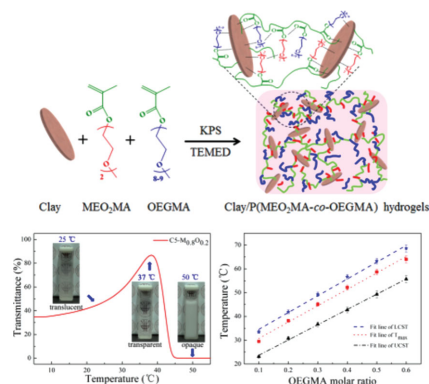


A Novel Nanocomposite Hydrogel with Precisely Tunable UCST and LCST

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Novel thermosensitive nanocomposite (NC) hydrogels consisting of organic/inorganic networks are prepared via in situ free radical polymerization of 2-(2-methoxyethoxy) ethyl methacrylate (MEO₂MA) and oligo(ethylene glycol) methacrylate (OEGMA) in the presence of inorganic cross-linker clay in aqueous solution. The obtained clay/P(MEO₂MA-co-OEGMA) hydrogels exhibit double volume phase transition temperatures, an upper critical solution temperature (UCST), and a lower critical solution temperature (LCST), which can be controlled between 5 and 85 °C by varying the fraction of OEGMA units and the weight percentage of cross-linker clay. These new types of NC hydrogels with excellent reversible thermosensitivity are promising for temperature-sensitive applications such as smart optical switches.



1. Introduction

Smart hydrogels possess specific tunable stimuli-responsive properties, which enable them to respond to external changes, such as temperature, pH, light, electric field, magnetic field etc.^[1] These hydrogels have been utilized as novel materials in many applications, such as intelligent sensors,^[2] artificial skin,^[3] drug delivery,^[4] and tissue engineering.^[5] Among these smart hydrogels, thermosensitive hydrogels on the basis of poly(*N*-isopropylacrylamide) (PNIPAM) have attracted extensive attention because of

their facile phase transition temperature near 32 °C, which is close to the human body temperature.^[6] Numerous strategies have been developed to prepare novel PNIPAM-based hydrogels with controllable thermosensitivity, superior mechanical properties, and specific swelling/de-swelling behaviors.^[7] For example, organic/inorganic hybrid PNIPAM-based nanocomposite (NC) hydrogels, which utilize inorganic clay as physical cross-linker instead of conventional organic cross-linker, exhibited extraordinary mechanical properties, perfect optical properties, special swelling/de-swelling behavior, and reversible stimuli-responsiveness.^[8] However, phase transition regions of most reported NC hydrogels based on *N*-substituted alkyl acrylamide monomers can only be controlled in a narrow range around 32 °C, which restricted the applications for temperature-controlled switches, drug delivery systems, and biomedical materials.^[9]

To exploit new and alternative thermosensitive hydrogels, poly(2-(2-methoxyethoxy) ethyl methacrylate) (PMEO₂MA) was investigated to replace PNIPAM, because the phase transition temperature can be fine-tuned from 25 to 90 °C by simply copolymerizing oligo(ethylene

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glycol) methacrylate (OEGMA) monomers.^[10] More importantly, the obtained P(MEO₂MA-co-OEGMA) copolymers combine both reversible thermosensitivity properties of PNIPAM and nontoxicity properties of poly(ethylene glycol).^[11] Consequently, for these advantageous properties, numerous smart hydrogels, polymer micelles and polymer brushes based on MEO₂MA and OEGMA have been studied in detail.^[12] To the best of our knowledge, only a few studies have been focused on P(MEO₂MA-co-OEGMA)-based NC hydrogels.^[13] Herein, we fabricated a series of novel thermoresponsive clay/P(MEO₂MA-co-OEGMA) NC hydrogels that use inorganic clay (Laponite, XLS) as physical cross-linker during in situ free radical copolymerization of MEO₂MA and OEGMA. These physically cross-linked clay/P(MEO₂MA-co-OEGMA) NC hydrogels are expected to exhibit a lower critical solution temperature (LCST) transition with a precisely tunable thermosensitivity from 25 to 90 °C. Such specific thermoresponsive hydrogels would be promising environmental temperature sensors due to the well-controlled phase transition temperature over a wide range.

2. Experimental Section

2.1. Materials

2-(2-Methoxyethoxy) ethyl methacrylate (MEO₂MA, $M_n = 188 \text{ g mol}^{-1}$) and OEGMA ($M_n = 475 \text{ g mol}^{-1}$) were purchased from Sigma-Aldrich Chemical Co. Ltd., and purified through chromatography on a silica gel column prior use. *N*-isopropylacrylamide (NIPAM) was purchased from Acros Co. Ltd., and purified by recrystallization from a toluene/*n*-hexane mixture. The synthetic hectorite, Laponite XLS (92.32 wt% [Mg_{5.34}Li_{0.66}Si₈O₂₀(OH)₄]Na_{0.66} and 7.68 wt% Na₄P₂O₇) with platelets ca. 30 nm in diameter and 1 nm thick, was provided by Rockwood Ltd. UK. Potassium persulfate (KPS), *N,N,N',N'*-tetramethyl ethylene diamine (TEMED), and *N,N'*-methylenebisacrylamide (BIS) were purchased from Sinopharm Chemical Reagent Co. Ltd., and used as received without any further purification. The water was obtained from a water purification system (Heal Force Bio-Meditech Holdings Ltd.), which had a water resistivity of 18.2 MΩ cm, and was purged with nitrogen gas for more than 2 h before use to exclude oxygen.

2.2. Synthesis of Nanocomposite Hydrogels

The synthetic procedure to prepare clay/P(MEO₂MA-co-OEGMA) NC hydrogels is similar to previous reports.^[14] In brief, NC hydrogels were prepared using initial solution consisting of water (18 mL), inorganic cross-linker clay, MEO₂MA and OEGMA comonomer (4 g), the aqueous solution of the initiator (KPS 0.04 g in water 2 mL) and accelerator TEMED (30 μL) were subsequently added to the initial reaction solution. Next, in situ free radical polymerization was carried out at room temperature for 24 h. Here, the sample nomenclature for clay/P(MEO₂MA-co-OEGMA) NC hydrogels are generally defined in terms of C_m-M_{1-x}O_x, where C, M, and O stand for clay, MEO₂MA and OEGMA, respectively,

whereas the subscript *m* is the weight percentage of clay and *x* is the molar ratio of OEGMA in NC hydrogels. The same synthesis procedure was used for the organic cross-linked (OR) hydrogels except that an organic cross-linker BIS was used instead of inorganic cross-linker clay. C_m-PNIPAM hydrogel was prepared under the same condition, except for adding 4 g NIPAM monomer instead of comonomer MEO₂MA and OEGMA. All the sample compositions are listed in Table S1 (Supporting Information).

2.3. Characterization of Thermosensitive Hydrogels

¹H NMR spectra of clay/P(MEO₂MA-co-OEGMA) NC hydrogel prepared in D₂O instead of H₂O were acquired with a Bruker Avance-400 MHz spectrometer. The transmittance of thermosensitive OR and NC hydrogels were determined in the cuvette by turbidity measurement at 600 nm using a PerkinElmer UV-vis Lambda35 spectrophotometer equipped a thermoregulator (± 0.1 °C) with a heating rate of 0.5 °C min⁻¹ from 5 to 95 °C. Before each measurement, the sample was kept at 5 °C for 20 min. The values of volume phase transition temperature were determined at the middle point of transmittance change, T_{max} correspond to the temperature of maximum transmittance of hydrogel.

3. Results and Discussion

Thermosensitive hydrogels based on clay and P(MEO₂MA-co-OEGMA) have been prepared via facile in situ free radical polymerization. It is shown in Figure S1 (Supporting Information) that the C=C double bonds on the monomer completely disappeared in the ¹H NMR spectrum after polymerization, and the conversion of MEO₂MA and OEGMA was practically 100%. To evaluate the thermoresponsiveness of P(MEO₂MA-co-OEGMA)-based hydrogels with different types of cross-linking, temperature-dependent transmittance was recorded by a UV-vis spectrometer (Figure 1). As shown in Figure 1a, the organic cross-linked OR-M_{1-x}O_x hydrogels exhibit a clear plateau of transmittance below LCST, and then undergo a volume collapse transition above LCST. This result was in well agreement with that of traditional temperature-responsive hydrogels.^[7b,15] The LCST of OR-M_{1-x}O_x hydrogels could be tuned from 20 to 85 °C by varying the molar ratio of OEGMA from 0% to 100%, which is in accordance with the result of linear polymer reported by Lutz et al.^[10a] The addition of inorganic cross-linking agent clay improved the network structure and enhanced the mechanical property of the hydrogels dramatically.^[7a,14b,16] In the case of C5-M₁O₀ and C5-M₀O₁ hydrogels (Figure 1b), the thermoresponsive behavior was similar to that of traditional temperature-responsive hydrogels, and only one volume phase transition was observed. However, it was surprisingly found that the temperature transmittance curve of C5-M_{0.8}O_{0.2} hydrogel featured two volume phase transition temperatures: a upper critical solution temperature (UCST) at 30.8 °C and an LCST at 41.9 °C, both of which are

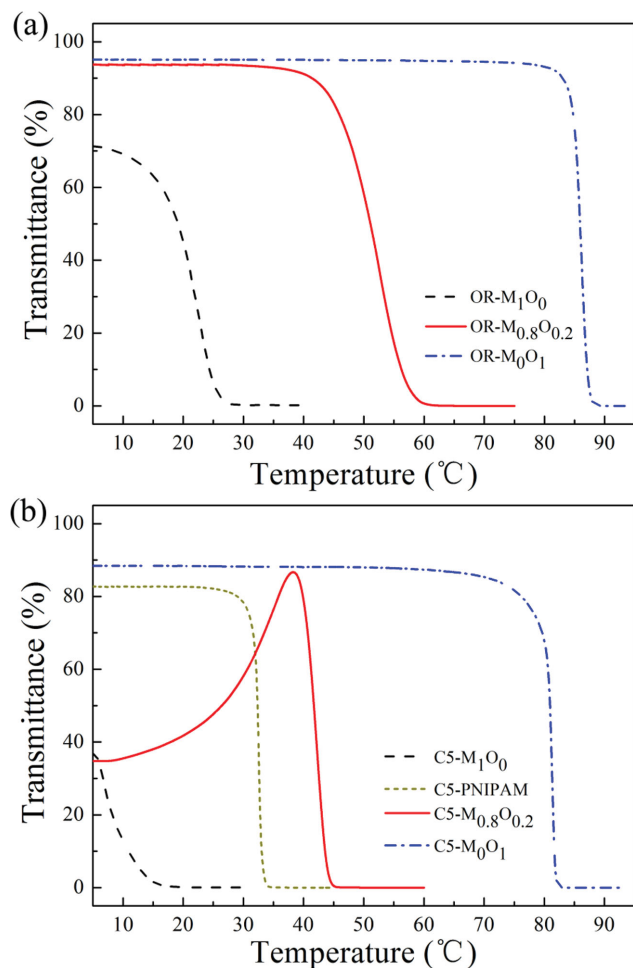


Figure 1. The transmittance versus temperature plots for a) OR- $M_{1-x}O_x$, b) C_5 - $M_{1-x}O_x$ and C_5 -PNIPAM hydrogels at a wavelength of 600 nm with a heating rate of $0.5\text{ }^\circ\text{C min}^{-1}$.

close to the human body temperature. It should be noted that novel clay/P(MEO₂MA-co-OEGMA) hydrogels differ obviously from organic cross-linked P(MEO₂MA-co-OEGMA) hydrogels and/or PNIPAM hydrogels, with the latter exhibiting only an LCST transition. This dual responsiveness of clay/P(MEO₂MA-co-OEGMA) hydrogels with both UCST and LCST is highly interesting and has not been reported yet. Furthermore, the LCST values of C_5 - $M_{1-x}O_x$ hydrogels were slightly lower than that of OR- $M_{1-x}O_x$ hydrogels, due to the restricted local mobility of polymer chains by covalent cross-linking in OR- $M_{1-x}O_x$ hydrogels. All in all, clay/copolymer hydrogels exhibited both UCST and LCST transitions, while clay/homopolymer and OR- $M_{1-x}O_x$ hydrogels possessed only one LCST transition. This double thermosensitivity might be attributed to the consecutive changes by the clay/copolymer structural micro- and macroaggregation of clay/P(MEO₂MA-co-OEGMA) hydrogels: from loose clay/polymer microaggregation ($T < \text{UCST}$), over homogeneous network structure ($\text{UCST} < T < \text{LCST}$), to dense clay/polymer macroaggregation ($T > \text{LCST}$).^[12a,b,17]

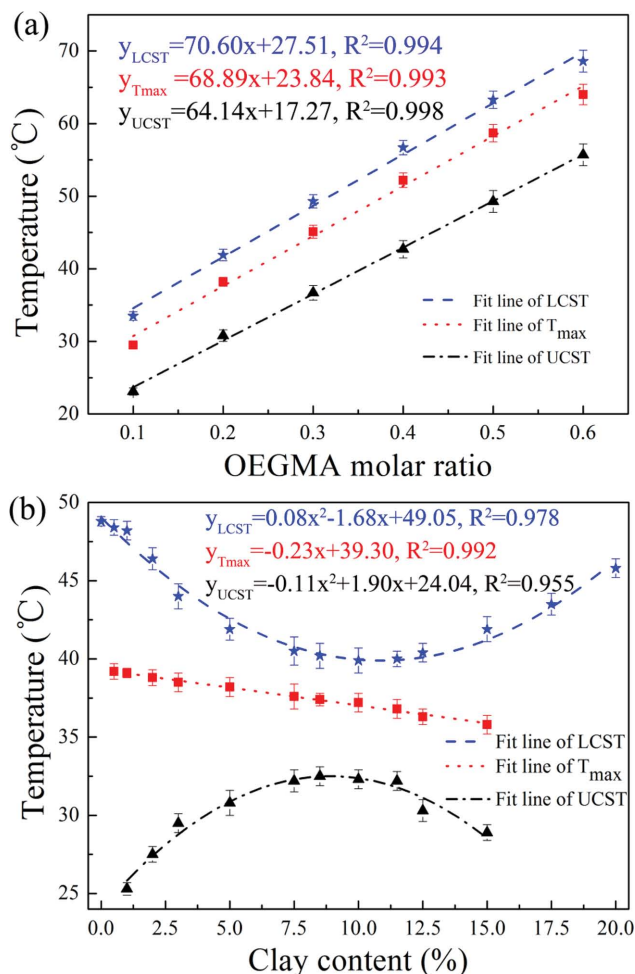


Figure 2. Temperature dependence of clay/P(MEO₂MA-co-OEGMA) NC hydrogels with different a) OEGMA molar ratios and b) clay contents. Plots of the measured transition temperatures (UCST: triangle, T_{max} : square, LCST: star) as a function of a) OEGMA molar ratio for C_5 - $M_{1-x}O_x$ hydrogels and b) clay content for C_m - $M_{0.8}O_{0.2}$ hydrogels.

In order to engineer these thermoresponsive behaviors, full control of UCST and LCST is highly desirable. According to our study, the double thermosensitivity of C_m - $M_{1-x}O_x$ NC hydrogels is expected to realize such a prediction by varying the organic/inorganic components. It is obvious that the concentration of OEGMA and clay is important for the dual responsiveness of clay/P(MEO₂MA-co-OEGMA) NC hydrogels (Figure 2). Notably, a series of C_5 - $M_{1-x}O_x$ NC hydrogels exhibits similar thermal transition profiles, showing an increasing volume phase transition temperature (UCST and LCST) with increasing OEGMA amount (Figure S2, Supporting Information). Each C_5 - $M_{1-x}O_x$ NC hydrogel in the cuvette was translucent at an initial temperature $T_0 = 5\text{ }^\circ\text{C}$, and the transmittance increased gradually, reaching a maximum transparent value ($\text{Trans}_{\text{max}} > 85\%$) with the temperature increasing to T_{max} . As temperature increased beyond T_{max} , the NC

hydrogels immediately became opaque. The initial transparency of C5- $M_{1-x}O_x$ NC hydrogels improved with the increase of the hydrophilic OEMGA units. The C5- $M_{1-x}O_x$ hydrogels exhibited an LCST ranging from 33.5 °C at $x = 0.1$ to 68.6 °C at $x = 0.6$. Similarly, the UCST and T_{max} also varied from 23.1 to 64.0 °C when the amount of OEMGA increased. Moreover, we found that the correlation between the measured temperature (UCST, T_{max} , LCST) and the OEMGA units in NC hydrogels is a linear function of OEMGA molar ratio (Figure 2), where y_{UCST} , y_{max} , and y_{LCST} correspond to the temperature of $Trans_{UCST}$, $Trans_{max}$, and $Trans_{LCST}$, respectively. In other words, both UCST and LCST of NC hydrogels not only shift to a higher temperature, but also can be tuned from 5 to 85 °C by increasing its hydrophilic nature. To the best of our knowledge, such NC hydrogels featuring double volume phase transitions over a wide temperature range have not been reported to date.

Furthermore, the concentration of clay varied from 1 wt% to 20 wt% and affected the thermoresponsive behavior of Cm- $M_{0.8}O_{0.2}$ hydrogels. All hydrogels were thermally stable and continuously changed from translucent over transparent to opaque upon heating (Figure S3, Supporting Information). But the dependence of UCST and LCST on the clay content showed a parabolic function as shown in Figure 2b, and the phase diagram of Cm- $M_{0.8}O_{0.2}$ hydrogels also presented reversible transitions at UCST and LCST. The temperature region between UCST and LCST was quite sensitive to external temperature. When the concentration of clay was higher than 15 wt% or lower than 1 wt%, Cm- $M_{0.8}O_{0.2}$ hydrogels only showed an LCST-type thermosensitive transition in the same temperature range, which means that the clay content can significantly affect the UCST and LCST transitions. Up to now, the origin of this double volume phase transition mechanism is not entirely clear yet and will be discussed in a forthcoming study.

To gain a first insight, the temperature stability of the NC hydrogels was investigated. The clay/P(MEO₂MA-co-OEGMA) NC hydrogels possess a double thermosensitivity and are expected to show durability for repeated heating/cooling cycles. Thus, we carried out the transparency reversibility tests of Cm- $M_{1-x}O_x$ hydrogels with a heating/cooling rate of 0.5 °C min⁻¹. All hydrogel samples exhibited good

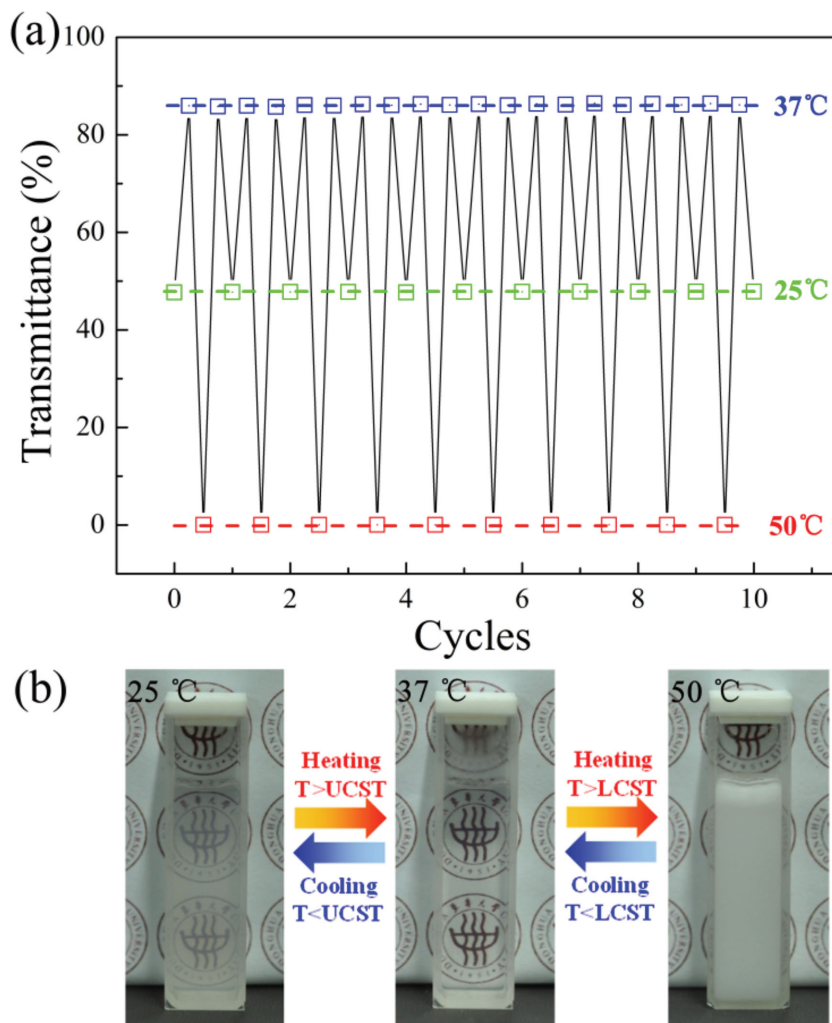


Figure 3. a) Temperature cycling of transmittance and b) photographs of C5- $M_{0.8}O_{0.2}$ hydrogel at different temperatures (25, 37, and 50 °C), demonstrating reversibility.

reversible transitions at UCST and LCST without any hysteresis. The result of a representative C5- $M_{0.8}O_{0.2}$ hydrogel that has been cycled for 10 times is shown in Figure 3a, in which the transmittance at 25, 37, and 50 °C are 48%, 86%, and 0%, respectively. No obvious degradation of the hydrogel was observed even after the 10th cycle, which indicated that the two phase transitions of C5- $M_{0.8}O_{0.2}$ hydrogels were completely reversible. Visually observable changes of two phase transitions of C5- $M_{0.8}O_{0.2}$ hydrogel at 25, 37, and 50 °C are shown in Figure 3b, C5- $M_{0.8}O_{0.2}$ hydrogel remained stable and exhibited the same reversible thermosensitivity even after several months. In addition, temperature dependence swelling/de-swelling behavior studies of Cm- $M_{0.8}O_{0.2}$ NC hydrogels with different clay content were performed (Figure S4, Supporting Information). Clay/P(MEO₂MA-co-OEGMA) NC hydrogels exhibited remarkable de-swelling in response to the increase of temperature, the swelling ratio of all the samples decreased moderately as the temperature gradually increased.

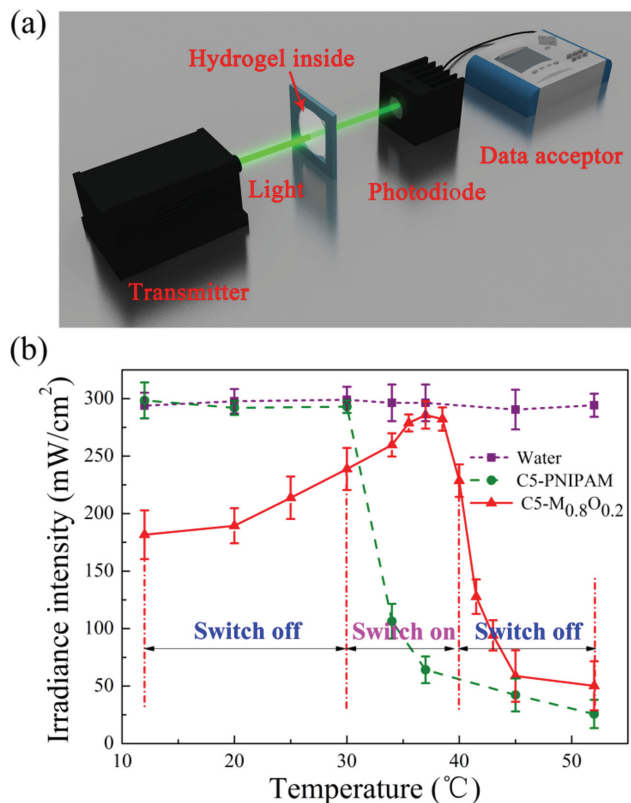


Figure 4. a) The illustration of the hydrogel as an optical transducer for detecting the environment temperature changes. The laser is emitted from the transmitter, passed through the hydrogel, and detected by photodiode. b) The temperature-switching behavior of hydrogels under 636 mW cm^{-2} laser (wavelength 532 nm) irradiation.

The clay/P(MEO₂MA-co-OEGMA) NC hydrogels exhibited a peculiar thermosensitivity over a wide temperature range. Such unique features could be fully taken advantage of in well-defined optical transducer to demonstrate temperature changes by detecting the irradiance intensity of the laser as a function of temperature, as illustrated in Figure 4a. We recorded the irradiance intensity with a photodiode after the laser light passed through the hydrogel. The irradiance intensity of a laser can be effectively altered by the transmittance changes of the hydrogel induced by temperature variations. As a reference, the irradiance intensity of laser passing through water was not changed with varying temperature, while the intensity decreased rapidly around LCST after the laser passing through the traditional thermoresponsive hydrogel such as C5-PNIPAM (Figure 4b). In the case of C5-M_{0.8}O_{0.2} NC hydrogel, the irradiance intensity was about 200 mW cm^{-2} at $10 \text{ }^\circ\text{C}$, and gradually increased to 300 mW cm^{-2} , then sharply decreased to below 50 mW cm^{-2} as soon as the temperature was above LCST. Moreover, the irradiance intensity of laser light passing through C5-M_{1-x}O_x hydrogels can reach relative higher values (switch on) in a

narrow temperature region between UCST and LCST, while the temperature-switching off occurred when the temperature was below UCST or above LCST. Therefore, temperature-controlled optical transducer based on double thermosensitivity hydrogel can be used as a switch, which could be well-tuned in different temperature range by adjusting the organic/inorganic components, making the clay/P(MEO₂MA-co-OEGMA) NC hydrogel a facile, controllable, and reversible switch. In a word, the unique advantages of double thermosensitive hydrogels with precise responses to temperature provide the opportunities to achieve switchable and repeatable intelligent materials for stimulus-responsive devices.

4. Conclusion

A series of clay/P(MEO₂MA-co-OEGMA) NC hydrogels featuring double thermosensitivity has been synthesized via in situ free radical polymerization. These novel physically cross-linked clay/P(MEO₂MA-co-OEGMA) NC hydrogels exhibited not only reversible UCST and LCST transitions, but also a precisely tunable thermosensitivity over a wide temperature window by adjusting the fraction of OEGMA units and clay content. Moreover, the double thermosensitive NC hydrogels were application in smart device to monitor surrounding temperature variation, which showed superior thermoresponsive properties compared to corresponding normal LCST-typed clay/PNIPAM hydrogels. These thermosensitive NC hydrogels with both predictably tunable UCST and LCST provide a new insight to develop novel multiple thermosensitive hydrogels as promising functional devices with a number of interesting properties in the future.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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