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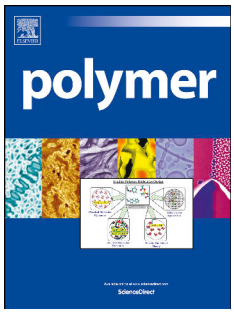

Self-switchable polymer reactor with PNIPAM-PAm smart switch capable of tandem/ simple catalysis

Wenjing Wei, Vijay Kumar Thakur, Songjun Li, Iva Chianella

PII: S0032-3861(21)00888-0

DOI: https://doi.org/10.1016/j.polymer.2021.124265

Reference: JPOL 124265

To appear in: *Polymer*

Received Date: 28 May 2021

Revised Date: 27 September 2021

Accepted Date: 9 October 2021

Please cite this article as: Wei W, Thakur VK, Li S, Chianella I, Self-switchable polymer reactor with PNIPAM-PAm smart switch capable of tandem/simple catalysis, *Polymer* (2021), doi: https://doi.org/10.1016/j.polymer.2021.124265.

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Polymer, Volume 235, November 2021, Article number 124265
DOI:10.1016/j.polymer.2021.124265

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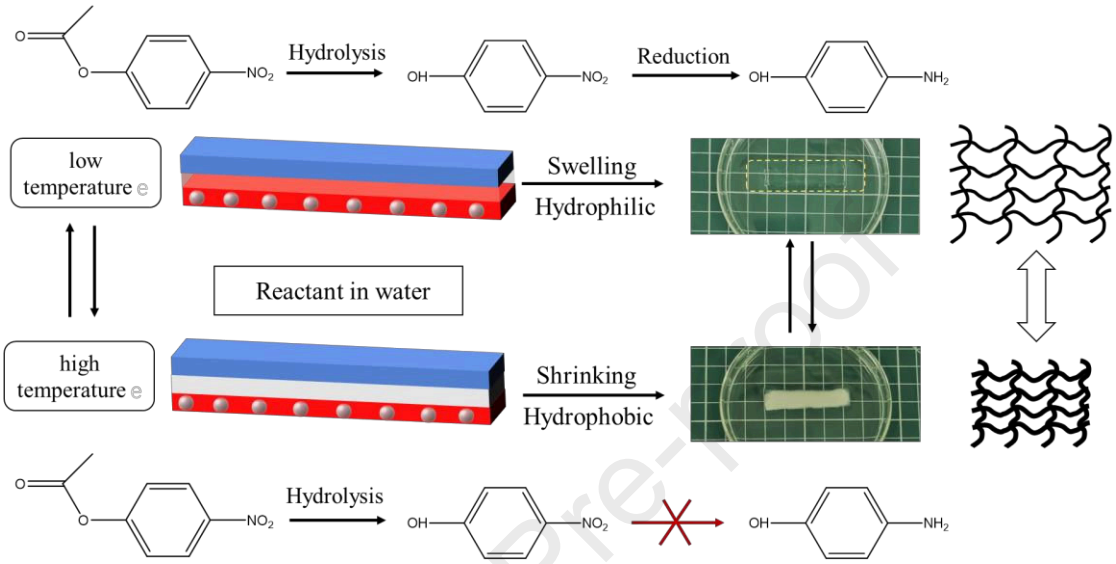
Graphical Abstract



The switchable mechanism of the three-layer polymer reactor.

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Self-switchable polymer reactor with PNIPAM-PAm smart switch capable of tandem/simple catalysis

Wenjing Wei [a,b], Vijay Kumar Thakur [c], Songjun Li*[a], Iva Chianella*[b]

Abstract

In this paper, we report a novel three-layer polymer reactor capable of simple/tandem self-controlled catalysis. The top and bottom layers were composed of two different molecularly imprinted polymers respectively containing two catalytic sites (an acidic site catalyzing hydrolysis and metal nanoparticles catalyzing reduction), performing two selective tandem reactions without interference between each other. The middle layer was composed of a copolymer of poly-N-isopropylacrylamide (PNIPAM) and polyacrylamide (PAm) in different ratio, acting as a temperature-responsive switch for the tandem catalysis process. In an aqueous environment, when the temperature is lower than the Lower Critical Solution Temperature (LCST) of the copolymer, the reactor exhibited an open middle access (hydrophilic condition) of intermediate, allowing the tandem processes from hydrolysis to reduction. When the temperature is higher than the LCST, the channels of the middle layer were closed (hydrophobic condition), which obstructed the access of reactants. As a result, the reactor could only conduct simple hydrolysis processes. Therefore, with the three-layer structure, the polymer reactor has led to a self-controlled catalysis. This new multi-layer polymeric reaction concept can expand the practical use of functional catalysts by permitting the control of processes in large temperature ranges.

Keywords: temperature-responsive polymer; tandem catalysis; LCST; smart catalysis.

1 Introduction

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Discovering new methodologies to prepare complex organic molecules has been the desire in the catalytic field for a long time [1, 2]. Tandem catalysis, performing reactions in a one-pot sequentially, is among the most popular solutions. In tandem processes, a series of catalytic cycles proceed one by one without interference, which not only saves time and energy but also decreases the loss of reagents [3-5]. However, as there are always more than one active sites (catalysts) in tandem reactors, it is critical to separate different sites and ensure each step is conducted individually [6, 7]. Based on the need, herein, we introduce different molecularly imprinted polymers as the carriers of different active sites. Molecularly imprinted polymers (MIPs) are synthetic receptors with recognizable ability of targeted substrates, which is similar to the interaction of antibody-antigen and enzyme-substrate in biological systems. As the catalysts are separated in different supportive polymers, tandem processes can be performed without interference. Also, the unique molecular recognition properties of MIPs enable the catalytic process to take place only with specific reactions [8]. On the other hand, additional control over the reactions is required because of the multi-steps and complex processes.

Due to their self-controlled abilities, thermo-responsive polymers, sensitive to different temperature conditions, were introduced here to allow a greater degree of control over the reactions. Poly-N-isopropylacrylamide (PNIPAM) has attracted a lot of interest [9-11] as one of the most prominent thermo-responsive polymers. PNIPAM exhibits a lower critical solution temperature (LCST) at around 31°C to 33°C in water (regardless of the polymer concentration) [12]. PNIPAM, as a result of its hydrophilic and hydrophobic units, goes through clear phase transitions from a water-soluble state to a water-insoluble state as the temperature increases. PNIPAM has repeating hydrophilic amide groups and hydrophobic isopropyl groups. Below the LCST, the amide groups have strong interactions with water through the formation of hydrogen bonds. However, above the LCST, as the hydrogen bonds are disrupted, the hydrophobic interactions between the main chain and isopropyl groups become dominant [13], causing a change from coil chains to the collapsed globule state. As PNIPAM is rather soft in its hydrated condition, it is necessary to improve its

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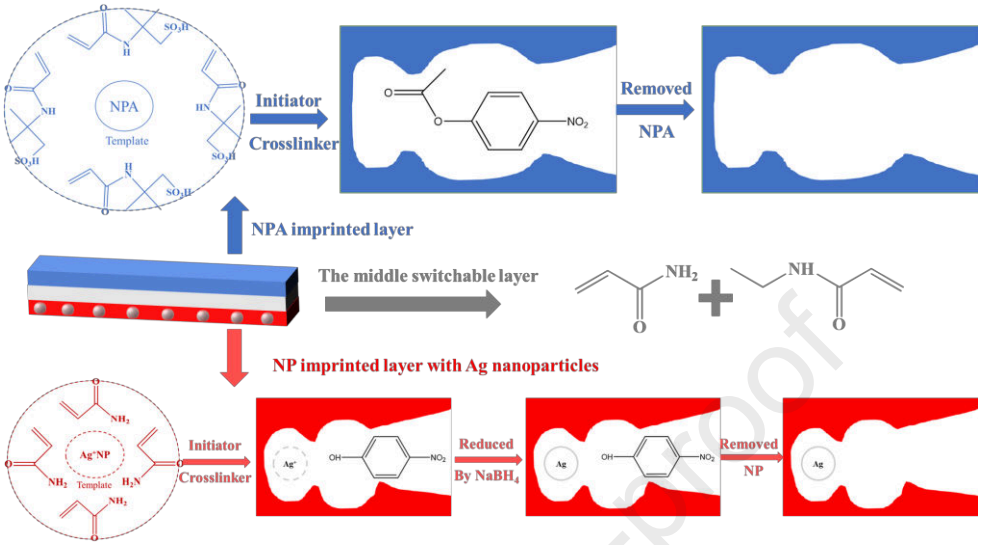
mechanical stability for practical use. There are a variety of different methods to modulate its mechanical stability. One of the most popular ways is to introduce another hydrophilic or hydrophobic comonomers to copolymerize with it. The copolymerization processes will change the LCST of PNIPAM. Also, the tuning of the LCST of PNIPAM to a broad range of temperature provides a variety of applications in different fields such as drug delivery and smart catalysis [14, 15]. For example, it has been shown that the temperature-responsive behavior can be tuned by adjusting the random ratio between NIPAM and N, N-diethylacrylamide (DEA) [16]. Furthermore, it has been reported that the copolymerization of NIPAM and the hydrophilic monomer N, N-dimethylaminopropylacrylamide (DMAPAAm) has shown to lead to an increase of LCST, as a result of enhancing the hydrogen bonds between polymer chains and water molecules [17-19]. Among the variety of comonomers, as a polar, uncharged, hydrophilic monomer, acrylamide (Am) is one of the most well-known candidates. PAm is not a thermo-responsive polymer, but it will increase the LCST of PNIPAM because of its hydrophilic nature [20]; at the same time, it will improve the mechanical properties of the resulting material by forming a semi-interpenetrating polymer networks with PNIPAM [21].

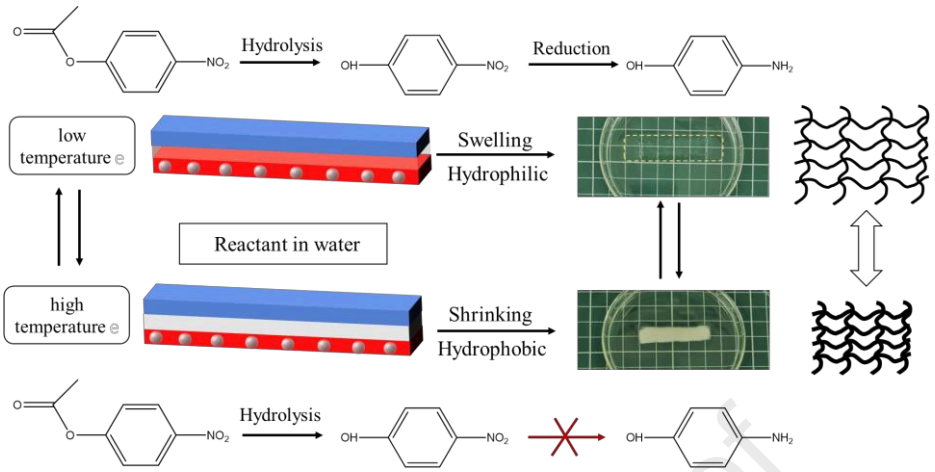
In this research, we prepared a three-layer polymer reactor with different active sites consisting of two imprinted polymer layers separated by a self-controlled switch middle layer. The top and bottom layers were made of molecularly imprinted polymers, acting as the carriers of two different catalytic sites (acidic sites for hydrolysis and metal nanoparticles sites for a reduction reaction). In this way, each step in tandem catalysis can be conducted separately without undesired interferences. Moreover, this polymer reactor has selective reaction capability through the recognition of the imprinted substrate. As shown in **Scheme 1**, the top layer was made by poly (2-acrylamido-2-methylpropanesulfonic acid) (PAMPS), which contains acidic sites, responsible for catalytic hydrolysis. The bottom layer was prepared by polyacrylamide (PAm) with Ag nanoparticles encapsulated in it, responsible for the catalytic reduction process. Nitrophenol acetate (NPA) and 4-nitrophenol (NP) were selected as the substrates for the catalysis and the templates for the imprinting of the two MIPs layers.

As it is well known, NPA can undergo a tandem catalytic process from hydrolysis to reduction with NP being the hydrolyzed intermediate and 4-aminophenol (AP) the final product [22]. As a result, the tandem catalysis process can be performed sequentially.



Scheme 1 The preparation of the three-layer switchable polymer reactor.

In between these two imprinted layers, a switchable layer, made of PNIPAM and PAm was prepared. PNIPAM acts as a self-controlled switch to adjust the simple/tandem catalytic process. Meanwhile, to improve the mechanical ability of PNIPAM as well as to enhance the repeatability of the catalysis process and increase the affinity between the top and the bottom layers, PAm was introduced to copolymerize with PNIPAM. As we can see in **Scheme 2**, at low temperatures, the middle layer swells and becomes hydrophilic, which allows the intermediate to pass through. In this way, the tandem catalysis from hydrolysis to reduction can be performed. However, in high temperature, the middle layer shrinks and become hydrophobic, which obstructs the intermediate to go through and undergo the reduction reaction. As a result, only the simple hydrolysis reaction is conducted in this condition. In our previous work, we have studied similar smart tandem catalysts with bilayer or three-layer architectures [22, 23]. In this work, a novel improved switchable layer was prepared and we further studied the responsive time range, response sensitivity and the repeated catalytic abilities, so as to prepare a novel reactor with higher sensitivity and ability for more stable switchable catalysis.



Scheme 2 The switchable mechanism of the three-layer polymer reactor.

2 Experimental section

2.1 Materials

All the chemicals used in the experiments including N-isopropylacrylamide (NIPAM; 99%), acrylamide (AM; 99%), N, N'-methylene bisacrylamide (MBA; 99%), ammonium persulfate (APS, 99%), 2-acrylamido-2-methylpropane sulfonic acid (AMPS, 99%), 4-nitrophenyl acetate (NPA, 98%), 4-nitrophenol (NP; 99%), silver nitrate ($AgNO_3$, 99.9999%), sodium borohydride (99%), methanol (99.9%), acetic acid (99.9%), dimethyl sulfoxide (DMSO, 99.9%) were purchased from Sigma-Aldrich and used as received.

2.2 Preparation of the polymer reactors

The three-layer polymeric reactor was prepared by synthesizing two molecularly imprinted polymer layers with different catalytic sites (top: acidic site; bottom: Ag nanoparticles) and a middle-temperature responsive layer (PNIPAM-PAm) in between them (**Scheme 1**). To connect the different layers in the preparation processes, after finishing the synthesis of the top layer in a glass petri dish, the middle layer solution was added on the top and polymerized to form the interpenetrated network in the jointed part. Similarly, the solution of the bottom layer was added on the top of the two synthesized layers to get diffusion and connection after synthesis. In this way, the

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resulting three layers were tightly connected with each other. After synthesis, the round three-layer polymeric reactor was cut in rectangular shapes for testing.

For the synthesis, firstly, the monomer 2-acrylamido-2-methylpropane sulfonic acid (AMPS) (2.33 g), crosslinker N, N'-methylene bisacrylamide (MBA) (0.35 g), initiator ammonium persulfate (APS) (0.075 g) and template NPA (0.36 g) were dispersed in 10 mL dimethyl sulfoxide (DMSO). The solution was then fully dissolved using an ultrasonic bath and deoxygenated by flushing it with Nitrogen gas (N_2). Then it was put in a vacuum at 70°C for 3 hours to polymerize. After polymerization, the first layer polymer was immersed in the pre-polymerization solution of the middle layer. This solution was composed of N-isopropylacrylamide (NIPAM; 2.26 g) and acrylamide (Am) with different molecular ratio (6:1; 5:1; 4:1; 3:1; 2:1), MBA (0.3 g) and APS (0.075 g) in 10 ml DMSO. After dissolution and full deoxygenation, the first layer with the solution of the second layer on the top was put in the vacuum oven at 70°C for 3 hours to polymerize. Followed by this, the top two layers were immersed in the bottom imprinted layer solution composed of Am (1.6 g), MBA (0.34 g), APS (0.075 g) and the complex template $[Ag\ (NP)_2]^+$ (2.25 mmol $AgNO_3$ and 2.25 mmol NP mixed together in 2 mL DMSO for 30 minutes) in DMSO (8 mL), and following deoxygenation the synthesis was performed at 70°C for 2 hours. After finishing preparing the three-layer reactor, then the Ag ions were reduced using an excess of sodium borohydride ($NaBH_4$) (10-fold to Ag ions). After reduction, a large amount of deionized water was used to wash the reactor repeatedly to remove the excess of $NaBH_4$. Then NPA and NP templates in the imprinted parts in the top and bottom layers, were washed out using 250 mL methanol including 10% acetic acid (changing solution every 12 hours and using UV-Vis to detect the templates until they were totally removed). The tri-layer polymer reactor PRS (switchable polymer reactor) ready for use was obtained (**Scheme 1**).

To further investigate the self-controlled catalytic ability of PRS, two controls, polymer reactor open (PRO) and polymer reactor close (PRC) were then prepared in comparable conditions. Specifically, PRC means that the reactor is always closed ("C"). PRC also has the acidic MIP top layer and metal-encapsulated MIP bottom layer, while

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the middle layer was replaced by polystyrene, which is always hydrophobic. PRO means the reactor is always open (“O”). PRO has the same top/bottom MIPs layers, while the middle layer was composed of polyacrylamide alone. As a result, PRC will only conduct a one-step simple reaction because of the obstructed middle layer. PRO will permit tandem catalysis processes in both high and low temperatures. On the other hand, the PRS reactor developed in this work can conduct tandem catalysis at low temperature (like PRO), while it can only catalyze simple reaction (hydrolysis) at high temperature (like PRC), hence enabling self-controlled catalysis.

2.3 Characterization methods

The connecting boundaries and morphology images of the polymer reactor were collected by Scanning Electron Microscope (SEM) (TESCAN VEGA 3). The functional groups of the middle polymer layer and the imprinted parts were investigated by Fourier Transform Infrared Spectrometer (FTIR) (Jasco FT/IR-6200). Energy Dispersive spectra (EDS) were used to study the composition of different elements. To confirm the existence and type of metal nanoparticles, X-ray diffraction (XRD) (Siemens D5005) spectra of different samples were collected.

2.4 Thermo-responsive behaviors

Thermo-responsive behaviors of the polymer reactors were studied by dynamic light scattering technique (DLS, Malvern Zen1600) from 25°C to 60°C. Here, the dynamic diameters were used to show the changing thermal behavior of the copolymers. For the analysis, the polymeric samples were grounded into fine powder. Then the crushes samples were dispersed in water and filtered using a syringe filters (0.22 μm) to reach a size small enough for the DLS tests. The temperature of the sample was set to the desired starting value and measurement were carried after 10 minutes to make sure that a thermal equilibrium was reached [24].

The DLS measurements enabled to determine the lower critical solution temperature (LCST) for the reactor and this was further confirmed by Differential Scanning Calorimetry (DSC, Q200) performed in the same temperature range with a

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scanning rate of 2°C per minute. The solid content of the samples for the DSC test was 10% (w/v).

2.5 Self-controlled catalysis

UV spectrophotometer (Jasco V-670) was used to study the self-controlled catalysis processes against time in a batch system [23, 25]. Firstly, the spectra of initial substrate NPA (0.25 μmol/ml), the intermediate NP (0.1 μmol/ml) and the final product AP (0.1 μmol/ml) were recorded. In all the tests carried out with different samples and at different temperatures (30 °C and 60 °C), the concentration of the polymer reactor was kept constant at 0.1 mg/ml. To measure the samples at the two different temperatures, these were maintained at the desired temperatures on a hot plate. Then aliquots of the solutions were transferred on the spectrophotometer and measured every 10 minutes up to a total time of 90 minutes. The initial concentration of NPA was 0.1 μmol/ml (20 ml PBS, pH 7.0). An excess of the reducing reagent sodium borohydride (fourfold to NPA) was also added to the catalytic system. To obtain a reliable result, the final conversion efficiency was determined by the average of three tests. In addition, to eliminate the effect of self-hydrolysis of NPA, the hydrolysis of NPA was conducted in comparable conditions without the catalyst. Then the self-hydrolysis performance was deducted from the system, which enables to assess the catalytic ability of the polymer reactor without the influence of self-hydrolysis.

3 Results and discussion

3.1 The optimized ratio between PNIPAM and PAm

In order to improve the affinity among the polymeric layers of the catalytic reactor, in the middle layer, the hydrophilic monomer Am was copolymerized with PNIPAM. Am is able to increase the adhesion ability of PNIPAM to the other two layers and at the same time enables to modulate the temperature sensitivity. As a result, in this work, a series of copolymers with the different molecular ratio between PNIPAM and PAm were prepared (6:1; 5:1; 4:1; 3:1; 2:1) to identify a suitable ratio with good thermo-sensitivity.

Herein, DLS tests were firstly used to test the LCST of the resulting switchable layers. The LCST data of polymer made with different ratio between PNIPAM and Am are presented in **Table 1**. As it can be seen, the LCST values of PNIPAM copolymers increased significantly from 33°C to 53°C while increasing the Am content. This is attributed to the stronger hydrogen bond between the functional groups of Am and water molecules [26]. However, when it comes to the 2:1 ratio (NIPAM: Am), due to the high content of Am, a significant LCST was not observed. As a result, the ratio between NIPAM and Am in the copolymers should be kept higher than 2:1 to ensure the temperature-responsive ability. To display the changing trends of LCST, the profiles of the diameter (D) of the hydrodynamic particles *versus* the temperature (T) were plotted and are shown in **Figure 1a**. Furthermore, **Figure 1b**, which shows the first derivative of D *versus* T, provides a clearer view of the sensitivity of different samples to the temperature. **Figure 1** shows that PNIPAM possesses the biggest change in D, while the changes become smaller with the addition of Am with the smallest change observed when the molecular ratio was 3:1. After comparing the several molecular ratios, 5:1 was chosen as the best, as it contained enough Am to assure good adherence ability and at the same time exhibiting good thermal sensitivity (Figure 1b).

Table 1 LCST data of different ratio between PNIPAM and PAm collected by DLS and DSC.

Sample Name (PNIPAM/PAM)	LCST (°C)	
	From DLS curve	From DSC curve
PNIPAM	33	33
6:1	43	42
5:1	47	48
4:1	51	51
3:1	53	54
2:1	N/A	N/A

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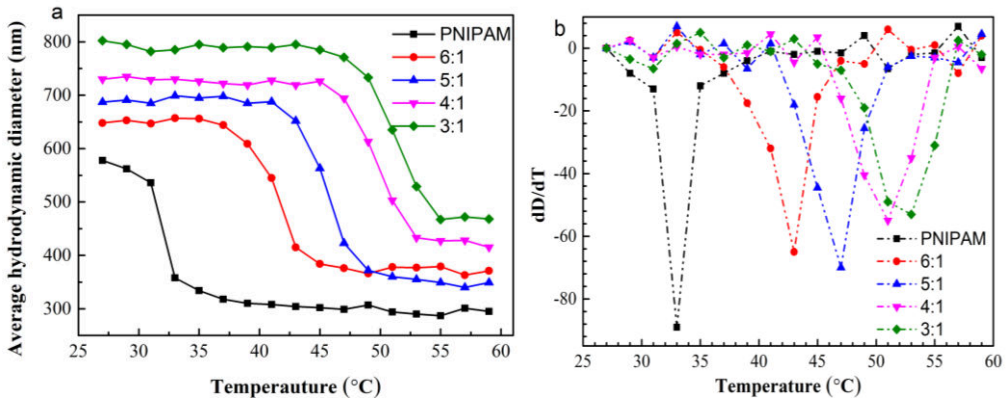

Figure 1 DLS spectra of different ratio samples of copolymer PNIPAM-PAm with hydrodynamic diameter changing as a function of temperature (a) Normal; (b) differential

The thermo-responsive ability of the samples with different ratios were further studied by non-isothermal DSC (**Figure 2**). The temperature of the minimal endothermic peak, which was defined as phase transition temperature (LCST), exhibited similar results to those obtain by DLS. As shown in **Figure 2**, the thermal sensitivity became weaker as more Am was introduced in the system. In fact, the ratio 4:1 and 3:1 displayed a poorer sensitivity compared with the 5:1. These results confirmed that the ratio 5:1 was indeed the best to obtain samples with good thermal sensitivity. This thermal characterization of the polymers produced has evidenced that the LCST of PNIPAM can be tuned between 33°C to 53°C by adjusting the hydrophilic units, providing insights of further applications of PNIPAM-based temperature-responsive polymers, which can be used in a larger temperature range.

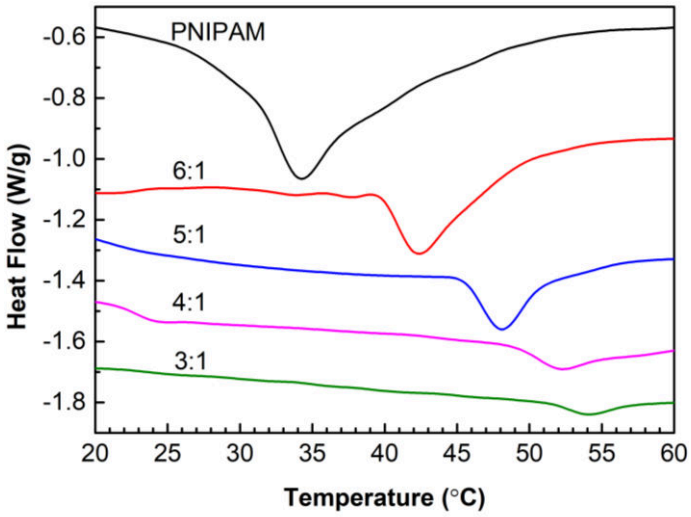

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Figure 2 Non-isothermal DSC profiles at a heating temperature of 2°C min^{-1}.

3.2 Characterization of composition and structure

The three-layer switchable polymer reactor PRS was prepared by two molecularly imprinted polymers containing two different catalytic sites and a temperature-responsive layer in between them. SEM was firstly used to study the three-layer structure and the morphology of three polymeric layers. As shown in **Figure 3a**, the polymer reactor exhibited three distinct layers as well as tight boundaries among the layers. To further examine the three-layer structure, images of the boundaries between the top and the middle layer, as well as the middle layer and the bottom layer are shown in **Figure 3b** and **3c**. The cross-linked network between the polymers created tight boundaries between the layers. The morphologies of the three different layers are shown in **Figure 3d**, **3e** and **3f**. Compared with the middle layer, the MIP-PAMPS and MIP-AgPAM layers demonstrated a rougher surface because of the washing of the imprinted parts in the preparation processes. Meanwhile, high content of silver nanoparticles well dispersed and with similar size was seen in the MIP-AgPAM layer, confirming the presence of metal nanoparticles in the reactor. Therefore, the SEM results have confirmed that the basic structure of the reactor was prepared as expected.

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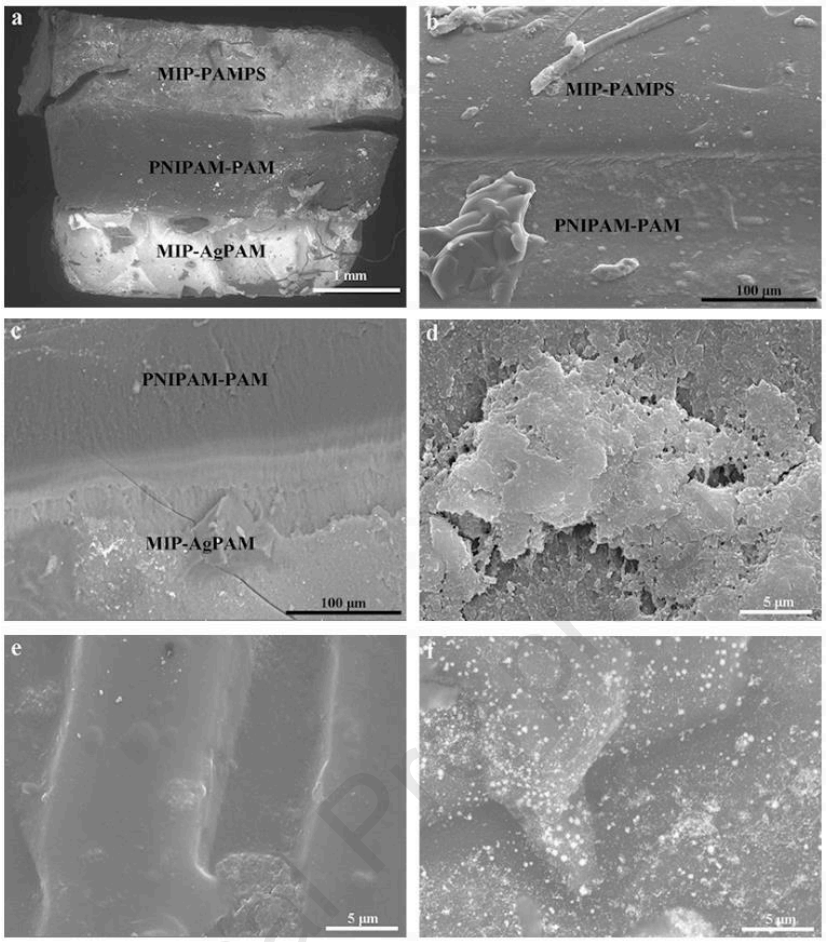

Figure 3 SEM images of PRS (a:three-layer structure of PRS; b: the boundary of MIP-PAMPS and PNIPAM-PAM; c: the boundary of PNIPAM-PAM and MIP-AgPAM; d: MIP-PAMPS layer; e: PNIPAM-PAM layer; f: MIP-AgPAM layer)

To study the chemical composition of the reactor in the three layers, FTIR was used to characterize the functional groups. As we know, the top layer was composed of PAMPS MIP and the bottom layer was composed of PAm MIP with Ag nanoparticles, while the middle layer consisted of PNIPAM and PAm. The FTIR results for the full polymer reactor and the three layers separately, shown in **Figure 4**, evidenced four main bands (1000-1200, 1000-1400, 1600-1800 and 2900-3700 cm^{-1}), which were attributed to the compositions of the three-layer polymer, specifically related to the stretching vibration of S=O, C-C/C-N, C=O and O-H/N-H bonds [27, 28]. **Figure 4** also showed the spectra of three different layers separately. Compared with the other two layers, the characteristic peak of the S-O group appeared around 1025 cm^{-1} confirming the existence of AMPS in the MIP-PAMPS layer, which also appeared in the spectrum

of the three-layer reactor. As for the middle and bottom layer, they demonstrated similar peaks because of their similar composition in functional groups, except for the vibration peak at 1370 cm^{-1} assigned to isopropyl group of PNIPAM [29]. The FTIR results of the three layers and the whole reactor suggested the successful copolymerization of PNIPAM and PAm in the middle layer and the basic composition of the top and bottom layers.

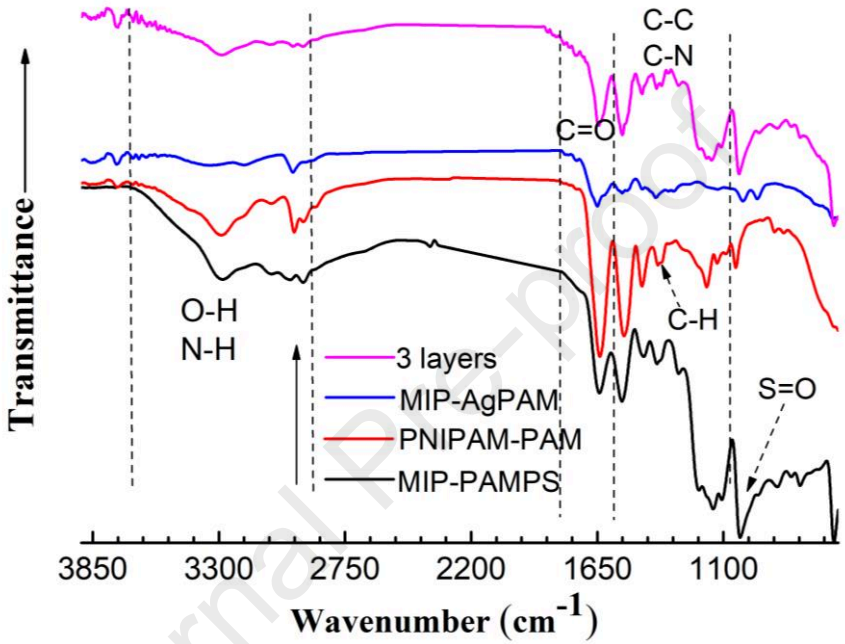

Figure 4 FTIR spectra of polymer reactor PRS and three layers respectively

FTIR was also used to characterize the imprinted structure of the top and bottom layers. As shown in **Scheme 1** of the preparation route, the imprinted polymers firstly were synthesized with the catalysis substrates as templates and then the template molecules were removed by washing obtaining the polymeric layers with the free imprinted cavities. The unwashed imprinted polymers are identified here as "precursor". In order to show the effect of the washing step, the FTIR spectra of the washed imprinted layers were compared respectively with the precursor spectrum before washing as well as with the spectrum of the template itself (**Figure 5a**, **5b**). **Figure 5a** shows that the precursor contained both the characteristic peaks of PAMPS and template NPA. After the washing processes, the polymer MIP-PAMPS showed a spectrum without most of the vibration peaks of the template, proving the success of

the washing step. Similar behavior was observed for the other imprinted layer (**Figure 5b**), where the spectrum of the precursor exhibited the main bands of both MIP-AgPAm and the template NP, while after the washing process the spectrum of the resulting polymer did not show the main bands of the template. Therefore, the test confirmed the presence of the imprinted cavities in the polymer reactor as well as the efficacy of the washing step.

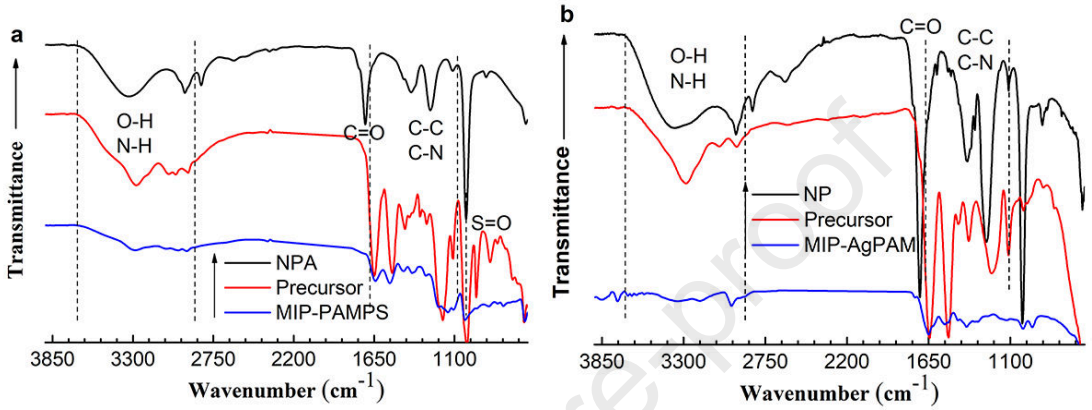

Figure 5 Imprinted behaviors of two different molecularly imprinted layers (a: MIP-PAMPS layer; b: MIP-AgPAM layer)

The composition of the metal nanoparticles and the elemental analysis of the polymer reactor was further investigated by XRD and EDS. XRD results from the powder form of all the three different layers in PRS separately and together are presented in **Figure 6**. Both the top and middle layers were prepared without Ag nanoparticles. As we can see, all the samples displayed a broad peak at around 22°, which is related to the amorphous properties of the polymer. At the same time, the single-layer MIP-AgPAM and the three layers together samples showed sharp peaks assigned to the Ag nanoparticles. The signals appeared at 2 theta values of 38.7°, 44.4°, 64.4°, 77.5° and 82°, which are consistent with the characteristic signals of Ag nanoparticles [30, 31]. The elemental composition of the polymers was assessed by EDS and results are shown in **Figure 7**. Expect for the common elements C, N and O, the MIP-PAMPS layer contained S because of PAMPS, while MIP-AgPAm layer contained Ag element, confirming the composition of the preparation. These characterization tests reinforced further that the composition and the structure of the polymer reactor were as expected and as shown in **Scheme 1**.

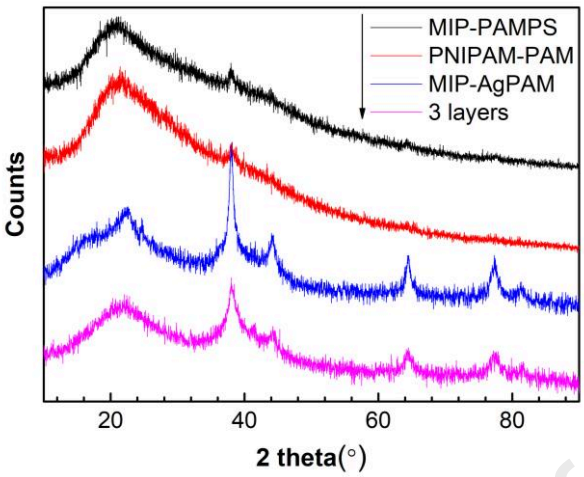

Figure 6 XRD spectra of polymer reactor PRS (three layers respectively and together)

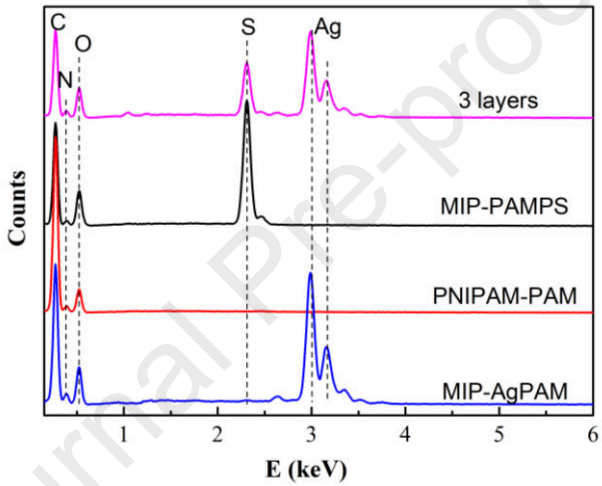

Figure 7 EDS spectra of PRS (three layers together and three different respectively)

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3.3 Thermo-responsive transition behavior

After identifying the best molecular ratio 5:1 between PNIPAM and PAm as explained in section 3.1, the switchable reactor PRS was prepared with the optimized composition. In addition, the other two reactors PRO and PRC were synthesized in comparable conditions, as controls, to confirm and study the self-controlled behaviors of PRS. The middle layers of the three reactors were then characterized by DLS and the results are presented in **Figure 8a** and **8b**. As it can be seen, the two controls that have PAM and PS in the middle layer did not show a clear correlation with temperature in **Figure 8a**. However, the middle layer PNIPAM-PAm of the reactor PRS showed a sharp decrease in the changing process. To better identify the specific LCST, the differential graph of the process was calculated and it is shown in **Figure 8b**. As we can see, the

biggest changing point (transition point) was at 47 °C, which was therefore identified as the LCST of the reactor PRS. Below such temperature, the switchable middle layer exhibited a larger diameter due to swelling occurring in the hydrophilic condition, which would allow access to the reactant between the top and bottom layers. On the other hand, above 47°C, the diameter became much smaller due to the polymer shrinking in the hydrophobic conditions, which would close the access of the reactant from the top to the bottom layer. Therefore, DLS analysis has confirmed that the PRS reactor possessed a switchable behavior regulated by temperature.

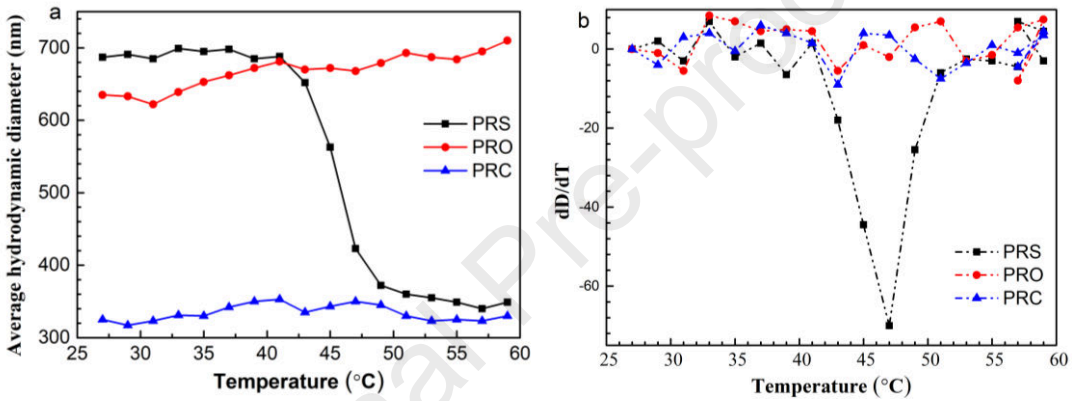


Figure 8 DLS spectra of three different polymer reactors with hydrodynamic diameter changing as a function of temperature (a) Normal; (b) differential

As is depicted in **Scheme 2**, the middle layer experienced a change from transparent to opaque due to the phase transition from coils to globules at different temperatures [32]. The morphological change of the three-layer reactor is also presented in **Figure 9a** and **9b**. According to the phase transition temperature of PRS (47°C), two temperatures, 30°C and 60°C were chosen to observe the morphological changes of the temperature-responsive layer. With the increase of the temperature, the initially transparent (hydrophilic) middle layer became hydrophobic (opaque), inhibiting the tandem catalysis. To observe the changing conditions more clearly, the pictures of only the middle layer are presented separately in **Figure 9c** and **9d**. These results are consistent with the DLS test.

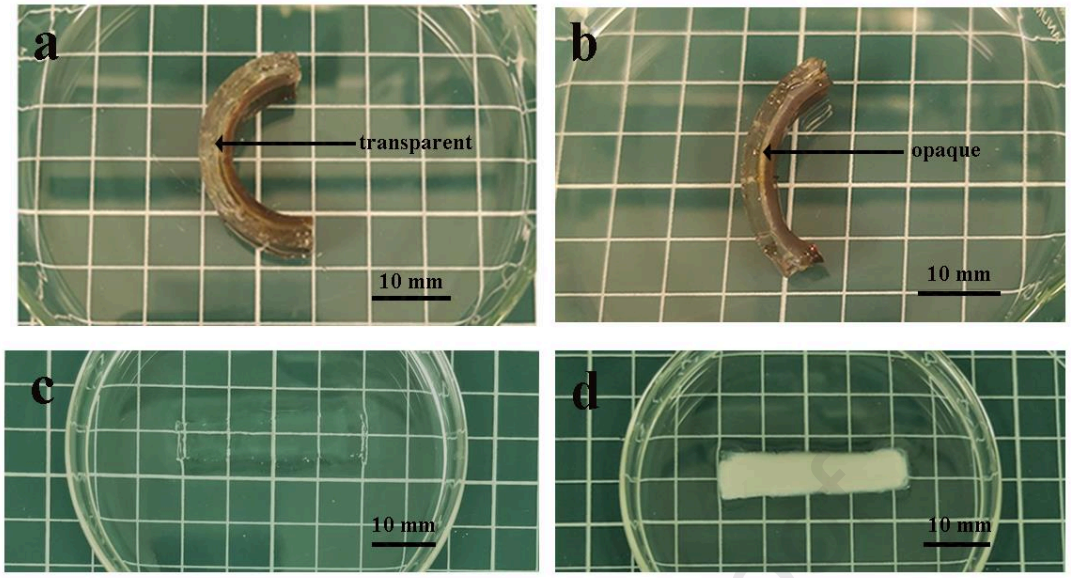
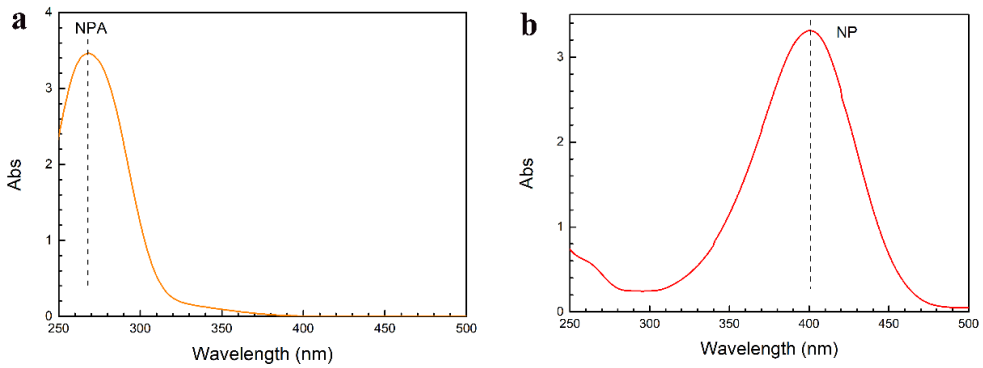


Figure 9 Digital images (a) PRS in 30°C; (b) PRS in 60°C; (c) The middle layer of PRS in 30°C; (d) The middle layer of PRS in 60°C.

3.4 Self-controlled catalytic processes

To further understand the self-controlled properties of the polymer reactor, an UV spectrophotometer was used to record the complete catalytic processes at both low and high temperatures. In order to better study catalysis, the UV spectra of initial reactant NPA (270 nm), intermediate product NP (400 nm) and final product 4-aminophenol (AP; 295nm) were first recorded as a reference (**Figure 10a**, **10b** and **10c**). Meanwhile, as the LCST of the polymer reactor PRS was identified to be around 47°C, 30°C (lower than LCST) and 60°C (higher than LCST) were carefully chosen as examples of low and high temperatures for the measurements.



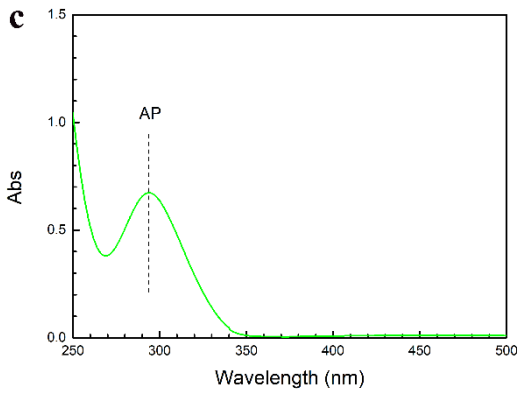


Figure 10 UV spectra of initial reactant, intermediate product and final product (a 4-nitrophenol acetate; b 4-nitrophenol; c 4-aminophenol)

When the two controls without temperature-responsive abilities were tested, similar catalytic spectra were obtained in both low and high temperature respectively. As is shown in **Figure 11a**, when PRC was tested at 30°C, NPA peak (271 nm) decreased due to the catalytic hydrolysis, resulting in an increase of NP peak (400 nm). When PRC was tested at 60°C, although the conversion of NPA improved because of higher temperature, PRC still exhibited a one-step simple reaction because of the close access of the middle layer (**Figure 11b**). As for the control PRO, the reaction processes appeared more complicated. In **Figure 11c**, at a lower temperature, the initial reactant NPA (270 nm) underwent the catalytic hydrolysis to intermediate NP (400 nm). Then this was reduced to the final product AP (295 nm) in the presence of sodium borohydride, completing the tandem catalysis. Nevertheless, when tests were performed at the higher temperature, PRO was still able to achieve a similar tandem process (**Figure 11d**), as the middle layer (PAm) was always open lacking self-control ability.

Both controls can only achieve the simple or tandem reactions at different temperatures without any control on the processes. As for the switchable polymer reactor, PRS, with the thermal-sensitive middle layer, it demonstrated distinct self-controlled catalytic processes. At 30°C, PRS showed free access of the intermediate NP, because of the hydrophilic and open status of the middle layer, succeeding in finishing the tandem reactions. The spectra (**Figure 11e**) from NPA (270 nm) to final product AP (295 nm) were similar to the reactor PRO with permanent open access. However, when

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the temperature rose, PRS only exhibited the one-step hydrolytic catalysis, which was the same as the permanently closed reactor, PRC, because of the blocked access (**Figure 11f**). Therefore, only the reactor PRS was able to provide control over either the complex tandem reactions (hydrolysis to reduction) at low temperature (lower than 47°C) or only the simple hydrolysis reaction at high temperature (higher than 47°C).

Compared with other types of tandem catalyst with different structures and components, for example the metal–organic framework [33], metal/metal oxide [34] catalysts, our PRS consisted of two MIP layers, as the carrier of different active sites and a control layer in between them. The MIPs layers were able to separate the two active sites, which avoided the agglomeration of metal nanoparticles and also prevented the interference of different active sites. The middle layer was able to act as a switch to control the process of tandem reactions, enabling either the simple or the tandem reactions just by changing the temperature.

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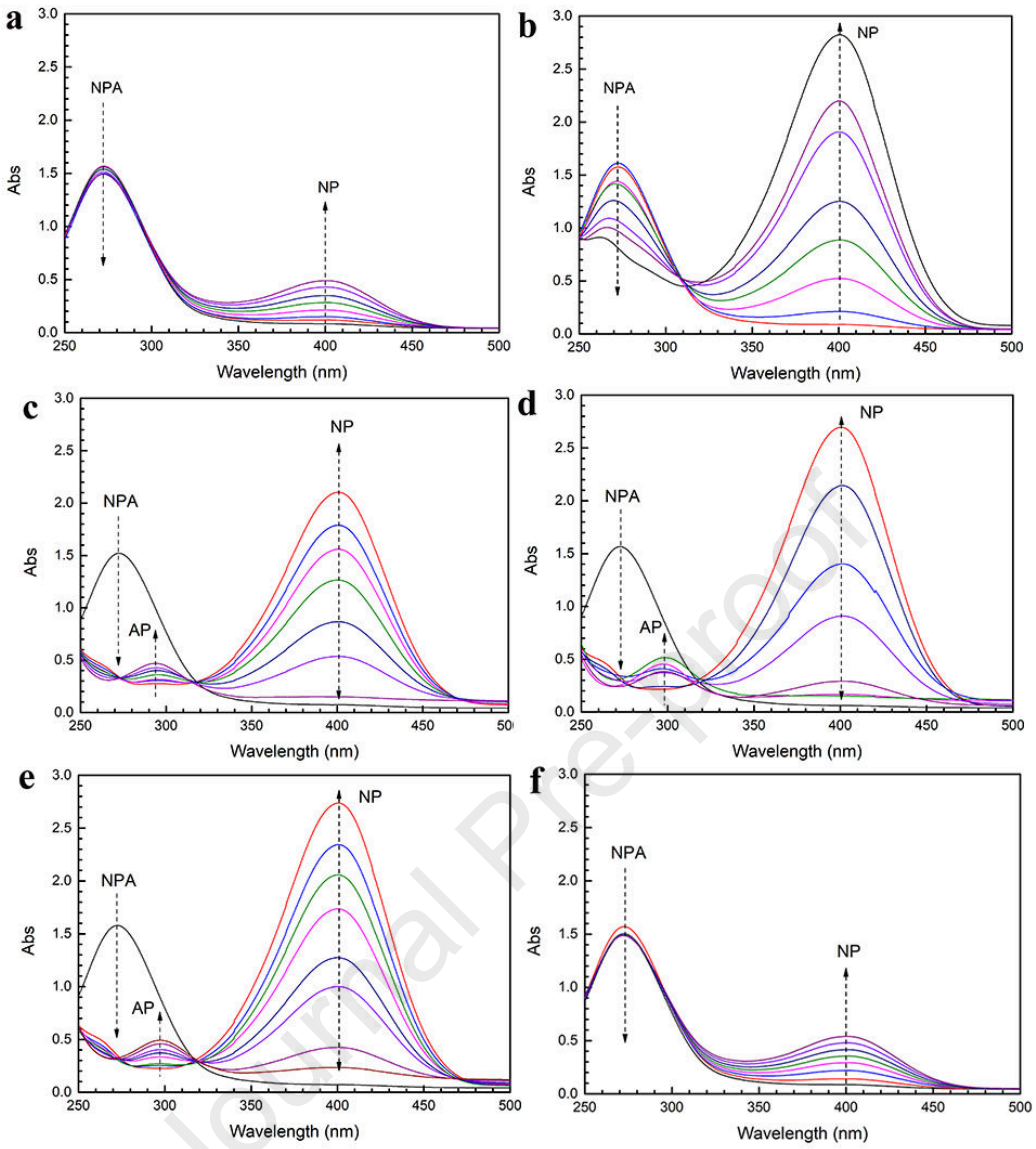

Figure 11 UV spectra of the catalytic performance of PRS and two controls in 30°C and 60°C (a PRC in 30°C; b PRC in 60°C; c PRO in 30°C; d PRO in 60°C; e PRS in 30°C; f PRS in 60°C)

By recording the conversion of NP repeatedly, the switchable repeating properties of the reactor PRS was estimated and it is shown in **Figure 12**. The polymer reactor demonstrated the ability to switch to a different status from tandem catalysis to simple catalysis for multiple times without obvious loss in catalytic abilities (conversion of intermediate NP). Due to the enhanced mechanical stability deriving from the copolymerization of PNIPAM and PAm with a suitable ratio, the three-layer reactor was able to perform repeating catalysis without showing deterioration. Hence, PRS demonstrated robust tandem /simple self-controlled ability in aqueous solutions.

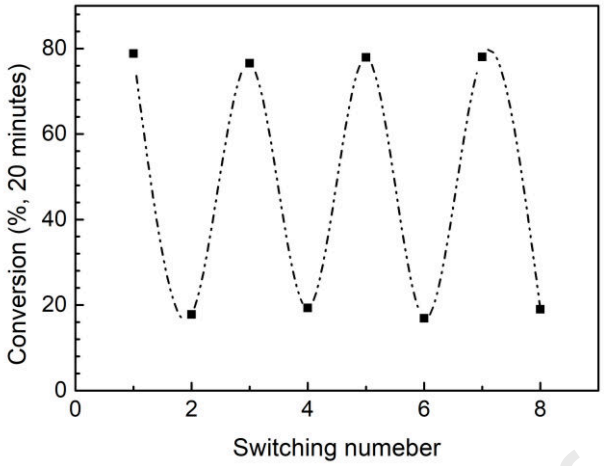

Figure 12 Repeating switchable performance of polymer reactor PRS

4 Conclusion

A self-controlled catalytic polymer reactor PRS containing two molecularly imprinted polymer layers and one temperature-responsive layer in between was prepared. Here, two different catalytic active sites were separated in two different molecularly imprinted polymers to ensure that two consecutive steps in tandem catalysis could be conducted without interference. The middle layer made of PNIPAM and PAm acted as a switch to control the simple/tandem reaction process by varying the temperature. Below the LCST of the copolymer (47°C), the middle layer would allow the access of the intermediate from the top layer to the bottom layer, conducting the tandem catalysis from hydrolysis to reduction. While above the LCST, the middle layer would stay closed, inhibiting the access of the intermediate to the bottom layer, enabling only progression of the hydrolysis reaction. Therefore, this PRS reactor has demonstrated the ability to achieve a self-controlled catalytic process. Furthermore, by adding the suitable ratio of copolymer acrylamide (Am), the reactor PSR showed excellent adherence and mechanical stability of the middle layer as the catalytic process could be repeated multiple time with good temperature sensitivity and enhanced mechanical stability. Hence this novel polymer reactor has shown the ability to achieve stable and robust self-controlled catalysis. At the same time, by tailoring the composition of the middle switchable layer, it has demonstrated the potential for

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practical applications of functional catalysts in different temperature ranges.

Acknowledgements

The authors want to show gratitude to the Dual PhD Degree Programme between Jiangsu University and Cranfield University.

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Highlights

- A three-layer polymer reactor with non-tandem/tandem self-controlled catalytic abilities was prepared.
- The middle layer made of PNIPAM-PAM acts as a molecular switch to control the tandem catalysis.
- Tandem catalysis without interference was obtained by using molecularly imprinted polymers as carriers.
- A temperature controlled and stable smart tandem catalysis was achieved.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Self-switchable polymer reactor with PNIPAM-PAm smart switch capable of tandem/simple catalysis

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2021-10-11
Elsevier
https://doi.org/10.1016/j.polymer.2021.124265
Wei W, Kumar Thakur V, Li S, Chianella I. (2021) Self-switchable polymer reactor with PNIPAM-PAm smart switch capable of tandem/simple catalysis. Polymer, Volume 235, November 2021, Article number 124265

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