Investigation of New Cooling Paints Based on Copolymers of N-Isopropylacrylamide with Butyl Acrylate and N,N-Dimethylacrylamide

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Authors' contributions

*This work was carried out in collaboration among all authors. All authors read and approved the final
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Article Information

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ABSTRACT

New cooling paints were developed by exploiting the vaporization heat of water. These systems
were prepared using various ratios of three copolymer components N-isopropylacrylamide
(NIPAAm), butyl acrylate (BA), and N,N-dimethylacrylamide (DMAAm). The homopolymer of
NIPAAm dissolves in water below about 32℃ (hydrophilic) and becomes insoluble above this
temperature (hydrophobic). On the basis of the hydrophobic/hydrophilic switch of NIPAAm
polymers, cooling paints consisting of copolymers of NIPAAm with coating materials were
investigated. Copolymers of NIPAAm with BA (NIPAAm-co-BA) showed cooling effects; however,
the hydrophobic/hydrophilic switch temperature decreased with the BA ratio. Copolymerization of
NIPAAm-co-BA and DMAAm allowed us to adjust the switch temperature to about 30℃. In

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addition, when the copolymers were pasted on the wall of a model house, at night (temperatures below approximately 30℃), water molecules from the ai r were adsorbed on the materials, and when the outside temperature increased, the temperature of the room decreased. These new coating materials could cool the room on hot days without the need for electrical energy or labor.

1. INTRODUCTION

An enormous amount of energy is consumed by air conditioners, which are used to adjust room temperature especially in the summer. The demand for energy is expected to further increase with the increasing urban population in the world. Thus, there is an urgent need for materials that reduce energy consumption. In ancient times, in order to cool the atmosphere during hot days, people often used to sprinkle water on streets. More recently, wall and roof greening projects have been investigated, which can reduce the electrical energy consumption during summer; however, these approaches require electrical energy and labor for their functionality and for plant growth (e.g., water has to be pumped up to the roofs for roof greening). This energy loss is due to the use of water in the liquid state: if moisture can be converted to liquid water without the need for electrical energy, a considerable amount of energy can be saved.

We have previously proposed a new cooling system consisting of the temperature-responsive polymer, poly(N-isopropylacrylamide) (P(NIPAAm)) [1,2]. P(NIPAAm) has a lower critical solution temperature (LCST) of about 32℃ in aqueous solution [3]; it can dissolve in water at temperatures below the LCST (hydrophilic) and becomes insoluble above this temperature (hydrophobic). This hydrophilic/ hydrophobic property change is proposed to occur via the coil-to-globule transition of the P(NIPAAm) main chains. At temperatures below the LCST, the polymer adopts a coiled conformation and solvent molecules can bind to the side chains of P(NIPAAm); in contrast, at higher temperatures, the polymers condense in solution [4-25]. Based on the mechanism, NIPAAm, i.e., the monomer of P(NIPAAm), have no LCST in aqueous solution. Molecular dynamics (MD) simulation demonstrates that the oligomers with 26-unit of NIPAAm have the LCST [26]. The property of LCST is exploited in the investigation of drug delivery [27-32], separation techniques [33-39], thermoresponsive self-assembling micelles [40], etc. The behavior of P(NIPAAm) in solid state has been reported to be similar to that in solution: the polymer swollen in a small amount of water shows a phase transition at a temperature close to the LCST [1,2,41]. Two kinds of cooling systems can be obtained by using only temperature and humidity changes: (i) P(NIPAAm) included in mesoporous materials [1] and (ii) NIPAAm copolymerized with coating materials [2]. At night (below 30℃), both systems can adsorb water molecules from the air; and the water molecules are desorbed and vaporized when the outer temperature rises. In addition, at temperatures < 30℃, P(NIPAAm) and the copolymers are hardly desorbed from each system into the water phase (water-proof). P(NIPAAm) in mesoporous materials can successfully decrease the temperature in a box by about 4℃ with respect to the outside temperature [1]. However, only few constructions consist of mesoporous materials of nm size (some architectural materials have pores in the μm order); thus, application of this system to existing buildings is limited. In contrast, the later system (paints) has various applications, e.g., houses, trains, cars, etc. Cooling pastes have been obtained by copolymerization of NIPAAm with butyl acrylate (BA) which is a main component of commercial paints. The cooling effects of the copolymer, however, have been recorded for only 3 hours, whereas the homopolymer of P(NIPAAm) can cool the room for a day [2]. This unsatisfactory result is due to two factors: (i) the average temperature of hydrophilic/hydrophobic switch decreases with the BA ratio in the copolymer, and (ii) this switch temperature is distributed over the copolymer, i.e., in some areas of the copolymer it is about 28℃ whereas in other areas it is about 25, 22, 19C, etc. On the basis of this distribution, water molecules can be adsorbed on part of the copolymer in the summer nights, if the outer temperature is decreased to around 25℃. This distribution is caused by the homogeneous polymerization of NIPAAm with BA: because NIPAAm and BA monomers have similar behavior in radical reactions [2,42], various chemical environments of NIPAAm are detected in the copolymer, e.g., -BA-NIPAAm-BA-, -BA-NIPAAm-NIPAAm-BA-, -BA-NIPAAm-NIPAAm-NIPAAm-BA-, etc. In order to be able to apply the

cooling paints to vast areas of the world, it is important to control the temperature of hydrophilic/hydrophobic switch. In this study, we introduce N,N-dimethylacrylamide (DMAAm) to NIPAAm-co-BA, because BA and DMAAm can be classified into hydrophobic and hydrophilic polymers, respectively.

In addition, DMAAm is widely employed for the copolymerization with NIPAAm. Because DMAAm can adjust the LCST of P(NIPAAm) to approximately 40°C, which is slightly higher than normal human body temperature, the copolymers of NIPAAm with DMAAm (NIPAAm-co-DMAAm) have been used for drug delivery systems with various chemicals, including aminoethyl methacrylate, aspartic acid, dextran, glycolide, lactide, propylene, and succinimide [43-54].

NIPAAm-co-DMAAm can dissolve in water below the LCST; thus, a coating material is required in order to use this system outside of buildings (application of NIPAAm-co-DMAAm on the outside of a house on cool and rainy days is difficult).

In this work, we investigate new cooling paints based on copolymers of P(NIPAAm) with BA and DMAAm (the chemical structures are displayed in Fig. 1 and an image of this system is illustrated in Fig. 2). Because these new paints can be applied on many materials and provide cooling effects on hot days without the need for electrical energy or labor, they can find application in wide areas of the world, especially in Southeast Asia.
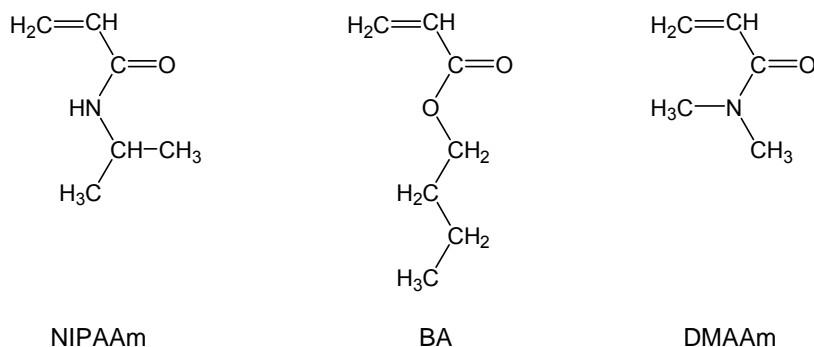

Fig. 1. Chemical structures of N-isopropylacrylamide (NIPAAm), butyl acrylate (BA), and N,N-dimethylacrylamide (DMAAm)
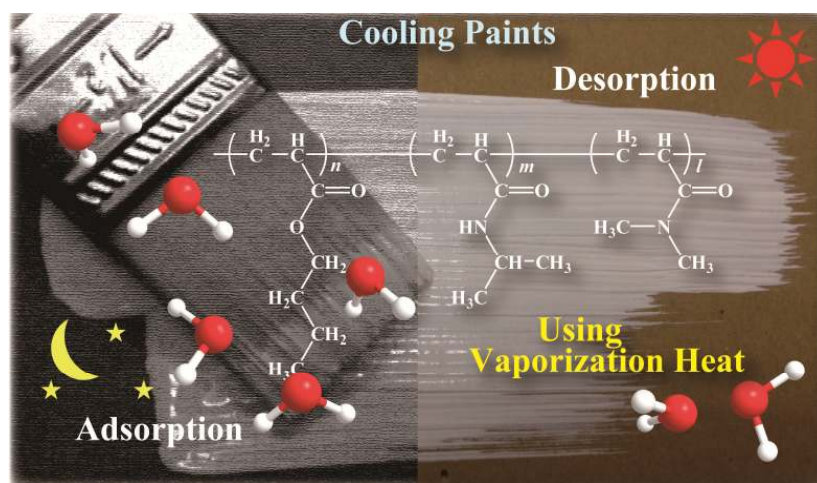

Fig. 2. Graphical abstract of this study. Water molecules are adsorbed on NIPAAm-co-BA-co-DMAAm in night and desorbed from the copolymer on hot daytime. By the vaporization heat of water, rooms can be cooled. This system can actuate without the need for electrical energy or labor
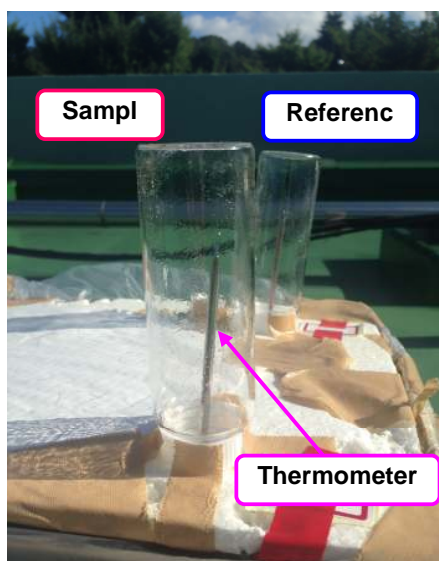
Fig. 3. Photograph of apparatus used for measuring temperatures in glass bottles outdoors

2. EXPERIMENTAL

Homopolymers of P(NIPAAm) and P(DMAAm) were prepared according to the procedures described in a previous report [2]. Copolymers of NIPAAm and DMAAm (NIPAAm-co-DMAAm), and NIPAAm, BA, and DMAAm (NIPAAm-co-BA-co-DMAAm) were obtained by the following procedure: NIPAAm, BA, and DMAA (monomers used in the ratios listed in Table 1) were dissolved in 56.6 mL of *tert*-butanol and radical polymerization was initiated by adding 0.136 g of ofα,α'-azobisisobutyronitrile (AIBN). The temperature of the solution was kept at 60°C for 20 h, after which the copolymers were obtained. In this work, two notations are used to indicate the monomer ratios in the copolymers: mole ratios of NIPAAm:BA:DMAAm or NIPAAm:BA and mole% ratios of DMAAm to total amount of (NIPAAm + BA) for simple presentation of the component ratios and DMAAm ratios. The translation between the two notations is outlined in Table 1.

Differential scanning calorimetry (DSC) data were recorded on a Shimadzu DSC-60 calorimeter using Al_2O_3 as a reference material. The samples were heated from about 273 K at a rate of 3 K min^{-1}. ^{1}H NMR spectra of the samples dissolved in deuterium-substituted CDCl$_3$ and dimethyl sulfoxide-*d*6 (DMSO-*d*6) were recorded at a Larmor frequency of 600.13 MHz using a Bruker Avance 600 spectrometer (14.10 T). ^{1}H NMR chemical shifts (CSs) were calibrated using an impurity peak of CHCl$_3$ (δ= 7.26 ppm) and CHD$_2$(SO)CD$_3$ (δ = 2.49 ppm) in CDCl$_3$ and DMSO-*d*6, respectively, as an internal standard. The cooling effects of the copolymers were estimated on the basis of the following

Table 1. The mole ratios of NIPAAm, BA, and DMAAm

NIPAAm-co-DMAAm			
DMAAm to NIPAAm	**(NIPAAm: DMAAm)**	**NIPAAm/g**	**DMAAm/g**
10 mol%	(0.91 : 0.09)	3.00	0.26
20 mol%	(0.73 : 0.17)	3.00	0.53
30 mol%	(0.77 : 0.23)	3.00	0.79
50 mol%	(0.67 : 0.33)	3.00	1.32
100 mol%	(0.50 : 0.50)	3.00	2.63
150 mol%	(0.40 : 0.60)	3.00	3.94
175 mol%	(0.36 : 0.64)	3.00	4.60
200 mol%	(0.33 : 0.67)	3.00	5.26

NIPAAm-co-BA-co-DMAA				
DMAAm ratios to (NIPAAm: BA)	**(NIPAAm: BA: DMAAm)**	**NIPAAm/g**	**BA/mL**	**DMAAm/g**
20 mol% (0.95 : 0.05)	(0.79 : 0.04: 0.17)	5.37	0.36	0.94
20 mol% (0.90 : 0.10)	(0.75 : 0.08: 0.17)	5.09	0.71	0.90
20 mol% (0.80 : 0.20)	(0.66 : 0.17: 0.17)	4.52	1.42	0.79
40 mol% (0.95 : 0.05)	(0.68 : 0.04: 0.28)	5.37	0.36	1.88
40 mol% (0.90 : 0.10)	(0.65 : 0.07: 0.28)	5.09	0.71	1.78
40 mol% (0.80 : 0.20)	(0.57 : 0.15: 0.28)	4.52	1.42	1.58
50 mol% (0.95 : 0.05)	(0.63 : 0.04: 0.33)	5.37	0.36	2.35
50 mol% (0.90 : 0.10)	(0.60 : 0.07: 0.33)	5.09	0.71	2.23
50 mol% (0.80 : 0.20)	(0.54 : 0.13: 0.33)	4.52	1.42	1.98

measurements: The copolymers were painted on different glass bottles with an outer diameter of 40 mm and a height of 120 mm. These bottles (sample) and blank (reference) were placed outside of a building, as shown in Fig. 3. The temperature inside the glass bottles was continuously recorded using data loggers of Sato Keiryou SK-L210T instrument.

3. RESULTS AND DISCUSSION

The introduction of DMAAm has been reported to increase the LCSTs of NIPAAm copolymers with various components [43-54]; thus, we prepared a copolymer of NIPAAm and DMAAm (NIPAAm-co-DMAAm) and we evaluated its hydrophilic effects before studying the three-component copolymer, NIPAAm-co-BA-co-DMAAm. In order to determine the hydrophobic/hydrophilic switch temperature of the copolymer, DSC measurements were performed after exposure to water vapor under ambient conditions. The DSC thermograms of the copolymers are displayed in Fig. 4. In order to confirm that the switch temperature corresponds to the LCST, a 532 nm laser light was employed. The solution can transmit the laser light below the LCST; in contrast, above the LCST, the solution becomes cloudy. The LCSTs determined using laser irradiation are plotted in Fig. 5. Comparison of the switch temperatures (Fig. 4) with the LCSTs (Fig. 5) reveals that the LCST corresponds to the temperature obtained by DSC measurements (LCST is determined in aqueous solution, the samples studied in this work are in solid state). Our findings show that the switch temperature increased with increasing DMAAm concentration in the copolymer. This tendency is similar to that

reported for copolymers formed by NIPAAm and DMAAm with various components [43-54]. In order to compare DMAAm with BA, the same measurement using laser light was performed for NIPAAm-co-BA in aqueous solution (Fig. 5). Because DMAAm and BA have opposite effects on the switch temperature of NIPAAm, we prepared three component copolymers (NIPAAm-co-BA-co-DMAAm) with various monomer ratios.

In order to confirm copolymerization of NIPAAm with BA and DMAAm, and to reveal molar ratios of NIPAAm, BA, and DMAAm in the copolymer, ^{1}H NMR spectra measurements of P(NIPAAm), PBA, P(DMAAm), and NIPAAm-co-BA-co-DMAAm were carried out. Based on the NMR lines displayed in Fig. 6, it is revealed that the copolymer of NIPAAm-co-BA-co-DMAAm is successfully obtained in our manipulation (signals of -C$\underline{H}_3$ in NIPAAm, BA, and DMAAm components were detected at 1.02, 0.85, and 2.77 ppm on the NMR spectrum of the copolymer, respectively). Since ratios of each peak's area were similar to those of monomers in preparation (the fact that NIPAAm and DMAAm have two -C$\underline{H}_3$ groups in each molecule is counted in this estimation), it can be considered that the copolymerization reaction is homogeneously progressed.

In order to evaluate the hydrophobic/hydrophilic effects on the switch temperature in NIPAAm-co-BA-co-DMAAm, the LCSTs of copolymers with various NIPAAm:BA:DMAAm mole ratios in aqueous solution were determined and are plotted in Fig. 7. The LCST decreased with increasing BA ratios and increased slightly with
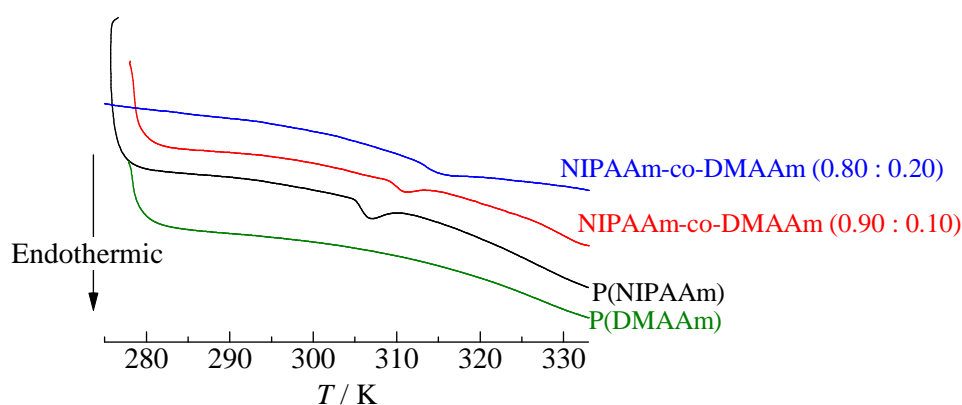

Endothermic

NIPAAm-co-DMAAm (0.80 : 0.20)

NIPAAm-co-DMAAm (0.90 : 0.10)

P(NIPAAm)
P(DMAAm)

280   290   300   310   320   330

T / K

Fig. 4. DSC thermograms of P(DMAAm), P(NIPAAm), and NIPAAm-co-DMAAm with mole ratios of 0.90:0.10 and 0.80:0.20

increasing DMAAm ratios. This tendency is similar to that observed for NIPAAm-co-BA and NIPAAm-co-DMAAm, shown in Fig. 5. DSC measurements of these copolymers were also attempted; however, the signal intensity was very weak. This can be explained by the different chemical environments of the NIPAAm regions in the copolymer of NIPAAm-co-BA-co-DMAAm as compared with those in NIPAAm-co-BA and NIPAAm-co-DMAAm; the switch temperatures in the three component copolymer are therefore distributed over a wide range: NIPAAm can take many chemical environments in the copolymer, e.g., -BA-$(NIPAAm)_m$-BA-, -BA--$(NIPAAm)_n$-DMAAm-, -DMAAm--$(NIPAAm)_l$-DMAAm-, (m, n, and l can have various values) etc. Therefore, the switch temperature can be considered to be distributed over wide temperature range as compared with the homopolymer of P(NIPAAm).
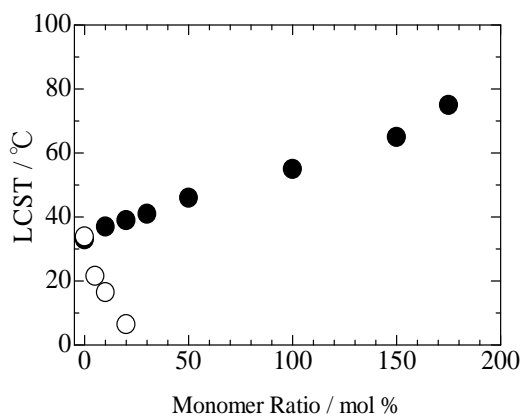

Fig. 5. Monomer ratio dependences of LCSTs observed for aqueous solution of NIPAAm-co-DMAAm(●) and NIPAAm-co-BA(○)

In order to evaluate the cooling effects of NIPAAm-co-BA-co-DMAAm, copolymers with various DMAAm ratios were coated onto the outer surface of glass bottles. After vaporization of t-BuOH solvent, the glass containers were placed in the apparatus together with the reference container, as displayed in Fig. 3. The temperature variations inside the containers are plotted in Fig. 8. The spikes of temperature difference (ΔT = reference - sample) recorded at around 6 and 17 o'clock can be attributed to the different heat capacity of the copolymer and the reference. As shown in Fig. 8(a), when the outer temperature was above approximately 30℃, the inner temperature of the bottles coated with 20 mol% copolymer (0.90:0.10) was lower than that of the reference. However, in the afternoon, ΔT

was reduced to about 0℃ although the outer temperature remained >30℃. This tendency is similar to that observed with NIPAAm-co-BA [2].
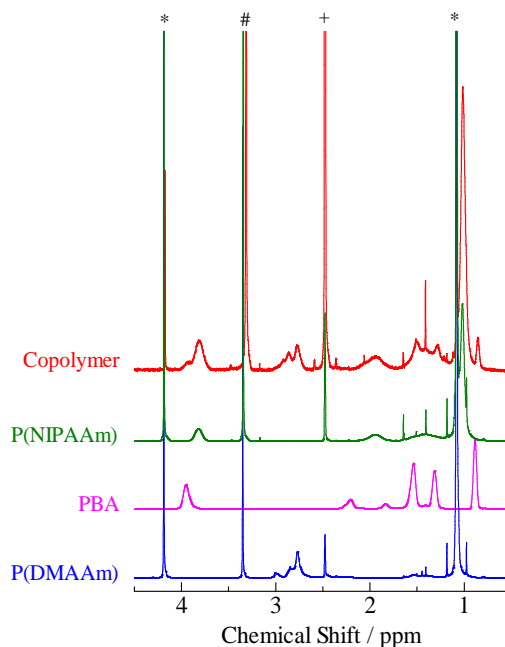

Fig. 6. ^{1}H NMR spectra of NIPAAm-co-BA-co-DMAAm (Copolymer), P(NIPAAm), PBA, and P(DMAAm) in DMSO-d6(+) solution (PBA was dissolved in CDCl$_3$ solution). Here, * and # denote peaks of t-BuOH and H$_2$O in the solutions
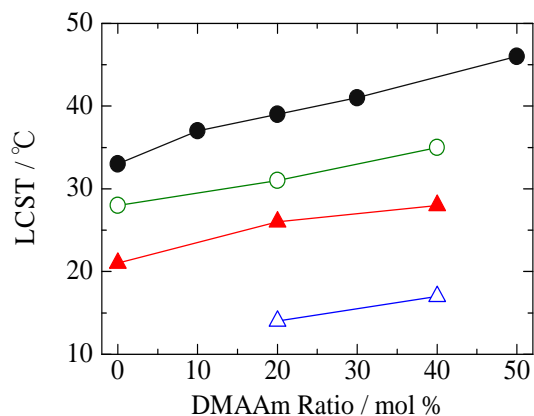

Fig. 7. LCSTs observed for NIPAAm-co-BA-co-DMAAm as a function of DMAAm ratios. In this figure, ratios of DMAAm are plotted as a function of total amount of NIPAAm and BA (ratios of NIPAAm:BA are 1.00:0.00 (●), 0.95:0.05 (○), 0.90:0.10 (▲), and 0.80:0.20 (△), respectively)

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(a) NIPAAm-co-BA (0.90 : 0.10)   DMAAm 20 mol%

(b) NIPAAm-co-BA (0.90 : 0.10)   DMAAm 40 mol%

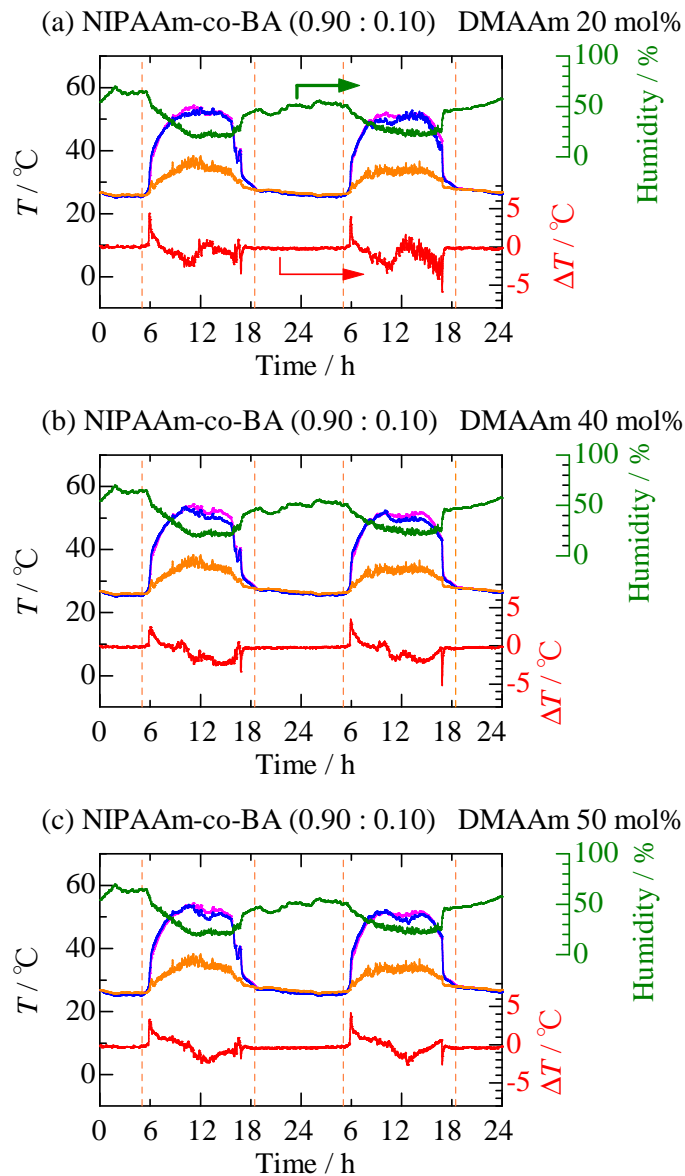### (c) NIPAAm-co-BA (0.90 : 0.10)   DMAAm 50 mol%

Fig. 8. Temperature changes in glass bottles coated with copolymer of NIPAAm-co-BA-co-DMAAm. DMAAm concentrations of (a) 20, (b) 40, and (c) 50 mol% relative to total amount of NIPAAm and BA with a mole ratio of 0.90:0.10. Temperatures of outer environment, reference, and sample are shown by orange, purple, and blue solid-lines, respectively. Temperature difference between sample and reference, and humidity are displayed by red and green curves, respectively. In this figure, sunrise and sunset times are shown by orange dotted lines

In contrast, negative ΔT values were recorded for 40 mol% (0.90:0.10) and 50 mol% (0.90:0.10) of NIPAAm-co-BA-co-DMAAm over a wide period of time when the ambient temperature was above approximately 35℃, as shown in Figs. 8(b) and (c). This tendency of the actuated temperature to increase with increasing DMAAm concentration is similar to that of the LCST, as

displayed in Fig. 7. Thus, the negative ΔT can be attributed to the cooling effect of the copolymer. In the case of the 20 mol% (0.90:0.10) copolymer (Fig. 8(a)), the cooling effect was observed for a short period, although the outer temperature exceeded 30℃ until evening. This can be explained by the same argument used for NIPAAm-co-BA [2]: because an average switch

temperature of 25℃ was measured for the copolymer, as displayed in Fig. 7, it can be considered that a small amount of water molecules was adsorbed on the copolymer during the night. In contrast, the LCST of the copolymers with DMAAm ratios of 40 and 50 mol% was about 30℃. Because the outer temperature decreased below this value at night, it can be deduced that the copolymer adsorbed water molecules at night and the cooling effect continued into the next day. In order to determine the amount of water molecules adsorbed on the copolymers, the weight changes of the copolymer were observed as a function of time (*t*) at 38℃ (although this temperature is much higher than the LCST of PNIPAAm and room temperature, it is reported that the whole polymers of P(NIPAAm) can't be condensed in aqueous solution at around 32℃ (the condensation is continued until approximately 36℃) [1]). Prior to this measurement, the NIPAAm-co-BA-co-DMAAm copolymers were exposed to water vapor at room temperature (about 20℃). The weight ratios, defined by the following equation, were plotted versus *t* (Fig. 9).

weight ratio =

$$\frac{\text{weight of sample}(t) - \text{weight of dried sample}}{\text{weight of dried sample}} \times 100 \quad (1)$$

At a constant temperature of 38℃ (humidity of about 50%), the ratios decreased gradually with *t*. These weight reductions are due to the vaporization of the water molecules from the copolymer. After the first cycle of measurements, the same samples were again exposed to water vapor at room temperature (about 20℃) and then reheated (second cycle). The weights of the copolymers at the beginning and at the end of the second cycle were comparable to the values measured in the first cycle. Thus, it can be concluded that the water molecules are repeatedly absorbed and removed from the copolymers. The values reported for P(NIPAAm) adsorbed on mesoporous silica [1] and NIPAAm-co-BA [2] are also displayed, to show the effect of DMAAm on the adsorbed water weight. These data revealed that a larger amount of water molecules was repeatedly adsorbed on NIPAAm-co-BA-co-DMAAm as compared with that adsorbed on NIPAAm-co-BA. In addition, the values of water ratio recorded at *t* = 0 in the first cycle is decreased with decreasing DMAAm concentration in NIPAAm-co-BA-DMAAm. Similar ratios were recorded for 50 mol% NIPAAm-co-BA-co-DMAAm and for P(NIPAAm)

in mesoporous silica at the beginning and at the end of the first and second cycle; this suggests that an amount of water molecules sufficient to cool the atmosphere is linked to the copolymers of 50 mol% NIPAAm-co-BA-co-DMAAm. These tendencies are consistent with the cooling effects observed for the copolymers and reported for P(NIPAAm) in mesoporous silica and NIPAAm-co-BA: P(NIPAAm) in mesoporous silica [1] and NIPAAm-co-BA-co-DMAAm repeatedly show the cooling effect during daytime, whereas NIPAAm-co-BA can serve until noon [2].
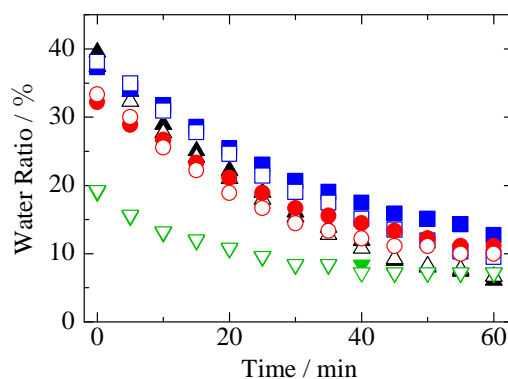

Fig. 9. Weight ratios of NIPAAm-co-BA-co-DMAAm in the first (solid) and second (open symbols) cycles at 38℃ as a function of time. Red circles, and blue squares indicate DMAAm ratios of 20, and 50 mol% relative to total amount of NIPAAm and BA (0.90:0.10), respectively. Data reported in P(NIPAAm) adsorbed on mesoporous silica [1] and NIPAAm-co-BA [2] are also displayed as black triangle and green opposite-triangle, respectively

4. CONCLUSION

We developed new cooling paints based on NIPAAm-co-BA-co-DMAAm, which exploit the vaporization heat of water from the coating materials. The copolymers present a hydrophobic/hydrophilic switch at approximately 30℃. These systems can be widely applied to buildings, trains, cars, etc. Thus, the temperature of a room painted with the copolymers decreases if the external temperature increases to above 30℃. Because this cooling system is based on the absorption of water molecules from air during the night (if the temperature is < 30℃), it can be activated using only temperature changes, without the use of electrical energy and labor. Thus, this system depends on climatic conditions and can be therefore applied in Southeast Asia,

where temperature and humidity are high and the increasing urban population would require an enormous amount of energy in the future.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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