed using a Seiko DSC 220C, which was calibrated for both temperature and enthalpy using an indium standard, under a nitrogen gas atmosphere with powder samples, heating from −70 to 250 °C at a rate of 10 °C/min. The glass transition temperature, T_g, was defined as the midpoint of the change in heat capacity, and lower critical solution temperature (LCST) as the intersection point of the baseline and the tangent of the endothermic curve.

2.3. N-isopropylacrylamide polymerization procedure and kinetics

A series of parallel polymerizations were carried out under argon, and a detailed polymerization recipe is given in Table 1. For a typical procedure, 2.000 g of NIPAM, 50.0 mg of **1**, 20.0 mg of AIBN and 5.0 ml of 1,4-dioxane were charged into a Schlenk flask equipped with a magnetic stirrer. The mixture was deoxygenated by purging argon for 20 min and then heated at 75 °C under argon in a thermostated oil bath for 3 h. The polymer mixture was precipitated in a large excess of diethyl ether, and isolated by filtration and dried at 50 °C under vacuum to give 0.442 g of poly(*N*-isopropylacrylamide) polymer **PNIPAM-3**. The conversions of the monomer NIPAM were determined to be 19.5% by gravimetrical method. SEC: $M_n = 2090$, $M_w = 2410$, $M_w/M_n = 1.15$.

2.4. Synthesis of $Ru(bpy)_3^{2+}$-centered poly(N-isopropylacrylamide) metallopolymers

$Ru(bpy)_2Cl_2 \cdot xH_2O$ (55.0 mg, 108.6 μmol) was dissolved in MeOH (15 ml), and then $AgPF_6$ (170.5 mg, 0.674 mmol) was added. The purple-red solution was heated at reflux under argon for 19 h. The resultant reddish methanol solution containing a white precipitate was filtered, and then the filtrate was transferred into a 25 ml Schlenk flask and evaporated to almost dryness. Bipyridine-centered PNIPAM polymer **PNIPAM-1** (1.000 g, 29.9 μmol based on the molecular weight of $M_{n,\text{th}} = 33,450$ g/mol), and MeOH (20 ml) were added into the flask. The reaction mixture was deoxygenated by purging argon for half hour, and then heated at reflux for 3 days. The reaction was cooled to room temperature, and then evaporated to almost dryness, followed by the addition of diethyl ether. The precipitated complex was filtered, and further dialyzed for 7 days against deionized H_2O with 1000 MWCO dialysis tubing, then the water was removed under vacuum, followed by the addition of excess diethyl ether to recover the polymer complex. The dialyzed complex was dissolved in THF (30 ml)

Table 1
Experimental conditions and characterization data for RAFT polymerization of *N*-isopropylacrylamide at 75 °C using 1,4-dioxane as reaction media, **1** as a chain-transfer agent, AIBN as an initiator

Sample	NIPAM[a] (mol/l)	RAFT agent **1** (mol/l × 10−2)	AIBN[a] (mol/l × 10−2)	Time (h)	Conv (%)	M_n[b] (theory)	M_n[c] (NMR)	M_n[d] (SEC)	PDI[d]
PNIPAM-1	4.71	1.36	1.62	24	84.3	33,450		6470	1.29
PNIPAM-2[e]	3.54	2.05	2.44	12	60.2	12,260	12,990	3300	1.24
PNIPAM-3[e]				3	19.5	4300	4500	2090	1.15
PNIPAM-4[e]				4	26.8	5730	6040	2270	1.25
PNIPAM-5[e]				8	44.4	9170	9430	2790	1.28
PNIPAM-6[e]				10	52.8	10,810	11,420	3010	1.26

[a] Abbreviations: NIPAM, *N*-isopropylacrylamide; AIBN, 2,2′-azobis(isobutyronitrile).

[b] The theoretical molecular weight was calculated from the expression: $([M]_i/[CTA]_i)f\,M_0 + M_{CTA}$ where $[M]_i$ and $[CTA]_i$ are the initial concentrations of the monomer NIPAM and the transfer agent **1**, respectively, f is the fractional conversion, and M_0, M_{CTA} are the molecular weights of the monomer NIPAM and the used RAFT agent **1**.

[c] Determined by ^1H NMR spectroscopy according to the equation: $M_{n,\text{NMR}} = [I_{4.00}/(I_{8.45}/2)] \times 113.16 + 488.71$, where $I_{4.00}$ and $I_{8.45}$ are integral values of the peaks at $\delta = 4.00$ and 8.45; 113.16 and 488.71 are the molecular weights of NIPAM and **1**, respectively.

[d] Determined by SEC using THF as eluent, and molecular weights were reported as polystyrene equivalents; PDI $= M_w/M_n$.

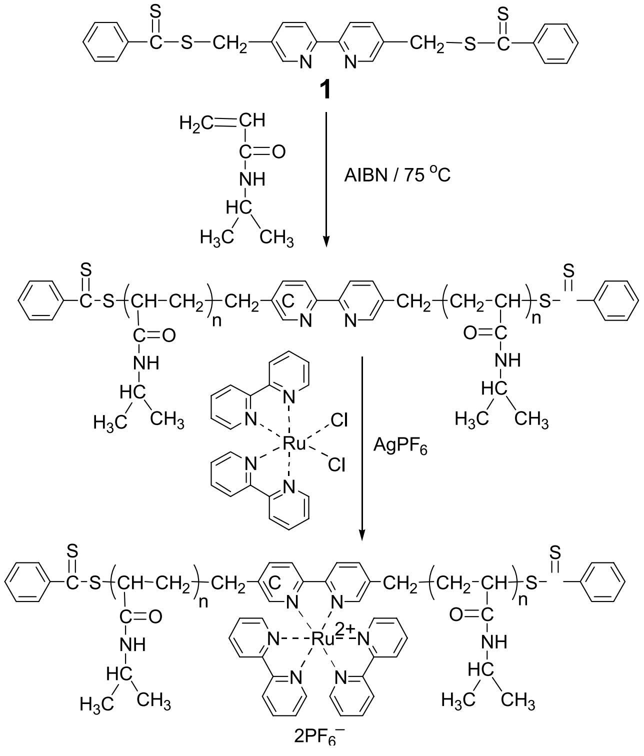
[e] Same experimental condition except polymerization time.

to give a clear solution, then hexane (22 ml) was added dropwise into the clear polymer solution. The uncomplexed poly(*N*-isopropylacrylamide) was left in solution. After the removal of the clear solution by pipette, the precipitate was dried in an oven under vacuum to give 819 mg of pure complex **PNIPAM-1-Ru** (80%).

PNIPAM-2-Ru was similarly prepared as described above using the following reagent loadings and purification conditions. For formation of **PNIPAM-2-Ru**: $Ru(bpy)_2Cl_2\cdot xH_2O$ (55.0 mg, 108.6 μmol), $AgPF_6$ (170.5 mg, 674.4 μmol) and **PNIPAM-2** (600.0 mg, 49.0 μmol based on the molecular weight of $M_{n,\mathrm{th}} = 12{,}257$ g/mol). For purification of **PNIPAM-2-Ru**: 25 ml of tetrahydrofuran (THF) vs. 18 ml of hexane. Yield: 416 mg, 66%.

3. Results and discussion

Since the first RAFT polymerization of NIPAM was reported by Gilbert et al. in 2000 [17], there has been much recent interest in RAFT polymerization of NIPAM with different RAFT agents [15,17–30]. In order to prepare bipyridine-centered thermosensitive polymers, a novel bipyridine-functionalized dithioester **1**, whose structure is shown in Scheme 1, was used for RAFT polymerization of NIPAM. Although **1** has been proven to be efficient for bulk polymerization of styrene [16], it is unclear whether it is efficient for polymerization of NIPAM. Therefore, a series of NIPAM polymerizations were carried out at 75 °C using 1,4-dioxane as reaction media, **1** as a chain transfer agent and AIBN as an initiator for various reaction times (Scheme 1). The polymerization condition and results (concentration, molecular weights, conversion) of these experiments are given in Table 1.



Scheme 1. Schematic representation for preparation of tris(2,2′-bipyridine) ruthenium(II)-centered poly(*N*-isopropylacrylamide) thermosensitive metallopolymers.

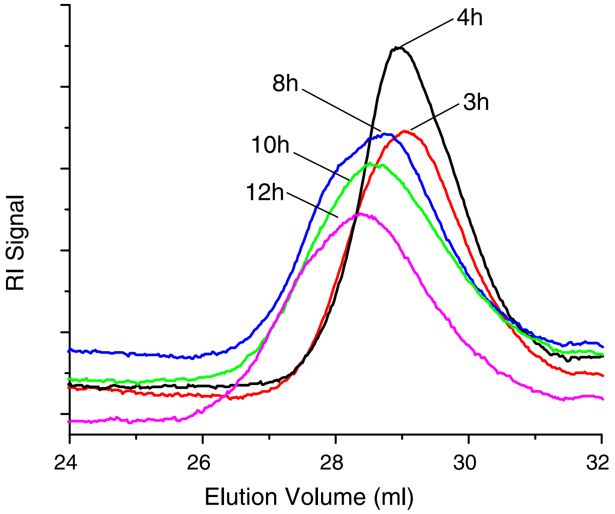


Fig. 1. SEC chromatograms (RI traces) of poly(*N*-isopropylacrylamide)s prepared by RAFT polymerization of NIPAM at 75 °C using 1,4-dioxane as reaction media, **1** as a transfer agent, AIBN as an initiator. [NIPAM] = 3.54 M, [**1**] = 2.05×10^{-2} M, [AIBN] = 2.44×10^{-2} M, [NIPAM]/[**1**]/[AIBN] = 173/1/1.19 (Sample **PNIPAM-2** to **PNIPAM-6** in Table 1).

Fig. 1 shows an overlay of the RI traces from the polymerization of NIPAM at different times. The traces clearly shift to lower elution times with increasing conversion, one indicator of a controlled polymerization. Fig. 2(a) shows the first-order rate plot of $\ln([M]_0/[M])$ vs. polymerization time. A linear relationship was observed which proved that the polymerization exhibits pseudo-first-order kinetics, consistent with a controlled polymerization. As observed from Fig. 2(b), the molecular weights determined by NMR and SEC increased linearly with conversion (the range 19–60%). However, there is marked deviation between the SEC-determined and theoretical molecular weights. The main cause for this discrepancy is that a polystyrene standard ($M_n = 9870$ g/mol) was used for calibration. All the polymerization characteristics indicate that the bipyridine-functionalized dithioester **1** is an efficient RAFT agent for the polymerization of NIPAM.

Fig. 3 is a typical ^{1}H NMR spectrum of RAFT-prepared PNIPAM. Peaks at 4.00 and 8.45 ppm correspond to methine protons of the isopropyl group ($-CH(CH_3)_2$) from repeating unit and the aromatic protons from the RAFT agent **1**, respectively. The molecular weight of PNIPAM was calculated by comparison of the peak area corresponding to polymer repeating unit protons to those corresponding to aromatic protons from the bipyridyl functional group in the center of the polymer chains. The calculated values deviated only slightly from theoretical values (Table 1 and Fig. 2(b)). The good agreement of $M_{n,\mathrm{NMR}}$ with theoretical number-average molecular weight $M_{n,\mathrm{th}}$ indicates that most of PNIPAM chains were centered by the bipyridine-functional group derived from the RAFT agent **1** used for polymerization. Certainly, a few polymer chains do not bear a bipyridine functional group at the center of chains because AIBN-decomposed radicals also

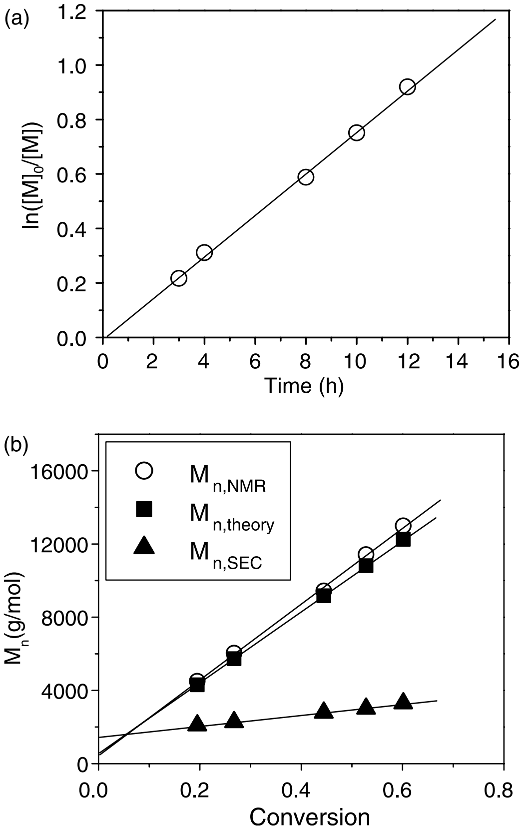


Fig. 2. (a) Pseudo-first order kinetic plot of $\ln([M]_0/[M])$ vs. polymerization time and (b) number-average molecular weights as a function of conversion for RAFT polymerization of NIPAM at 75 °C using 1,4-dioxane as reaction media, **1** as a transfer agent, AIBN as an initiator. $[\mathrm{NIPAM}]=3.54$ M, $[\mathbf{1}]=2.05\times 10^{-2}$ M, $[\mathrm{AIBN}]=2.44\times 10^{-2}$ M, $[\mathrm{NIPAM}]/[\mathbf{1}]/[\mathrm{AIBN}]=173/1/1.19$ (Sample **PNIPAM-2** to **PNIPAM-6** in Table 1).

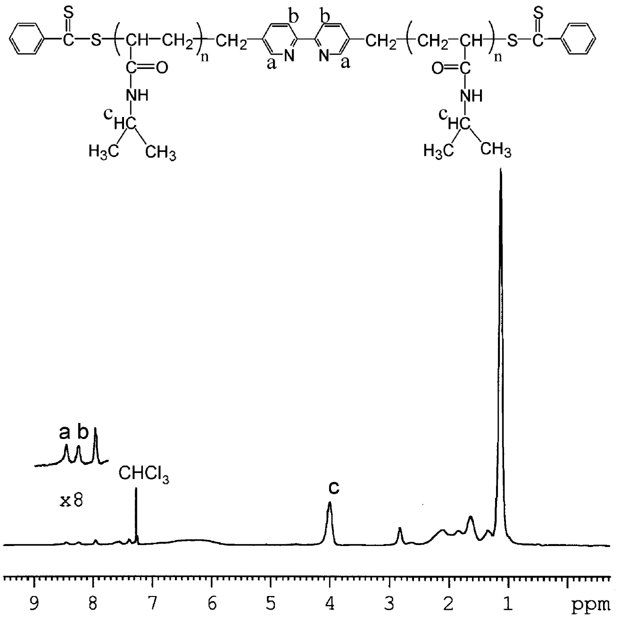


Fig. 3. ^{1}H NMR spectrum ($CDCl_3$) of the RAFT-prepared polymer **PNIPAM-3** using **1** as a RAFT agent.

participate in initiating polymerization. The content of the polymers without bipyridine functional groups depends mainly on the amount of the efficient radicals formed from initiators. In this case, the concentration of the initiator AIBN is a little high. This should result in the higher content of non-bipyridine-centered polymer chains in the resulting polymers. However, the good agreement between the theoretical and NMR-determined molecular weights indirectly reflected that the initiation efficiency of AIBN was quite low due to the incomplete removal of oxygen in polymerization mixture by purging argon.

To form thermosensitive metallopolymers, two RAFT-prepared bipyridine-centered PNIPAM polymers (**PNIPAM-1** and **PNIPAM-2** in Table 1), were further complexed with $Ru(bpy)_2(PF_6)_2(MeOH)_2$ in methanol prepared in advance under reflux for 3 days separately (Scheme 1). Meanwhile, the metallation reaction was monitored using UV–vis technique. A shift of MLCT (metal-to-ligand charge transfer) absorption maximum of the bis(bpy) system, $Ru(bpy)_2(PF_6)_2(MeOH)_2$, at 488 nm to the tris(bipyridine)Ru(II) at 453 nm after refluxing for 20 h (Fig. 4) was observed. After reacting for 72 h, the solvent (methanol) was removed under reduced pressure, and excess diethyl ether was added to precipitate the crude polymer complex.

The crude complex was further dialyzed for 7 days against deionized H_2O with 1000 MWCO dialysis tubing in order to remove excess of $Ru(bpy)_2(PF_6)_2(MeOH)_2$, then the water was removed under vacuum, followed by the addition of excess diethyl ether to recover the polymer complex. The uncomplexed poly(*N*-isopropylacrylamide) was removed according to the following typical procedure. The specific weight ratio χ_w in the THF-hexane mixture at room temperature, under which the complex can be precipitated out, was first determined ($\chi_w=1.870$ for **PNIPAM-1-Ru**, 1.834 for **PNIPAM-2-Ru**). Meanwhile, χ_w was also determined for precipitating its corresponding precursor polymer ($\chi_w=1.595$ for **PNIPAM-1**, 1.282 for **PNIPAM-2**), then an amount of the crude polymer

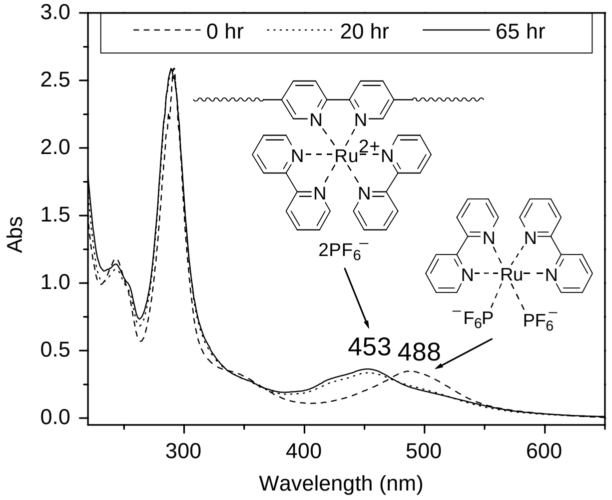


Fig. 4. The UV–vis spectra of the methanolic reaction mixture consisting of **PNIPAM-2** and the red precursor complex, $Ru(bpy)_2(PF_6)_2(MeOH)_2$, at various reaction times.

complex was dissolved in THF weighed in advance to give a clear solution, then a suitable amount of hexane was added dropwise into the clear polymer complex solution (the amount of hexane added can be calculated using χ_w for the complex and the amount of THF used). Specifically, the crude polymer complex **PNIPAM-1-Ru** was dissolved in a volume of THF to give a clear solution, then 0.71 fold THF (for the complex **PNIPAM-2-Ru**, 0.68 fold) volume of hexane was added dropwise into the clear polymer complex solution resulting in the precipitation of the complex while the uncomplexed poly(*N*-isopropylacrylamide) was left in the solution. The pure complex was obtained after the removal of the clear solution by pipette and dried under vacuum. Thus two pure complexes, **PNIPAM-1-Ru** and **PNIPAM-2-Ru**, were obtained.

The purified complexes were characterized by both UV–vis spectroscopy and fluorescence technique. Their UV–vis spectra (Fig. 5(a)) exhibit a new absorption band at 453 nm attributed to characteristic MLCT (metal-to-ligand charge transfer) absorption band of tris(bipyridine)Ru(II) unit as compared with the corresponding precursor polymers. Moreover, the fluorescence spectra of these complexes, **PNIPAM-1-Ru** and **PNIPAM-2-Ru**, are different from that of their corresponding precursor **PNIPAM-1** and **PNIPAM-2** (Fig. 5(a) and (b)). The emission spectrum of the complexes show only the well-known $Ru(bpy)_3^{2+}$ band with $\lambda_{max} = 605$ nm. This indicated the successful grafting of the ruthenium bis(bipyridine) onto the center of the polymers.

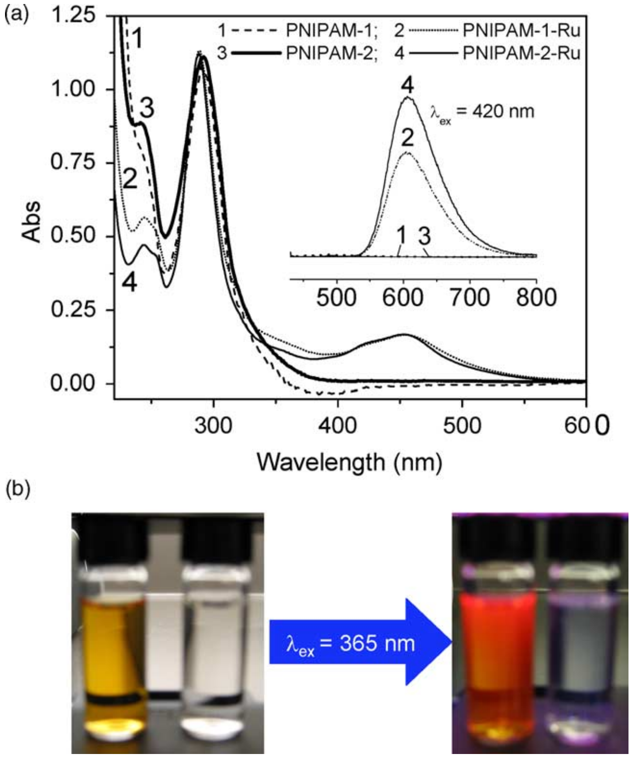


Fig. 5. (a) UV–vis spectra with insertion of emission spectra (H_2O) of the supramolecular polymeric ruthenium complexes **PNIPAM-1-Ru** and **PNIPAM-2-Ru** as well as their corresponding bipyridine-centered precursor polymers **PNIPAM-1** and **PNIPAM-2**. (b) Photos taken before and when exposed to 365 nm UV light of the polymeric ruthenium complexes **PNIPAM-2-Ru** (left vial) and its corresponding precursor **PNIPAM-2** (right vial) (0.1 wt% polymer in H_2O).

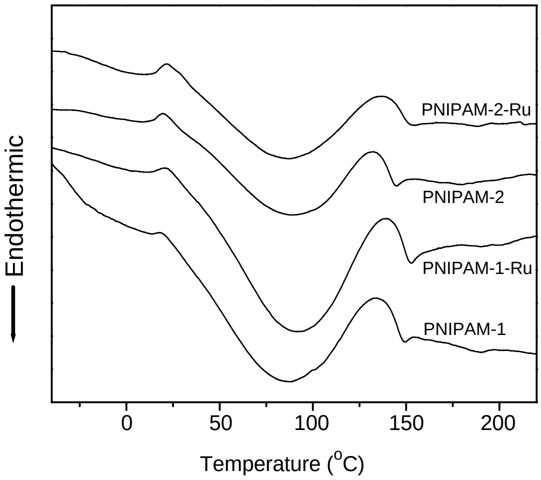


Fig. 6. DSC curves of the supramolecular polymeric ruthenium complexes **PNIPAM-1-Ru** and **PNIPAM-2-Ru** as well as their corresponding bipyridine-centered precursor polymers **PNIPAM-1** and **PNIPAM-2**.

Since the change of the microstructure of the polymer chains can affect the flexibility of the polymer chains, which is only one contributing factor to glass transition temperature, it is feasible to observe the change of the backbone structure through the measurement of the change of glass transition temperature. Therefore, thermal characterization of the two PNIPAM complexes **PNIPAM-1-Ru** and **PNIPAM-2-Ru** as well as their corresponding precursor polymers **PNIPAM-1** and **PNIPAM-2** were performed by differential scanning calorimetry (DSC). Their DSC curves are displayed in Fig. 6. In all cases, two transitions were evident in the DSC curve of each sample; the lower transition corresponds to the LCST, the higher transition is T_g. T_gs and LCSTs of these samples are listed in Table 2. The value of T_g for the precursor PNIPAM homopolymers found in this work (140 °C for **PNIPAM-2** and 142 °C for **PNIPAM-1**) is in accordance with the previously reported values 135 and 145 °C [31]. The glass transition temperatures of all polymer complexes are higher than their corresponding precursor polymers (Table 2) due to the incorporation of the hexacoordinated tris(bipyridine)ruthenium (II) complex into the center of the polymer chain.

The phase transition temperatures, LCSTs, of the two complexes and their corresponding precursor polymers were also measured by turbidimetric method. The data are summarized in Table 2. For each sample, its LCST determined

Table 2
Glass transition temperature (T_g) and LCST of the **PNIPAM** complexes and their corresponding precursor polymers

Sample	LCST (°C)[a]	$LCST_{DSC}$ (°C)[b]	T_g (°C)[b]
PNIPAM-1	32	32	142
PNIPAM-1-Ru	34	35	146
PNIPAM-2	31	31	140
PNIPAM-2-Ru	35	37	149

[a] Determined by turbidimetric method.
[b] Determined by DSC thermograms.

by turbidimetric measurements is in good agreement with that determined by DSC. The increase in both LCST and T_g of the PNIPAM complex as compared with its corresponding precursor polymer shows the RAFT-prepared bipyridine-centered PNIPAM was successfully complexed with ruthenium (II) metal ion to give a thermosensitive PNIPAM metallopolymer.

4. Conclusions

The novel bipyridine-functionalized dithioester **1** is an efficient RAFT agent for polymerization of *N*-isopropylacrylamide, thus the polymers produced were centered by a bipyridine functional group and its molecular weight was well-controlled. The bipyridine-centered PNIPAM polymers were further reacted with $Ru(bpy)_2(II)$ ion to produce thermosensitive metallopolymers. The successful metallation was confirmed by UV–vis, fluorescence, and DSC techniques as well as thermosensitive behavior. Moreover, the introduction of $Ru(bpy)_3^{2+}$ into the center of the polymer chains resulted in the increase in LCST of PNIPAM.

Acknowledgements

The financial support for this research work from the Office of Naval Research (ONR Grant # N00014-01-1-1042) is gratefully acknowledged. We thank Dr Airan Perez of the Office of Naval Research, Arlington, VA for helpful discussions.

References

[1] For example, see:McCormick CL, editor. Stimuli-responsive water soluble and amphilic polymers. ACS symposium series 780. Washington, DC: American Chemical Society; 2001.
[2] Heskins M, Guillet JE. J Macromol Sci Chem 1968;A2:1441–55.
[3] Haraguchi K, Takehisa T, Fan S. Macromolecules 2002;35:10162–71 [references therein].
[4] Lyons CH, Abbas ED, Lee JK, Rubner MF. J Am Chem Soc 1998;120: 12100–7.
[5] Yu SC, Gong X, Chan WK. Macromolecules 1998;31:5639–46.
[6] Knapp R, Schott A, Rehahn M. Macromolecules 1996;29:478–83.
[7] (a) Schultze X, Serin J, Adronov A, Fréchet JMJ. Chem Commun 2001; 1160–1.
(b) Serin J, Schultze X, Adronov A, Fréchet JMJ. Macromolecules 2002; 35:5396–404.
[8] (a) Smith AP, Fraser CL. J Polym Sci, Part A: Polym Chem 2002;40: 4250–5.
(b) Wu X, Collins JE, McAlvin JE, Cutts RW, Fraser CL. Macromolecules 2001;34:2812–21.
[9] (a) Holder E, Meier MAR, Marin V, Schubert US. J Polym Sci, Part A: Polym Chem 2003;41:3954–64.
(b) Marin V, Holder E, Schubert US. J Polym Sci, Part A: Polym Chem 2004.
[10] Marin V, Holder E, Hoogenboom R, Schubert US. J Polym Sci, Part A: Polym Chem 2004;42:4153–60.
[11] Marin V, Holder E, Meier MAR, Hoogenboom R, Schubert US. Macromol Rapid Commun 2004;25:793–8.
[12] (a) Pautzsch T, Klemm E. J Polym Sci, Part A: Polym Chem 2004;42: 2911–9.
(b) Pautzsch T, Blankenburg L, Klemm E. J Polym Sci, Part A: Polym Chem 2004;42:722–32.
[13] (a) Ito Y, Nogawa M, Yoshida R. Langmuir 2003;19:9577–9.
(b) Sasaki S, Koga S, Yoshida R, Yamaguchi T. Langmuir 2003;19: 5595–600.
[14] Yoshida R, Takahashi T. J Am Chem Soc 1996;118:5134–5.
[15] Zhou G, Harruna II. Macromolecules 2005;38:4114–23.
[16] Zhou G, Harruna II. Macromolecules 2004;37:7132–9.
[17] Ganachaud F, Monteiro MJ, Gilbert RG, Dourges M-A, Thang SH, Rizzardo E. Macromolecules 2000;33:6738–45.
[18] Schilli C, Lanzendörfer MG, Müller AHE. Macromolecules 2002;35: 6819–27.
[19] Schilli CM, Zhang M, Rizzardo E, Thang SH, Chong YK, Edwards K, et al. Macromoleculers 2004;37:7861–76.
[20] Costioli MD, Berdat D, Freitag R, André X, Müller AHE. Macromolecules 2005;38:3630–7.
[21] Arotçaréna M, Heise B, Ishaya S, Laschewsky A. J Am Chem Soc 2002; 124:3787–93.
[22] Ray B, Isobe Y, Matsumoto K, Habaue S, Okamoto Y, Kamigaito M, et al. Macromolecules 2004;37:1702–10.
[23] Zhu M-Q, Wang L-Q, Exarhos GJ, Li ADQ. J Am Chem Soc 2004;126: 2656–7.
[24] Convertine AJ, Ayres N, Scales CW, Lowe AB, McCormick CL. Biomacromolecules 2004;5:1177–80.
[25] Savariar EN, Thayumanavan S. J Polym Sci, Part A: Polym Chem 2004; 42:6340–5.
[26] Shan J, Nuopponen M, Jiang H, Kauppinen E, Tenhu H. Macromolecules 2003;36:4526–33.
[27] Shan J, Nuopponen M, Jiang H, Viitala T, Kauppinen E, Kontturi K, et al. Macromolecules 2005;38:2918–26.
[28] Hales M, Barner-Kowollik C, Davis TP, Stenzel MH. Langmuir 2004;20: 10809–17.
[29] Hong C-Y, You Y-Z, Pan C-Y. Chem Mater 2005;17:2247–54.
[30] Feng X-S, Pan C-Y. Macromolecules 2002;35:4888–93.
[31] (a) E Silva MESR, Dutra ER, Mano V, Machado JC. Polym Degrad Stab 2000;67:491–5.
(b) Bae SS, Chakrabarty K, Seery TAP, Weiss RA. J Macromol Sci Pure Appl Chem 1999;A36:931–48.