

Synthesis of Star-Shaped Poly(*N*-isopropylacrylamide) *via* Atom Transfer Radical Polymerization and Its Photocatalytic Oxidation of Rhodamine B

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Abstract: Zinc(II) tetra-(2-chloropropionylamido) phthalocyanine (TAPcCl) was synthesized as the initiator for atom transfer radical polymerization (ATRP). Using CuBr/tris(2-dimethylaminoethyl)amine as the catalyst system, ATRP of *N*-isopropylacrylamide (NIPAM) was performed to create a new star-shaped poly(*N*-isopropylacrylamide) (PNIPAM) with a zinc phthalocyanine core and PNIPAM arms (TAPc-PAM). The structures of the initiator and the polymers were characterized by means of Fourier transform infrared spectroscopy and proton nuclear magnetic resonance. The polydispersity index obtained by gel permeation chromatography indicated that the molecular weight distribution was narrow. The lower critical solution temperatures (LCST) for the TAPc-PAM aqueous solutions measured using the turbidimetry method were increased due to incorporation of the phthalocyanine core and decreased as molecular weight increased. TAPc-PAM possessed photocatalytic activity, a finding that was verified by Rhodamine B degradation in the presence of hydrogen peroxide under visible light. Moreover, the catalytic efficiency was higher at its LCST, which encouraged reuse of the photocatalyst.

Keywords: poly(*N*-isopropylacrylamide), phthalocyanine, atom transfer radical polymerization, photocatalytic oxidation, Rhodamine B.

Introduction

Owing to the intense absorption in the visible region at 600-800 nm (called Q band) and high quantum yield of excited triplet states, much attention has been paid on the phthalocyanine derivatives in many fields, such as chemical sensors, photodynamic therapy, electrochromic displays, catalysts for oxidative degradation, information storage systems, nonlinear optics and so on.¹⁻⁵ In the field of catalytic oxidation, metallophthalocyanines were of more efficient catalytic activity in the photocatalytic reactions. Among the metallophthalocyanines investigated, most were water-soluble with hydrophilic substitutions,^{6,7} *i.e.* sulfonic group, carboxyl group and their corresponding salts, which could contact with the substrate and form the coordination in the homogeneous solutions. The catalytic efficiency was high in the homogeneous system, but it was difficult to separate the catalysts from the system and caused the secondary pollution. The phthalocyanine complexes tended to aggregate in solution, which had direct influence on their physical and chemical properties. It was efficiently avoided by the method

of immobilizing the catalyst on the supporting medium,⁸⁻¹⁰ however, the transmittance of the solution was decreased by incorporation of the support, which lowered the catalytic activity consequently. Thus, it is of great significance to develop a photocatalyst which is water-soluble and facilitates the recycling.

As one of the most extensively studied stimuli-responsive polymer, poly(*N*-isopropylacrylamide) (PNIPAM) has a reversible phase transition at *ca.* 32 °C (the lower critical solution temperature, LCST).¹¹⁻¹³ It has been widely used in many fields, such as drug delivery systems, separation and purification, nanotechnology and bioengineering.¹⁴⁻¹⁹ The thermo-responsive property can be used to advantage for catalyst recycling by simple heating and filtration. Combining PNIPAM with phthalocyanine derivatives, the polymer possessed both the thermo-responsive property and the catalytic activity. This will avoid the aggregation behavior of the phthalocyanine in solutions and facilitates the recycling of the catalyst. Chen and coworkers reported the preparation of several novel polymeric catalysts containing phthalocyanine groups derived from the tetraaminophthalocyanines.^{20,21} The investigations showed the water-soluble photocatalysts possessed high catalytic activity on the oxidation of phenols

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and thiols under the visible light irradiation.

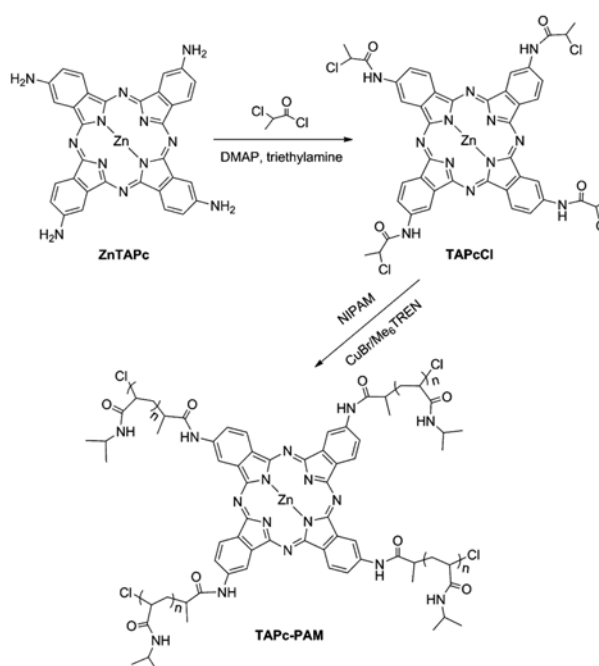
However, it is difficult to obtain the polymer with narrow molecular weight distribution and well-defined structure by traditional radical polymerization, which will affect the property accordingly. In the past few years, controlled/"living" radical polymerization (CRP) has been widely developed, which provides an efficient way of synthesizing polymers with designed structure and narrow molecular weight distribution. Atom transfer radical polymerization (ATRP), one of the most investigated CRP, can provide polymers with well-defined structure using suitable initiators.²²⁻²⁶ Recently, our group synthesized several end-functionalized PNIPAMs and the thermo-responsive properties were also studied.²⁷⁻²⁹

To the best of our knowledge, there were few reports on the ATRP of *N*-isopropylacrylamide (NIPAM) with phthalocyanine derivatives as the initiator. Using the "core-first" method, the star polymer TAPc-PAM, with zinc phthalocyanine as the core and PNIPAM as the arms, was synthesized *via* ATRP with zinc(II) tetra-(2-chloropropionylamido) phthalocyanine (TAPcCl) as the initiator and CuBr/Me₆TREN as the catalyst system in the mixed solvents of DMF and water at 70 °C. The polymer with low polydispersity possessed both thermo-responsive property and photocatalytic activity. Then the photocatalytic activity was tested on the oxidative degradation of Rhodamine B (Rh B) under the visible light irradiation and the recycling experiments were conducted.

Experimental

Materials. *N*-Isopropylacrylamide (99%, Aldrich) was recrystallized twice from benzene/hexane (10:1, v/v) prior to use; 2-chloropropionyl chloride (99%, Acros); copper(I) bromide (CuBr, 99%, Aldrich); 4-dimethylaminopyridine (DMAP, 99%, Alfa Aesar); cellophane tube (MWCO 2000, Solarbio); tris(2-(dimethylamino)ethyl)amine (Me₆TREN) was synthesized according to the literature;³⁰ The precursor zinc(II) tetraaminophthalocyanine (ZnTAPc) was synthesized by the literature method.³¹ All other chemicals were purchased from Sinopharm Chemical Reagent Co. and were used as received.

Characterization. All nuclear magnetic resonance (NMR) spectra were recorded on a Unity 400 (Varian) NMR spectrometer with DMSO-*d*₆ as the solvents. Fourier transform infrared (FTIR) spectra were recorded on a FTIR 8400S (Shimadzu) spectrometer. The spectra were collected at 40 scans with a resolution of 4 cm⁻¹. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) equipped with Waters 600 pump and Waters 410 differential refractometer at 25 °C. The eluent was THF at a flow rate of 1.0 mL/min. A series of low polydispersity polystyrene (PS) standards were employed for GPC calibration. Ultraviolet-visible (UV-vis) spectra were measured on a UV mini 1240 (Shimadzu)



Scheme I. Synthetic route for the star-shaped TAPc-PAM.

spectrophotometer.

Synthesis of Zinc(II) Tetra-(2-chloropropionylamido) Phthalocyanine (TAPcCl): The initiator TAPcCl was synthesized as shown in Scheme I. ZnTAPc (0.64 g, 1 mmol), DMAP (24 mg), triethylamine (1.2 mL) were added to the flask charged with DMF (20 mL) and cooled to 0 °C under a nitrogen atmosphere. 2-Chloropropionyl chloride (0.8 mL, 8 mmol) was added dropwise to the solution, the mixture was stirred for 1 h at 0 °C and then 48 h at room temperature. After filtration, the filtrate was evaporated under reduced pressure. The residue resolved in CHCl₃ and washed with 5% NaCO₃ aqueous solution and H₂O, then dried over anhydrous MgSO₄. After removal of the solvent, the crude product was purified by column chromatography (SiO₂, CHCl₃/methanol, 10:1). 0.86 g, Yield: 87%. FTIR (KBr, cm⁻¹): 1703 (C=O), 1629, 1510 (C=C-C). ¹H NMR (δ , DMSO-*d*₆, ppm): 10.61, 9.54, 9.05 (each s, 3H, ArH), 8.29 (s, 3H, NH), 5.00 (s, 3H, CH), 1.89 (t, 12H, CH₃).

Synthesis of Star-Shaped Polymer (TAPc-PAM): A general procedure employed for the preparation of TAPc-PAM was as follows. After deoxygenated by bubbling with nitrogen, NIPAM (1.13 g, 10 mmol), CuBr (29 mg, 0.2 mmol), Me₆TREN (22 μ L, 0.2 mmol) were dissolved in 5 mL of DMF/water (9:1, v/v), followed by degassing *via* three freeze-pump-thaw cycles. Deoxygenated solution of TAPcCl (50 mg, 0.05 mmol) in DMF (0.5 mL) was then added into the reaction flask to start the polymerization. The reaction was carried out for 8 h at 70 °C under a nitrogen atmosphere. Polymerization was terminated by exposed to air. Then the reaction mixture was diluted with THF and passed through an alumina column. The resulting polymer was purified by

dialysis using a cellophane tube (MWCO, 2000) in DMF. After removing the solvents, the residue was dried in *vacuo* for 24 h to give the polymer TAPc-PAM.

Cloud Points Measurement. Cloud points (CP) of the aqueous solution of TAPc-PAM were measured by UV-vis spectroscopy. The sample dissolved in water (2 mg/mL) was poured into a thermally controlled cell (1 cm×1 cm). Transmittance of the aqueous solution at 500 nm was monitored with heating rate of 0.5 °C/min.

Photocatalytic Degradation Test. Catalytic oxidation of Rh B was carried out in the aqueous solution at room temperature using hydrogen peroxide (H₂O₂) as the oxidant under the visible light irradiation (using a 500 W Halogen lamp through a glass filter ($\lambda > 450$ nm) as the irradiation source). The pH value of the solution was adjusted by adding standard buffer solutions, and the initial concentration of Rh B solution was 5×10^{-5} mol/L. After the polymeric catalyst TAPc-PAM ($M_{n,GPC} = 6,250$, $M_w/M_n = 1.13$) was added into Rh B solution under stirring, the samples (3 mL) were monitored immediately at given time intervals on a UV-vis spectrometer.

Results and Discussion

Synthesis and Characterization. The initiator TAPcCl was synthesized by the reaction of 2-chloropropionyl chloride with the amino groups in ZnTAPc in the presence of DMAP and triethylamine. After purification, the structure was characterized by ¹H NMR and FTIR. For the ¹H NMR spectrum of TAPcCl in Figure 1(a), the signals at 10.61, 9.54, 9.05, and 8.29 ppm were assigned to the protons in the

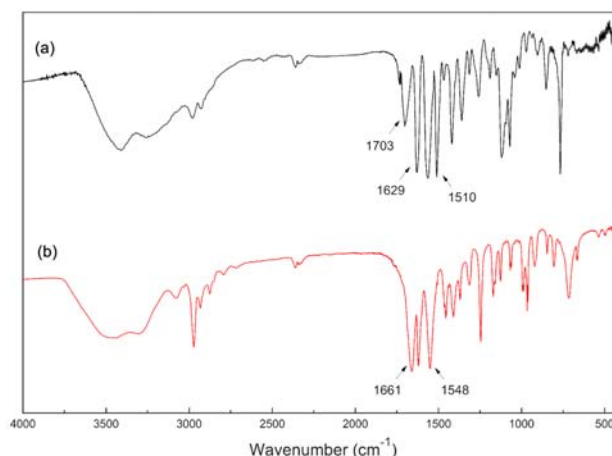


Figure 2. FTIR spectra of (a) TAPcCl and (b) TAPc-PAM.

imino group and aromatic ring in phthalocyanine, respectively. The signals of protons in the chloropropionate residues were located at 1.89 ppm. By the ¹H NMR analysis, the structure of TAPcCl was symmetrical tetrachlorophthalocyanine. It also can be obviously seen the characteristic absorption peaks of the carbonyl group (1703 cm⁻¹, $\nu_{C=O}$) and the skeleton in phthalocyanine (1629 and 1510 cm⁻¹, ν_{C-C}) in Figure 2(a), which indicated the incorporation of the chloropropionate residues.

As far as we knew, there were no reports on the ATRP of NIPAM with phthalocyanine derivatives as the initiator. In the present work, TAPcCl was employed as the initiator for the ATRP of NIPAM. The polymerizations were carried out in the mixed solvent of DMF/water (10:1, v/v) at 70 °C

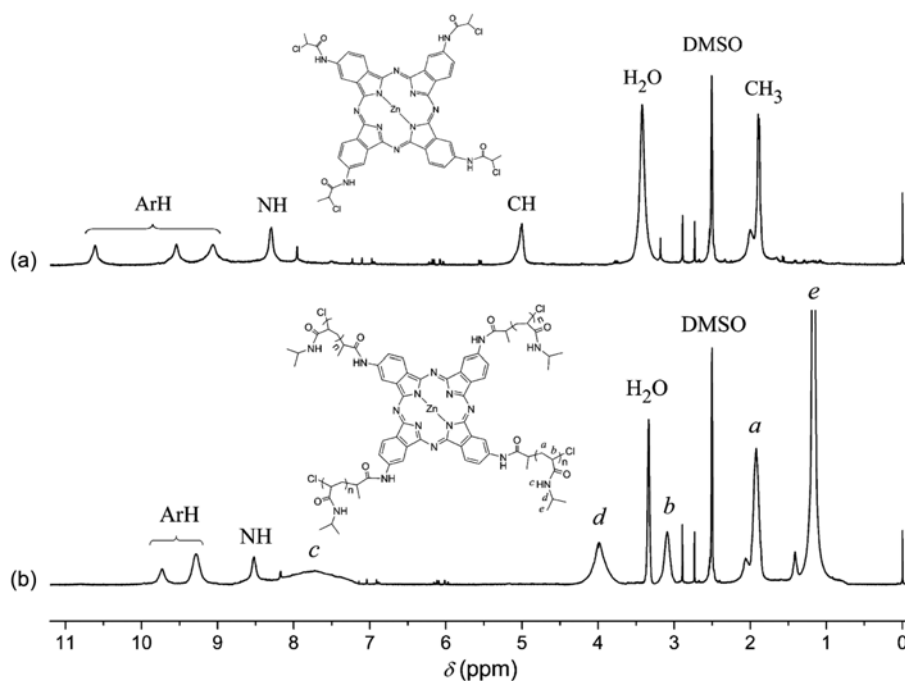
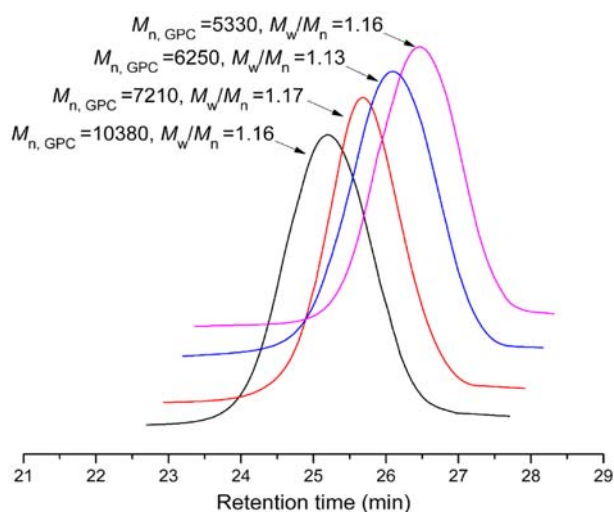


Figure 1. ¹H NMR spectra of (a) TAPcCl and (b) TAPc-PAM in DMSO-*d*₆.

Table I. Data of the Polymerization Reactions and LCST of TAPc-PAM Samples

Time (h)	Conv. ^a (%)	M_n^b	M_w^b	PDI ^b	LCST ^c (°C)
6	20	5,330	6,180	1.16	42.6
8	24	6,250	7,060	1.13	41.2
10	29	7,210	8,440	1.17	40.3
16	42	10,380	12,040	1.16	38.6

^aDetermined by gravimetric measurement. ^bDetermined by GPC using THF as eluent relative to polystyrene standards. ^cMeasured by turbidimetry using UV-vis spectrophotometer.

**Figure 3.** GPC traces of TAPc-PAM synthesized through ATRP.

using CuBr/Me₆TREN as the catalyst system. The feed ratio of [NIPAM]₀:[TAPcCl]₀:[CuBr]₀:[Me₆TREN]₀ was 200:1:4:4. Table I summarizes the results of the polymerization reactions. Considering the effect of the phthalocyanine core, the molecular weights of the polymer were relatively low. The relative molecular weight and the polydispersity index (PDI) were obtained through gel permeation chromatography (GPC). After a series of purifications, GPC traces of TAPc-PAM (shown in Figure 3) were relatively symmetric and showed no tailing at either side. It suggested the absence of any small molecule residues in the final product, such as the initiator, monomer or other byproducts, and it also provided an indication of efficient initiation and the symmetrical architecture of the polymer. Moreover, the polymers possessed low PDI with values between 1.13 and 1.17, which demonstrated that the polymerizations were performed in a controlled process.^{22,25}

¹H NMR spectrum of TAPc-PAM in DMSO-*d*₆ and the corresponding peak assignments are shown in Figure 1(b). The signals at 7.76, 4.0, 3.12, 1.94, and 1.16 ppm assigned to the protons in the repeated units NIPAM can be clearly observed. Moreover, the signals appear at 9.72, 9.28, and 8.52 ppm were attributed to the protons in phthalocyanine

core. ¹H NMR signals associated with 2-chloropropionate residues in TAPcCl are clearly discernible at 1.41 ppm (methyl proton). The molecular weight could be estimated by comparing the resonance signals in the aromatic part of the phthalocyanine group with those of the methine protons in NIPAM. The molecular weight of TAPc-PAM ($M_{n, GPC}$ = 6,250) determined by the ¹H NMR analysis was 6400, which was higher than that determined by the GPC analysis. This might be because the hydrodynamic volume of star-shaped polymer was somewhat smaller compared with that of the linear analogue of the same molecular mass.

The structure of TAPc-PAM was also characterized by FTIR spectrum (as shown in Figure 2(b)). The absorption peaks characteristic of PNIPAM can be clearly observed, as evidenced by the presence of a carbonyl stretching vibration (the secondary amide I band, $\nu_{C=O}$) with a weak red-shift to 1661 cm⁻¹ and the N-H bending vibration (the secondary amide II band, δ_{N-H}) at 1548 cm⁻¹. The strong absorbance at 3305 cm⁻¹ was assigned to the stretching vibration (ν_{N-H}) of acylamino group. And the characteristic peaks of the phthalocyanine skeleton located at 1620 and 1456 cm⁻¹. Thus, it was suggested that the star-shaped TAPc-PAM with phthalocyanine as the core and PNIPAM as the arms was successfully prepared through ATRP.

It is known that the phthalocyanine derivatives tend to aggregate in solution, which has direct influence on their properties. The electronic absorption spectra can be employed to reveal the aggregation behaviors of the phthalocyanine complexes.^{32,33} Figure 4(a) shows the UV-vis spectra of TAPcCl and TAPc-PAM in DMF. It is obviously seen that both have the B-band and Q-band characteristic of the phthalocyanine derivatives in the UV-vis range. The spectrum of TAPc-PAM has a strong sharp peak at 687 nm around which is the characteristic of nonaggregated zinc phthalocyanine. The maximum absorption wavelength (λ_{max}) of TAPc-PAM was somewhat blue-shifted relative to that of the initiator TAPcCl due to the PNIPAM arms. Besides, the solubility of TAPc-PAM was improved, which could dissolve in water and the common organic solvents. As can be seen from the UV-vis spectra of TAPc-PAM in aqueous solution with different concentrations in Figure 4(b), the Q-bands were not broadened and there were no shoulder peaks appeared with the increasing of the concentrations. It could be concluded that aggregations of the phthalocyanine complex were avoided efficiently by combination with PNIPAM.

Thermo-Responsive Property of TAPc-PAM. To determine the phase transition temperature of TAPc-PAM, the transmittance of the TAPc-PAM aqueous solution was measured using UV-vis spectroscopy. The aqueous solution of TAPc-PAM was clear at low temperature and became turbid by raising the temperature. Figure 5 shows the temperature-dependent transmittance of TAPc-PAM in aqueous solution. It is obvious that there is a sharp transition in the CP curve, which indicates the thermo-responsive property of TAPc-

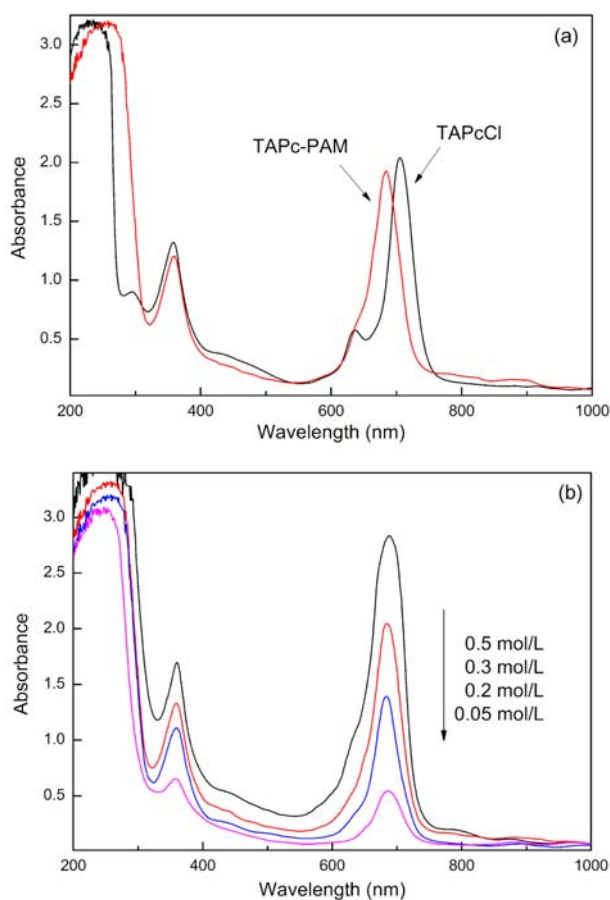


Figure 4. (a) UV-vis spectra of TAPcCl and TAPc-PAM in DMF (0.3 mol/L), and (b) UV-vis spectra of the aqueous solutions of TAPc-PAM with different concentrations.

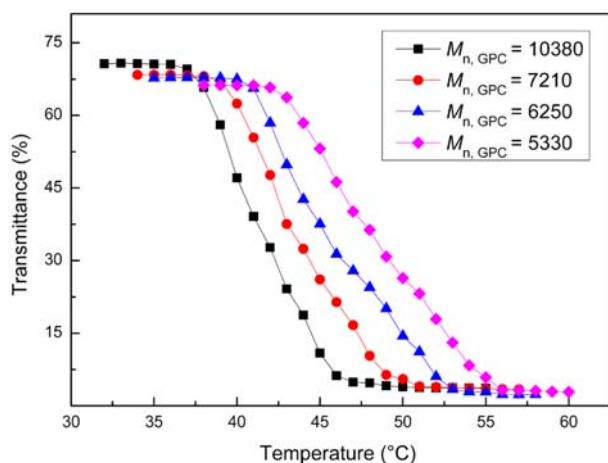


Figure 5. Temperature dependence of optical transmittance at wavelength of 500 nm obtained for aqueous solutions of TAPc-PAM (2 mg/mL).

PAM. In the current study, the LCST was arbitrarily defined as the temperature corresponding to a 10% decrease of the transmittance at 500 nm. The LCSTs of the aqueous solu-

tions of TAPc-PAM with the $M_{n,GPC}$ of 5,330, 6,250, 7,210, and 10,380 were 42.6, 41.2, 40.3, and 38.6 °C, respectively (as listed in Table I), which were higher than that of PNIPAM homopolymer. Unexpectedly, this phenomenon was not consistent with the reports that the hydrophobic groups decreased the thermal phase transition temperature of PNIPAM.^{34,35} We thought this might be because the amide group in the phthalocyanine core could form hydrogen bond with water, which increased the LCST of TAPc-PAM on the whole although TAPcCl was hydrophobic. In addition, the LCST values of the TAPc-PAM samples lowered and approached to 32 °C around commonly reported for PNIPAM with the increasing of molecular weight. This was attributed to the lowered proportion of phthalocyanine core in the polymer chain as the increasing of molecular weight, the effect of the phthalocyanine core on the performance of polymer became weaker accordingly.

Photocatalytic Activity of TAPc-PAM on Rh B. We choose Rhodamine B, a kind of commercial non-biodegradable toxic dye with aromatic structure, as the target to investigate the catalytic performance of TAPc-PAM under the visible light irradiation. The degradation of Rh B in aqueous solution was estimated by the changes of the absorption intensity at the maximum absorption wavelength (around 550 nm). The degradation rate (D) can be defined as the ratio of the absorbance decrement to the initial of the Rh B aqueous solution as described as follows,

$$D (\%) = \frac{A_0 - A}{A_0} \times 100$$

where A_0 is the initial absorption intensity at 550 nm, and A is the absorption intensity at any time during the measurement.

In previous works, the catalytic degradation of organic pollutants using H_2O_2 as the oxidant and metallophthalocyanine as the photocatalyst were investigated detailedly.³⁶⁻³⁸ To verify whether the polymers prepared possess the catalytic activity, controlled experiments of the degradation of Rh B were carried out. The results of the experiments under different conditions are displayed in Figure 6. Rh B was hardly degraded only in the presence of TAPc-PAM under visible light (curve d), and the semblable phenomenon was observed in the presence of TAPc-PAM and H_2O_2 without the light irradiation (curve c). More than 73% of Rh B were degraded by H_2O_2 under visible light in the presence of TAPc-PAM after 120 min (curve a), while limited oxidation occurred by H_2O_2 under the visible light (curve b). The degradation of Rh B was markedly accelerated by adding TAPc-PAM to the system. The oxidation efficiency was improved obviously in the presence of TAPc-PAM, which suggested TAPc-PAM possessed photocatalytic activity after the incorporation of PNIPAM chains.

Figure 7 shows the UV-vis spectral changes of Rh B dependence of irradiation time. It can be seen that the con-

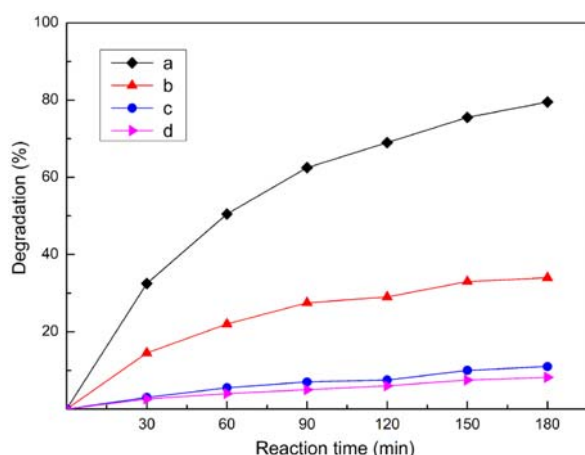


Figure 6. Comparison of experiments under different conditions for degradation of Rh B at 25 °C. (a) TAPc-PAM+H₂O₂+visible light; (b) H₂O₂+visible light; (c) TAPc-PAM+H₂O₂; (d) TAPc-PAM+visible light. Experimental condition: [Rh B]=5×10⁻⁵ mol/L, [TAPc-PAM]=2×10⁻⁵ mol/L, [H₂O₂]=40 mL/L, pH=2, λ>450 nm.

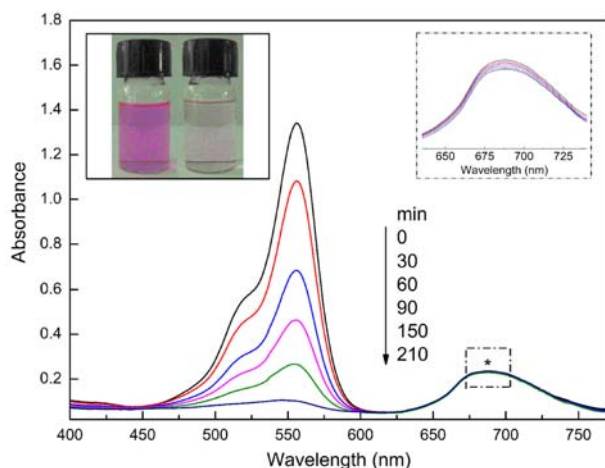


Figure 7. UV-vis spectral changes of Rh B in aqueous solution (initial concentration: 5×10⁻⁵ mol/L) as a function of irradiation time. [TAPc-PAM]=2×10⁻⁵ mol/L, [H₂O₂]=40 mL/L, pH=2, λ>450 nm.

centration of Rh B declined gradually with increasing reaction time in the Rh B/TAPc-PAM/H₂O₂ system. There were no other absorption peaks around 550 nm and the characteristic absorption band decreased in size rapidly and disappeared after degradation of 210 min. Concomitantly, the color of the reaction solution changed from the initial pinked to light transparent as shown in the inset of Figure 7 (left). In addition, the absorption peaks characteristic of TAPc-PAM at 687 nm were almost unchanged with the increasing reaction time (inset of Figure 7, right), suggesting the polymeric catalyst was relatively stable during the photodegradation of Rh B.

Usually, temperature has less effect on the catalytic activity of the metallophthalocyanine derivatives. Considering the polymeric catalyst possessed thermo-responsive prop-

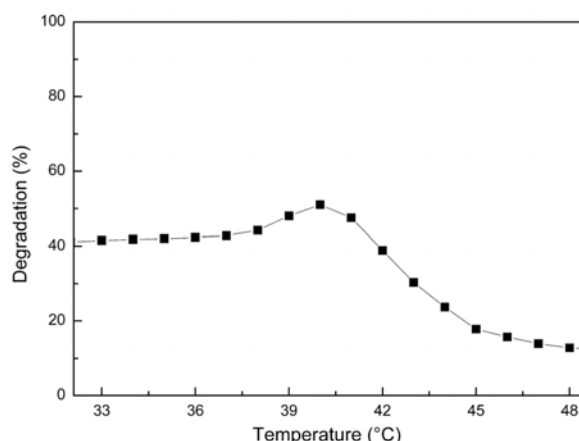


Figure 8. Effect of temperature on the degradation of Rh B in aqueous solution under visible light (λ>450 nm). [Rh B]=5×10⁻⁵ mol/L, [TAPc-PAM]=2×10⁻⁵ mol/L, [H₂O₂]=40 mL/L, pH=2.

erty, we investigated the effect of temperature on the oxidative degradation of Rh B. Figure 8 shows the dependence of the catalytic activity of TAPc-PAM on the reaction temperature within 50 min at pH 2. The degradation rate of Rh B had little change before 33 °C and the reaction system remained homogeneous. While the degradation rate evidently went up with the further increasing of temperature and reached peak value of 50.2% at 40 °C from 41.3% at 38 °C. Interestingly, the degradation rate declined upon rising temperature. The sudden change point was slightly lower than the LCST of TAPc-PAM determined. The interesting phenomenon might be attributed to the thermo-responsive property of the polymeric catalyst. To our knowledge, it can be explained that the polymer chain tuned to tightly packed globules from random coils to form a range micelles-like where Rh B was oxidized efficiently. Due to the thermo-sensitivity, TAPc-PAM precipitated from the aqueous solution when the temperature rising successively. The active center zinc phthalocyanine was embedded by the PNIPAM chains, which hindered the axial coordination between the oxidant H₂O₂ and the center metal atom Zn in phthalocyanine. The degradation system became heterogeneous and the degradation rate descended correspondingly.

Compared with the results of other homogeneous catalytic systems, the catalytic activity of TAPc-PAM was equivalent to other catalysts.^{20,21} The stability of the catalyst is also significant for its application in environmental technology. Recycling experiments were performed for the degradation of Rh B over the polymeric catalyst. In each run, a new fresh solution of Rh B was supplied for maintenance of its initial concentration. At the end of each run, the thermo-responsive catalyst was separated by elevating the temperature of the reaction system and dried in vacuum without further treatment. The catalytic activity was nearly unaffected in the reaction runs as shown in Figure 9. It suggested that the

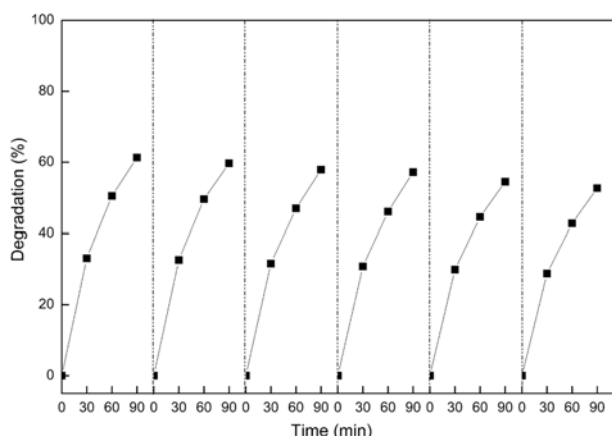


Figure 9. Recycling experiments for degradation of Rh B aqueous solution under visible light ($\lambda > 450$ nm). $[\text{Rh B}]_0 = 5 \times 10^{-5}$ mol/L, $[\text{TAPc-PAM}]_0 = 2 \times 10^{-5}$ mol/L, $[\text{H}_2\text{O}_2] = 40$ mL/L, $\text{pH} = 2$.

polymeric catalyst had a good stability during the recycling experiments. Differing from other homogeneous catalytic system, the thermo-sensitive catalyst could be reused for the degradation system through a simple operation.

Conclusions

A novel star-shaped polymer with zinc phthalocyanine as the core and PNIPAM as the arms was prepared through ATRP. The polymerization was performed at 70 °C in mixed solvents of DMF and water using TAPcCl as the initiator and CuBr/Me₆TREN as the catalyst system. The molecular weight distribution of the polymer was narrow, which indicated the polymerization was well controlled. Thermo-responsive property of TAPc-PAM was measured by turbidimetry method, the LCSTs increased due to the incorporation of the phthalocyanine core. It was verified that TAPc-PAM still possessed the photocatalytic activity by the oxidative degradation of Rh B aqueous solution. The polymeric catalyst had the higher activity around its LCST, it could be reused by the uncomplicated treatment utilizing its thermo-responsive property.

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