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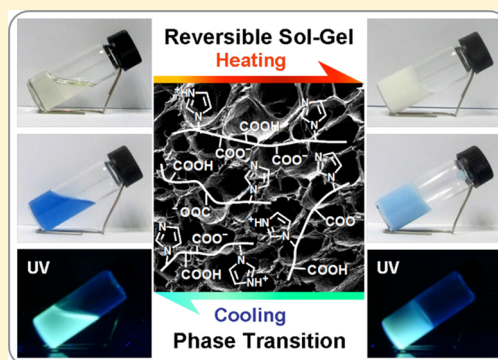
# Fabrication of Reversible Phase Transition Polymer Gels toward Metal Ion Sensing

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## Supporting Information

**ABSTRACT:** We report the synthesis of a new type of triple stimuli-responsive, i.e., thermo-, pH-, and metal ion-responsive copolymers based on poly(*N*-vinylimidazole-*co*-methacrylic acid) (poly(VI-*co*-MAA)) and their application as metal ion sensors. The copolymers exhibit reversible sol–gel phase transition behavior in aqueous media. The sol-to-gel transition temperature ( $T_{\text{sol-gel}}$ ) can be shifted in the range of 20–80 °C, by varying monomer ratio and feeding glycerol content, by adjusting the copolymer concentration in aqueous solution, by tuning the pH of the solution, or by adding various divalent metal ions. Metal ion sensors were designed upon an inverse opal photonic film loaded with aqueous solution of poly(VI-*co*-MAA), which allows the easy reorganization of various divalent metal ions by combining the diversity of  $T_{\text{sol-gel}}$  of the copolymers on different metal ions and flexible reflection spectra of the film. In addition, a fluorescent reversible sol–gel transition system was established by *in situ* generation of nanocrystals in the copolymer matrix. These extensions may provide the multiresponsive copolymers great flexibility for applications in biomedical, optical, and sensory fields.



## INTRODUCTION

Similar to living creatures responding to environmental changes, some polymers can undergo conformational changes in response to external stimuli, showing great promise in developing intelligent or smart materials.<sup>1–7</sup> Of particular interest are a typical class of stimuli-responsive polymers exhibiting a dramatic phase transition from a soluble sol to an insoluble gel state upon stimuli (such as temperature, pH, electric or magnetic field, light, or chemical), which are useful for applications in drug delivery, tissue engineering, sensors, logic gates, etc.<sup>1–3,8–10</sup> Most such polymers reported in literatures are thermo-sensitive; i.e., aqueous solutions of these polymers transform from solution to gelation upon heating and from gelation to solution upon cooling and are rather easy to recognize. To date, a variety of thermo-responsive polymers have been developed, including random, graft, or block copolymers of poly(*N*-isopropylacrylamide) (PNIPAm),<sup>11–15</sup> poly(ethylene glycol) (PEG),<sup>16–21</sup> polycaprolactone (PCL),<sup>19–21</sup> poly(ethylene oxide) (PEO),<sup>22–25</sup> polypeptides,<sup>26–28</sup> and poly(vinyl alcohol) (PVA).<sup>25,29</sup> Because of their inherent nature of reversible phase transition property near body temperature, these thermo-responsive polymers offer valuable opportunities of biomedical applications in such as drug delivery. Nevertheless, the challenge still remains to fabricate thermo-responsive polymers with wide sol–gel transition temperature ( $T_{\text{sol-gel}}$ ) regime. The narrow  $T_{\text{sol-gel}}$  range of polymers may restrict their applications to a large extent.

To achieve greater flexibility for their applications, another current design trend of stimuli-responsive polymers moves toward multiresponsive system, where the sol–gel phase transition can be triggered by more than one stimulus.<sup>17,23,30–37</sup> Realizing this potential might require functionalization of the polymer chains. For instance, the introduction of carboxylic or amino groups to the chain ends of polymers may confer the polymers with pH sensitivity through the protonation/deprotonation process during pH changes, and some dual thermo-/pH-responsive polymers have been obtained.<sup>17,30,31</sup> Besides, series of polymers behaving thermo- and light-sensitive,<sup>23,32,33</sup> thermo- and chemical-sensitive,<sup>34–36</sup> or thermo- and mechanical-sensitive<sup>37</sup> sol–gel transitions have also been synthesized.

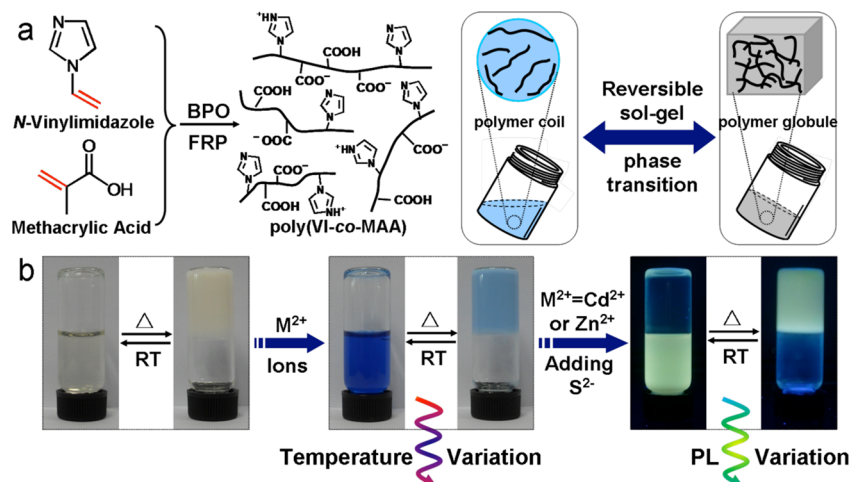
In this work, we report the preparation of a new member of triple stimuli-responsive polymers with wide adjustable  $T_{\text{sol-gel}}$  window (20–80 °C), as well as their potential applications in metal ion sensors and fluorescent reversible sol–gel transition system (Scheme 1). The free radical polymerization of *N*-vinylimidazole (VI) and methacrylic acid (MAA) yielded poly(VI-*co*-MAA) copolymers possessing thermally sensitive sol–gel transition behavior. Interestingly, the imidazole units/carboxyl groups along the polymer chain not only impart pH sensitivity to the copolymers, but also can bind with divalent metal ions ( $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ , etc.) to form

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**Scheme 1.** (a) Schematic Illustration for the Fabrication of Poly(VI-co-MAA) Copolymers with Triple Stimuli-Responsive Sol–Gel Transition Behavior and (b) Photographs of Thermo-Responsive Sol–Gel Transition of Aqueous Copolymer Solution (under Daylight), Cu<sup>2+</sup>-Loaded Copolymer Solution (under Daylight), and CdS Nanocrystal-Loaded Copolymer Solution (under UV, 365 nm Excitation)



**Table 1.** Summary of Preparation Parameters and GPC data of Poly(VI-co-MAA) Copolymers, and Their  $T_{\text{sol-gel}}$  in Aqueous Solutions

samples <sup>a</sup>	[VI]/[MAA] (mol/mol)	glycerol (wt %)	$M_n$ ( $\times 10^4$ )	$T_{\text{sol-gel}}$ of aqueous solution of copolymers with different concentration ( $^{\circ}\text{C}$ ) <sup>b</sup>				
				5 wt %	10 wt %	15 wt %	20 wt %	25 wt %
P-1(G10)	7:3	10	1.86	75	71	68	62	59
P-1(G20)	7:3	20	1.74	78	74	70	65	62
P-1(G30)	7:3	30	1.35	×	77	73	69	66
P-2(G10)	6:4	10	2.71	70	67	65	60	56
P-2(G20)	6:4	20	2.58	73	70	68	63	60
P-2(G30)	6:4	30	1.90	80	72	70	67	64
P-2(G40)	6:4	40	1.70	×	74	72	69	66
P-3(G10)	5:5	10	2.99	×	46	43	38	—
P-3(G20)	5:5	20	2.69	×	52	48	44	—
P-3(G30)	5:5	30	2.30	×	54	50	48	—

<sup>a</sup>The polymerization was conducted in a 70  $^{\circ}\text{C}$  water bath for 2h with oxidant benzoyl peroxide (BPO) of 0.1 wt % as initiator. <sup>b</sup>Key: ×, no gel but precipitate was formed upon heating; —, the copolymers were not completely dissolved.

complexes to selectively affect  $T_{\text{sol-gel}}$ . Therefore, the sol–gel transitions of the aqueous solutions of poly(VI-co-MAA) are thermo-, pH-, and metal ion-sensitive. On the basis of these triple stimuli-responsive copolymers, we designed a feasible metal ion sensor upon an inverse opal photonic structure of SiO<sub>2</sub> substrate for simple and fast recognition of divalent metal ions. Moreover, a fluorescent reversible sol–gel transition system was established by *in situ* generation of nanocrystals in the copolymer matrix, greatly extending the application of the copolymers. To the best of our knowledge, polymers with triple stimuli-sensitive sol–gel transitions are still rarely reported, and this work contributes a simple method to prepare new multiresponsive functional copolymers which may find potential applications in biomedical, optical, and sensory fields.

## RESULTS AND DISCUSSION

**Synthesis of Triple Stimuli-Responsive Copolymers Poly(VI-co-MAA) and Their Thermally Induced Sol–Gel Phase Transition Behavior.** The thermo-, pH-, and metal ion-sensitive copolymers poly(VI-co-MAA) were prepared from free radical polymerization of monomers *N*-vinylimidazole (VI) and methacrylic acid (MAA) in glycerol by using oxidant

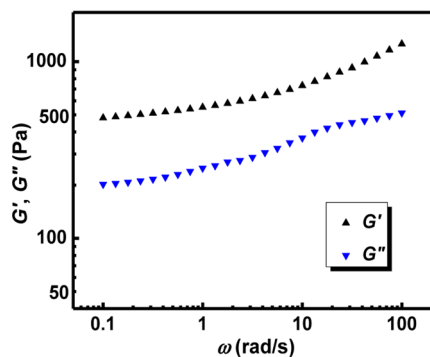
benzoyl peroxide (BPO) as initiator (Figure S1 and Table S1, Supporting Information). By varying monomer feed ratio ([VI]/[MAA] = 7:3, 6:4, 5:5, and 4:6 mol/mol, respectively) and feeding glycerol content (10, 20, 30, and 40 wt %, respectively), series of copolymers were synthesized, as listed in Table 1 and Table S2. The gel permeation chromatography (GPC) data were determined to show that the copolymers prepared from higher VI/MAA monomer ratio and higher feeding glycerol content have lower molecular weight ( $M_n$ ). For instance, with constant feeding glycerol content of 10 wt % was used during the synthesis of copolymers, the produced P-1(G10), P-2(G10), and P-3(G10) with VI/MAA molar ratio of 7:3, 6:4, and 5:5 mol/mol, respectively, have  $M_n$  of  $1.86 \times 10^4$ ,  $2.71 \times 10^4$ , and  $2.99 \times 10^4$ , respectively; with constant [VI]/[MAA] ratio of 6:4 mol/mol,  $M_n$  of P-2 groups decreases from  $2.71 \times 10^4$ ,  $2.58 \times 10^4$ , and  $1.90 \times 10^4$  to  $1.70 \times 10^4$  with an increase in the feeding glycerol content from 10, 20, 30, to 40 wt %. Interestingly, their aqueous solutions display obvious transformation from sol state to gel phase at appropriate concentrations when heating, and vice versa, which indicates the reversible thermo-responsive sol–gel transition behavior. The copolymers prepared with [VI]/[MAA]  $\leq$  4:6 mol/mol

are insoluble in water might due to the formation of three-dimensional networks, which fail to exhibit sol–gel transition.

We thoroughly investigated the impact of the monomer ratio, feeding glycerol content, as well as the copolymer concentration on  $T_{\text{sol-gel}}$  of aqueous solutions of as-prepared copolymers (Table 1). For each kind of copolymers,  $T_{\text{sol-gel}}$  decreases as the polymer concentration increases. For instance, as the concentration of aqueous solutions P-2(G30) increases from 5, 10, 15, and 20 to 25 wt %, their  $T_{\text{sol-gel}}$  varies from 80, 72, 70, and 67 to 64 °C, respectively. Moreover, with the other preparation parameters constant, the copolymers with higher ratio of [VI]/[MAA] have higher  $T_{\text{sol-gel}}$  at the same concentration. For example, 10 wt % aqueous solutions of P-1(G10), P-2(G10), and P-3(G10) show  $T_{\text{sol-gel}}$  of 71, 67, and 46 °C, respectively. In addition, the copolymers prepared with same monomer ratio have higher  $T_{\text{sol-gel}}$  when higher content of solvent glycerol is used during synthesis. As we can see from Table 1, 15 wt % aqueous solutions of P-2(G10), P-2(G20), P-2(G30), and P-2(G40) present  $T_{\text{sol-gel}}$  of 65, 68, 70, and 72 °C, respectively.

As reported, this sol–gel transition behavior is related to various factors, including molecular weight, the chain entanglement, the molecular transition at elevated temperatures from expanded coils to collapsed globules of a portion of the polymers, and the subsequent aggregation of collapsed globules to make weak physical junctions.<sup>2,12</sup> As evidenced in Table 1, both lower feeding glycerol content and lower VI/MAA molar ratio used during the synthesis lead to larger molecular weight of the copolymer, in which stronger physical junctions are formed between the polymer chains and ultimately, the transition temperature becomes lower. In addition, an aqueous solution of the copolymer above a critical concentration experiences four distinct phase upon heating, that is, clear solution, opaque solution, opaque gel and shrunken gel (Figure S2). Whereas, the copolymer solution below the critical concentration (e.g., P-2(G40)) undergoes clear solution, opaque solution and opaque precipitate (Figure S3, Table 1). The above results suggest in this system a wide range of monomer compositions as well as other preparation parameters can be chosen to prepare thermogelling materials. And different from thermo-responsive polymers reported before,<sup>12,16,19,24,27</sup> the VI-based polymer here experiences a higher  $T_{\text{sol-gel}}$  which may extend their potential application fields.

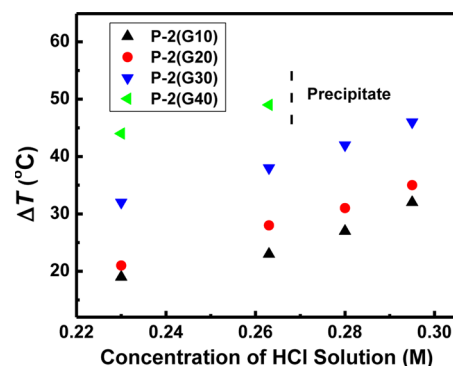
To verify the thermally induced sol-to-gel transition of the copolymers, rheological measurements were conducted. Figure 1 shows the rheological spectra of storage modulus ( $G'$ ) and



**Figure 1.** Dependency of the storage modulus ( $G'$ ) and loss modulus ( $G''$ ) on angular frequency ( $\omega$ ) for 20 wt % aqueous solution of P-2(G20) at 63 °C.

loss modulus ( $G''$ ) as functions of frequency for 20 wt % aqueous solution of P-2(G20) retaining at the fixed temperature of 63 °C (gel state). The  $G'$  values are larger than  $G''$  values over the entire range of frequencies, showing a substantial elastic response.<sup>13,30,38–40</sup> This feature demonstrates the successful transition from sol to gel at 63 °C.

**pH Dependence of  $T_{\text{sol-gel}}$  for Aqueous Solution of Poly(VI-co-MAA).** The incorporation of carboxylic acid and imidazole groups into the polymer backbone allows the  $T_{\text{sol-gel}}$  tuned continuously and reversibly by changing the pH value of aqueous solution of the copolymers. Take the copolymers of P-2 group as an example, as shown in Figure 2 and Table S3.

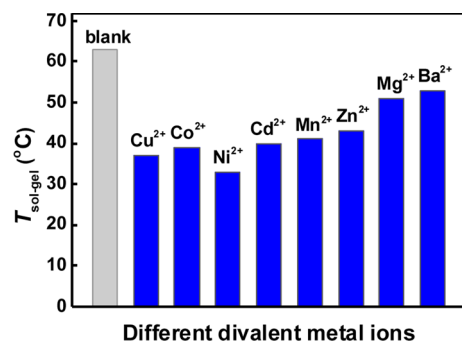


**Figure 2.**  $\Delta T$  of 20 wt % aqueous solutions of P-2(G10), P-2(G20), P-2(G30), and P-2(G40) under different HCl concentration (0.230, 0.263, 0.280, and 0.295 M).

Series of 20 wt % aqueous solutions of P-2(G10), P-2(G20), P-2(G30), and P-2(G40) with different pH values were prepared by dissolving the corresponding copolymers into different concentration of HCl aqueous solutions (0, 0.230, 0.263, 0.280, and 0.295 M). For each kind of copolymers,  $T_{\text{sol-gel}}$  decreases sharply as the pH value decreases. For instance, the pH value of original 20 wt % aqueous solution of P-2(G20) is 6.56, and its pH decreases in sequence to 6.25, 6.01, 5.86, and 5.63 by increasing HCl concentration, respectively, accompanying with  $T_{\text{sol-gel}}$  decreases from 63, 42, 35, 32 to 28 °C. Therefore,  $T_{\text{sol-gel}}$  can be tuned continuously and reversibly by changing the pH value of the copolymer solution. On the other hand, by adding the same amount of HCl, the copolymers synthesized from higher content of feeding glycerol show larger temperature change ( $\Delta T$ ) in  $T_{\text{sol-gel}}$ . For example, with inclusion of 0.263 M HCl, P-2(G40) behaves  $T_{\text{sol-gel}}$  drop from 69 to 20 °C ( $\Delta T$  of 49 °C) while  $\Delta T$  for P-2(G10) is 23 °C. It is worth noting that a pH decrease of less than 1 can lead to a significant drop in  $T_{\text{sol-gel}}$ , revealing the sol–gel phase transition of poly(VI-co-MAA) is highly sensitively pH-dependent. This may be attributed to the changes in ionization degree of both carboxylic acid and imidazole groups induced by pH changes.<sup>30,41,42</sup> The above results demonstrate the copolymers poly(VI-co-MAA) undergo dual pH/temperature-sensitive sol–gel transition in aqueous media, with extremely wide adjustable  $T_{\text{sol-gel}}$  range varying from 20 to 80 °C, which is meaningful for their practical applications.

**Metal Ion-Sensitive Sol–Gel Phase Transition of Aqueous Solution of Poly(VI-co-MAA).** We thoroughly investigated the effect of diverse divalent metal ions as well on  $T_{\text{sol-gel}}$  for aqueous solution of poly(VI-co-MAA). As shown in Figure 3, when various divalent metal ions ( $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ba}^{2+}$ ) with the same molar





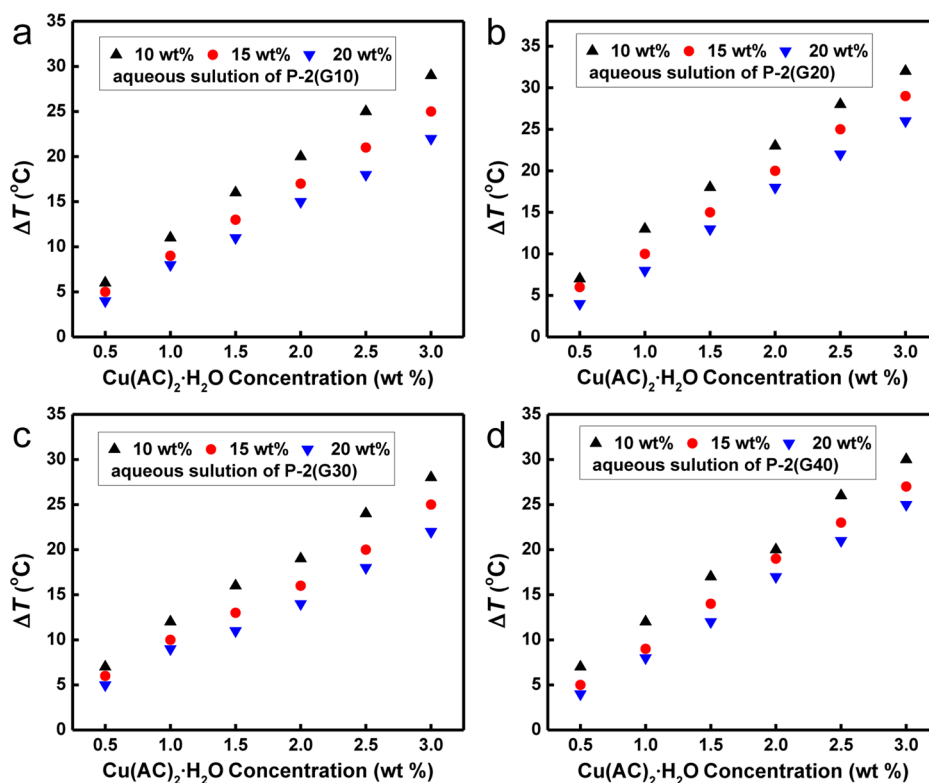
**Figure 3.**  $T_{\text{sol-gel}}$  of 20 wt % aqueous solution of P-2(G20) loaded with different divalent metal ions with same molar concentration (0.0375 M).

concentration (0.0375 M) are incorporated into 20 wt % aqueous solution of P-2(G20), the corresponding transition temperatures are 37, 39, 33, 40, 41, 43, and 51 °C, respectively. Similar procedure was carried out for aqueous solutions of P-2(G10), P-2(G30), and P-2(G40), and their  $T_{\text{sol-gel}}$  was listed in Table S4. We found the sol-gel transition temperature selectively responds to various divalent metal ions, which may be attributed to the discrepancy of coordination ability between carboxyl groups/imidazole units in the polymer chains with divalent metal ions.<sup>43,44</sup>

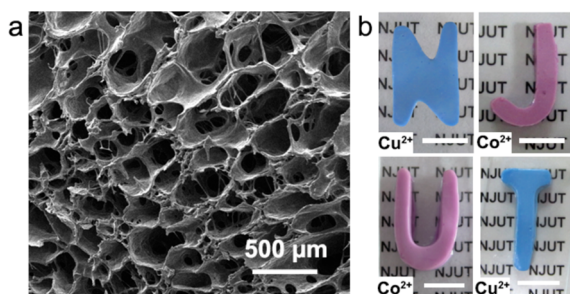
Simultaneously, the effect of metal ion concentration on  $T_{\text{sol-gel}}$  was investigated thoroughly. Take  $\text{Cu}(\text{AC})_2 \cdot \text{H}_2\text{O}$  for example, the addition of  $\text{Cu}(\text{AC})_2 \cdot \text{H}_2\text{O}$  with different concentrations into aqueous solutions of P-2(G10), P-2(G20), P-2(G30), and P-2(G40), causes  $T_{\text{sol-gel}}$  decrease to different levels (Figure 4 and Table S5). Generally, the transition

temperature is gradually lowered when the  $\text{Cu}^{2+}$  concentration becomes higher, which should be attributed to stronger binding as  $\text{Cu}^{2+}$  ions content increases. Moreover, the aqueous solution with lower polymer concentration exhibits larger variation in sol-gel transition temperature to  $\text{Cu}^{2+}$  ions. Specifically, with the addition of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 wt %  $\text{Cu}(\text{AC})_2 \cdot \text{H}_2\text{O}$ , 20 wt % aqueous solution of P-2(G20) displays an decrease in  $T_{\text{sol-gel}}$  from 63 to 59, 55, 50, 45, 41, and 37 °C, respectively, and hence the corresponding  $\Delta T$  is 4, 8, 13, 18, 22, and 26 °C, respectively. Meanwhile, by adding 2.0 wt %  $\text{Cu}(\text{AC})_2 \cdot \text{H}_2\text{O}$  into 10, 15, and 20 wt % aqueous solution of P-2(G20), the corresponding  $\Delta T$  is 23, 20, and 18 °C, respectively.

To further confirm the metal ion-induced sol-gel transition of aqueous solution of poly(VI-co-MAA),  $\text{Cu}^{2+}$  (3.0 wt %)-loaded 20 wt % aqueous solution of P-2(G20) was heated to 37 °C and then fast frozenly dried. Figures S5a and S4 show the morphology of the resulting sample by SEM and optical microscope measurements. It can be clearly seen that the samples exhibit well-defined and interconnected three-dimensional (3D) porous networks, indicating this copolymer solution loaded with  $\text{Cu}^{2+}$  ions has been completely transformed into gel phase at 37 °C. On the other hand, at this temperature, the original 20 wt % aqueous solution of P-2(G20) should be in a sol state since its sol-gel transition temperature is 63 °C. To investigate the gel characteristics of these metal ion-loaded copolymers, we molded out  $\text{Cu}^{2+}/\text{Co}^{2+}$ -loaded aqueous solution of poly(VI-co-MAA) into gels by heating (Figure S5). As depicted in Figure S5b, the gel letters “NJUT” (standing for “Nanjing University of Technology”) were obtained on glass substrates from P-2(G20) aqueous solutions (40 wt %) loaded with 3.0 wt %  $\text{Cu}(\text{AC})_2 \cdot \text{H}_2\text{O}$  (blue)



**Figure 4.** (a–d)  $\Delta T$  of 10, 15, and 20 wt % aqueous solutions of P-2(G10), P-2(G20), P-2(G30), and P-2(G40) loading with different concentration of  $\text{Cu}^{2+}$  ions.



**Figure 5.** (a) SEM images of 3.0 wt %  $\text{Cu}^{2+}$ -loaded 20 wt % aqueous solution of P-2(G20) heated to 37 °C followed by freeze-drying. (b) Optical photographs of letters “NJUT” molded out 40 wt % aqueous solutions of P-2(G20) with 3.0 wt % metal salts (blue,  $\text{Cu}(\text{AC})_2 \cdot \text{H}_2\text{O}$ ; purple,  $\text{Co}(\text{AC})_2 \cdot 4\text{H}_2\text{O}$ ; scale bar, 1 cm).

or  $\text{Co}(\text{AC})_2 \cdot 4\text{H}_2\text{O}$  (purple), showing good self-standing ability after the solutions turned into gels.

**Metal Ion Sensors Based on Inverse Opal Photonic Films for Easy Recognition of Various Metal Ions.** We further employed the thermo-, pH-, and metal ion-responsive copolymers poly(VI-*co*-MAA) as sensing platform for recognition of various transition metal ions. By incorporating the copolymers into inverse opal photonic (IOP) films, we designed desirable metal ion sensors. IOP structures are 3D periodic porous arrays with high surface-to-volume ratios and unique optical properties.<sup>45</sup> The  $\text{SiO}_2$ -based IOP film used here was fabricated according to a modified procedure.<sup>46,47</sup> The well-replicated IOP structures have a uniform pore size of  $\sim 250$  nm (Scheme 2) and present bright green colors (Figure S6 and

**Scheme 2. Schematic Illustration of Thermo-Responsive Sol–Gel Transition System Integrated in Inverse Opal Film (Scale Bar of SEM Image: 500 nm)**

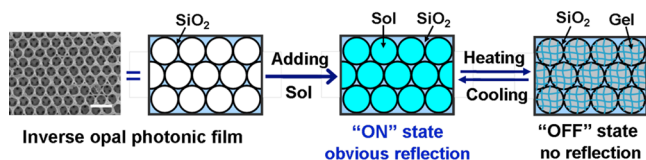
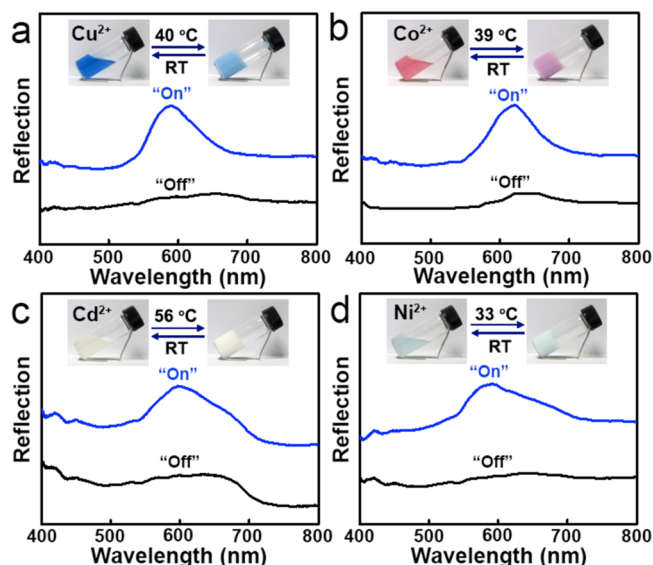


Figure S7) under daylight through the diffraction of light which results in the appearance of a photonic band gap that forbids propagation of certain wavelengths of light. As illustrated in Scheme 2, the incorporation of multiresponsive aqueous solutions of poly(VI-*co*-MAA) as fillers into the photonic structures is able to tune the band gap of the IOP films, and hence affects their reflection spectra. The IOP films display distinct optical properties when the filler, aqueous copolymer solution, is alternatively sol or gel. To be specific, when the IOP structures are filled with the copolymer at sol state, the whole film exhibits obvious reflection and presents bright green color under daylight (defined as “ON” state); whereas, the structures filled with the copolymer at gel state after heating show no reflection and structural color (defined as “OFF” state). This “on-off” switching will be observed for different divalent metal ions under different heating temperatures. As shown in parts a–d of Figure 6, the sensing platform shows “on-off” switching at 40, 39, 56, and 33 °C, respectively, for 0.0375 M aqueous solutions of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ni}^{2+}$  ions, respectively. It is difficult to distinguish light-colored aqueous solution of metal salts only by naked eyes. However, in this case, the molecular recognition based on the copolymer-filled IOP structures is



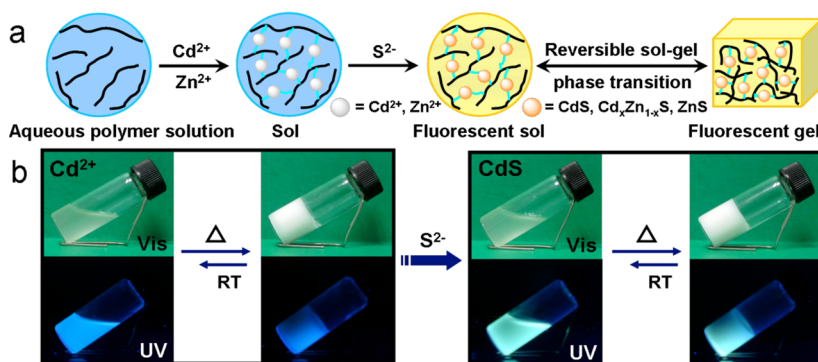
**Figure 6.** (a–d) Reflection spectra of IOP films filled with 0.0375 M  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ni}^{2+}$ -loaded 20 wt % aqueous solution of P-2(G20) at sol (“On”) and gel (“Off”) state, respectively. Insert: Photographs of reversible sol–gel phase transition process for  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ni}^{2+}$ -loaded 20 wt % aqueous solution of P-2(G20).

efficiently and easily achieved through output of a visible signal (from bright green to opaque color), without the need of molecular reporters and sophisticated devices. Therefore, this first example of combining the multiresponsive copolymer with IOP structures contributes a sensing platform for convenient and rapid reorganization of various divalent metal ions.

**Fluorescent Reversible Sol–Gel Transitions.** Notably, the multiresponsive copolymer system can serve as nano-reactors for *in situ* generation of nanocrystals, and then a fluorescent reversible sol–gel transition system is established. The addition of  $\text{Cd}^{2+}/\text{Zn}^{2+}$  ions into the aqueous solution of poly(VI-*co*-MAA), followed by the dropwise addition of  $\text{Na}_2\text{S}$  aqueous solution, gives *in situ* formation of  $\text{ZnS}$ ,  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ , and  $\text{CdS}$  nanocrystals in the polymer matrix, forming a fluorescent reversible sol–gel transition system (Figure 7). The favorable binding between the imidazole groups of the copolymers and  $\text{Cd}^{2+}/\text{Zn}^{2+}$  ions maintains the stable fluorescence performance of the nanocrystal hybrids (Figure S8 and Table S6). As we know, the fluorescent nanocrystal-carried sol–gel reversible transition systems are still rare, because the immobilization of nanocrystals into the polymer matrix may cause irreversible phase transition or disappearance of stimuli-responsive properties for the polymer, as well as the fluorescence diminishing/quenching for nanocrystals.<sup>48,49</sup> The successful combination of multisensitive copolymers with luminescent nanocrystals in this case may offer a novel fluorescent multiresponsive system for specific applications in such as optoelectronics, sensory, and biomedical areas.

## CONCLUSION

In conclusion, we demonstrate the preparation and application of new copolymers poly(VI-*co*-MAA) exhibiting thermo-, pH-, and metal ion-sensitive reversible sol–gel phase transition behavior. The sol–gel phase transition temperature can be controlled in a wide range of 20–80 °C, by adjusting the monomer ratio, vehicle glycerol content, the copolymer concentration and the pH value of the aqueous solution. The



**Figure 7.** (a) Schematic illustration of fabrication of fluorescent reversible sol–gel transition systems. (b) Photographs of reversible sol–gel transition behavior of  $\text{Cd}^{2+}$ - and CdS nanocrystal-loaded 15 wt % aqueous solutions of P-2(G20) under both daylight and a UV lamp (365 nm).

addition of different transition metal salts into the aqueous solution of copolymer causes the varying decrease in the phase transition temperature due to the interaction between carboxyl groups/imidazole units and divalent metal ions. Then the recognition of various transition metal ions has been easily realized via output of a distinct visible color signal on a sensing platform composed of multiresponsive copolymer-filled inverse opal photonic structures. In addition, a fluorescent reversible sol–gel transition system has been established via *in situ* generation of nanocrystals in the copolymer matrix. This work contributes a promising simple way to fabricate new triple stimuli-responsive copolymers might adaptable for more practice applications, for instance, in sensors, microreactors, optoelectronic devices, and medical systems.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Detailed experimental procedures and characterizations of copolymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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