Application of Copolymers of *N*-Isopropylacrylamide and Vinyl Acetates for use in Cooling Materials

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Abstract

New cooling paints are investigated, which exploit the vaporization heat of water to repeatedly cool a room on hot days without using electrical or human energy. When the coating materials are applied to the wall of a room, water molecules are adsorbed from air onto the coating materials at night (below ca. 30 °C), and if the outside temperature exceeds the stated temperature, the water molecules become desorbed and are vaporized. This system can be realized using *N*-isopropylacrylamide (NIPAAm). However, the homopolymer of NIPAAm dissolves in water below ca. 32 °C (hydrophilicity), whereas it is insoluble in water above the stated temperature (hydrophobicity); therefore, it is difficult to use the homopolymer outdoors. By copolymerization of NIPAAm with paint components, they can be anchored into walls. Since the hydrophilic/hydrophobic switch-temperature of NIPAAm depends on the coating components, a paint component that does not affect the switch temperature is required. In this study, it was revealed that a copolymer of NIPAAm with vinylacetate (VA) showed a switch temperature of ca. 30 °C, and that this temperature was largely independent of VA ratios.

Key Words:

Cooling Material, *N*-Isopropylacrylamide, Vinylacetate, Vaporization Heat

Introduction

Global warming and the urban heat island phenomenon are serious problems in the world. In addition, energy problems will occur from future urban development in developing nations. In the summer, an enormous amount of energy is used to cool rooms using air conditioners. People often use water to cool the atmosphere by sprinkling walls, lanes, gardens, etc. However, human and/or electrical energy are required to pump and sprinkle water. This energy requirement comes from the use of water in the liquid state; if moisture can be converted to liquid water without using electrical energy during summer nights, the energy required to cool rooms can be reduced. We previously proposed a new cooling system consisting of temperature responsive poly(*N*-isopropylacrylamide), abbreviated as P(NIPAAm), with a C_2H_4-inserted mesoporous silica [1]. The homopolymer of P(NIPAAm) has a known lower critical solution temperature (LCST) of ca. 32 °C in aqueous solution [2]: below the LCST, the polymer can dissolve in water; conversely, above that temperature, it is insoluble. Applying P(NIPAAm) to the C_2H_4-inserted mesoporous silica, the system absorbs water molecules from the air during the summer night and water is vaporized during the hot daytime. Based on this effect, the temperature inside a box can be successfully decreased without using electrical energy. In addition, NMR measurements reveal that P(NIPAAm) is hardly desorbed into water below the LCST. For more universal application of the cooling system, we also propose another cooling system in which NIPAAm forms copolymers with coating materials. By copolymerizing NIPAAm with butyl acetates (BA) and *N,N*-dimethylacrylamide (DMAAm), new cooling paints of the form NIPAAm-co-BA-co-DMAAm can be investigated [3]. The copolymers can be painted on various materials and cool a room in summer days using the vaporization heat of water. This system can be used on various subjects, e.g. houses, buildings, cars, trains, etc. The copolymer of NIPAAm-co-BA-co-DMAAm is a suitable paint for the cooling materials, however, the hydrophilic/hydrophobic switch-temperature is strongly dependent on BA and DMAAm ratios in the copolymer. The hydrophilic/hydrophobic switch-temperature is the same temperature as the LCST, however the LCST is used in aqueous solutions. In comparison to the copolymers, only a small amount of water is present in solid materials, and therefore the term switch-temperature is used. Increasing the BA concentration, results in a decrease of the switch-temperature, conversely, DMAAm components increase the switch-temperature [3]. If the switch-temperature is too low, e.g. 20 °C, copolymers adsorb too few water molecules from the air in summer nights. In contrast, if the switch temperature is too high, e.g. 40 °C, the copolymers can adsorb sufficient water, however they rarely desorb the water molecules and the system can only cool rooms for a

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few days each year. Therefore, it is important to investigate potential compounds where the switch-temperature is largely independent of the ratios of the copolymer components.

We employed vinyl acetates (VAs) (the chemical structures are displayed in Fig. 1) for copolymerization with NIPAAm in this study, because VAs are widely applied in industry. A homopolymer of VA, abbreviated to PVA, has a low softening temperature and is used in industry for pigments for paints, adhesives, molds in solid articles, etc. [4]. The molecular dynamics of PVA have been investigated by ^{1}H and ^{13}C NMR studies in solids and solutions [5-7]. Copolymers of VA with ethylene are studied and applied widely in many fields [8-34]. The NIPAAm homopolymer and copolymers are applied to drug delivery [35–40], separation [41–46], thermoresponsive self-assembling micelles [47]. P(NIPAAm) forms a coiled conformation at temperatures below the LCST, and the polymers condense together in aqueous solutions above this temperature [48-54]. In the solid-state of P(NIPAAm), similar behavior to that in solution has been reported: polymer swollen in a small amount of water shows a phase transition at a temperature close to the LCST [1, 3, 55]. In addition, it has been reported for solid-state P(NIPAAm) that the swollen polymer forms hydrogel walls in itself, and the walls prevent the polymer from absorbing and desorbing water molecules [1, 3, 56].

In this study, we investigated new cooling paints based on P(NIPAAm) with VA. The new materials can be painted on several surfaces and cool them on hot days without using any electrical or human energy.
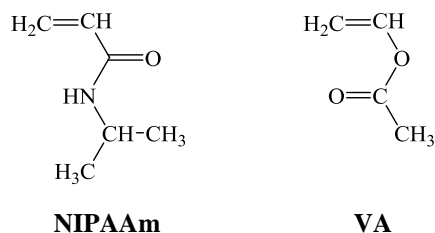

Figure 1: Chemical structures of *N*-isopropylacrylamide (NIPAAm) and Vinyl Acetylates (VA).

Experimental

P(NIPAAm) was prepared according to the recipe described in previous reports [3]. PVA and copolymers of NIPAAm-co-VA were prepared by a similar method: NIPAAm and VA (the monomer ratios of these copolymers are listed in Table 1) were dissolved in *tert*-butanol (56.6 mL) and radical polymerization was started by addition of α,α'-azobisisobutyronitrile (AIBN) (0.136 g) under a N_2 atmosphere. The temperature of the solution was maintained at 60 °C for 20 h, and the copolymers diluted in *tert*-butanol were obtained.

In order to estimate reaction rates, 1,10-phenanthroline (Phen) was dissolved in another reaction solution. Since this chemical substance was hardly reacted by monomers and AIBN in the reaction conditions, the concentration of the monomer was estimated based on the Phen concentration at each reaction time. The amount of monomer and Phen was estimated by the area of ^{1}H NMR signals.

^{1}H and ^{13}C NMR spectra of the specimens dissolved in deuterated solvents were recorded at Larmor frequencies of 600.13 and 150.92 MHz, respectively, using a Bruker Avance 600 spectrometer (14.10 T). ^{1}H and ^{13}C NMR chemical shifts (CSs) were calibrated using the solvent signals of $CDCl_3$ ([13]C: 77.16 ppm) as an internal standard. The sample temperature was controlled and recorded using a Bruker VT-2000 instrument.

Differential scanning calorimetry (DSC) spectra were obtained using a Shimadzu DSC-60 calorimeter, with a reference sample of Al_2O_3. The samples were heated from ca. 273 K at a rate of 3 K min^{-1}.

The cooling effects of the polymers were obtained based on the following measurements: the polymers of PVA and NIPAAm-co-VA were coated on a glass bottle (outer diameter, 40 mm; height, 120 mm) and the bottles (one coated; one blank) were set outside of a building as shown in Fig. 2. The temperatures in the glass bottles and moisture content were continuously recorded using a Sato Keiryou SK-L210T instrument.

Table 1: The mole ratios of NIPAAm and VA

Molar Ratio	VA / g	NIPAAm / g
10:90	0.43	5.09
20:80	0.86	4.52
30:70	1.29	3.96
40:60	1.72	3.39
50:50	2.15	2.83

Results and Discussion

Verification of Copolymerization

In order to assign NMR peaks, DFT simulations were carried out. In this calculation, we employed models of PVA (homopolymer of VA) and P(NIPAAm) constructed by five monomers, i.e. VA-VA-VA-VA-VA and NIPAAm-NIPAAm-NIPAAm-NIPAAm-NIPAAm. Atomic arrangements of the homopolymers and monomers were optimized by a function of B3LYP/6-31G** in the Gaussian 03 computer program [57]. Shielding tensors of each chemical were estimated by the same function of B3LYP/6-31G**. CS values were calculated by subtracting the isotropic values of the shielding tensor estimated in the molecules from those of a tetramethylsilane (TMS) molecule,
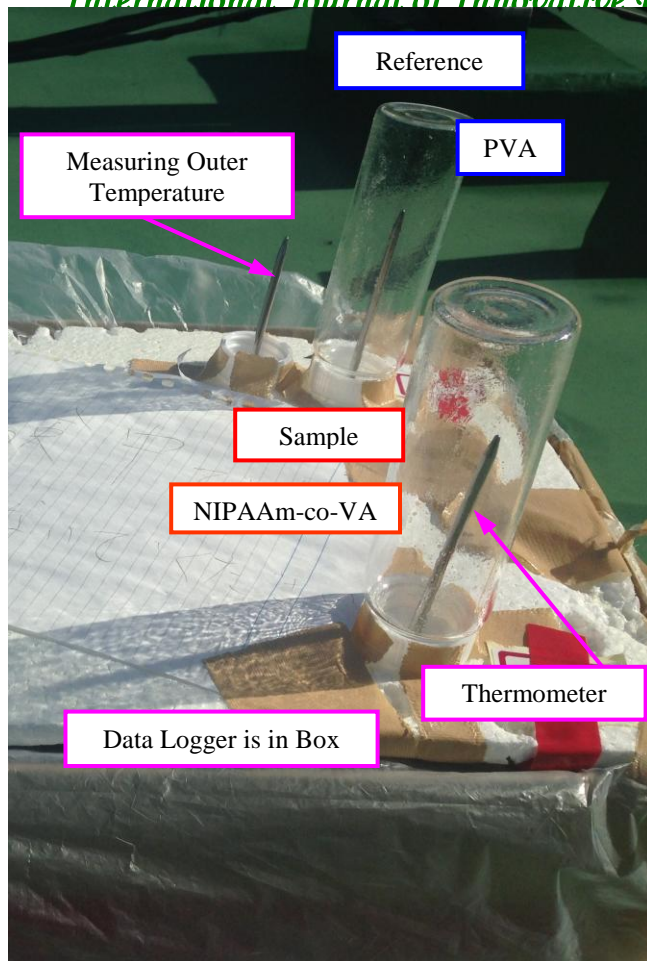
Figure 2: Photograph of apparatus used for measuring temperatures in glass bottles outdoors.

NIPAAm-co-VA. Based on our DFT estimation in the NIPAAm-NIPAAm-VA-NIPAAm-NIPAAm model, this new signal can be assigned to the C atom of $-\underline{C}H_2-CH(OCOCH_3)-$ in the copolymer. In contrast, the small CS shift was recorded in the NIPAAm parts by copolymerization. These two results recorded on the spectrum of the copolymer are consistent with our estimation model of NIPAAm-NIPAAm-VA-NIPAAm-NIPAAm, therefore, we can conclude that copolymerization was successfully achieved.

^{13}C	NIPAAM	P(NIPAAm)
CH_2	112.922	27.8076
CH	114.512	39.5535
CO	146.77	157.102
$C\underline{H}(CH_3)_2$	40.234	35.737
CH_3	10.2921	12.1425

Table 2: ^{1}H and ^{13}C NMR CS values estimated by a function of

^{13}C	VA	PVA	-VA-*
CH_2	80.7808	34.1147	31.4932
CH	127.099	61.4083	61.7664
CO	151.551	157.155	157.301
CH_3	9.5016	11.034	13.1029

B3LYP/6-31G**.

^1H	NIPAAm	P(NIPAAm)
CH_2	6.10275	1.64255
CH	5.69205	2.11805
CO	4.61725	8.76835
$C\underline{H}(CH_3)_2$	2.94405	4.38015
CH_3	1.39628	6.7927

^1H	VA	PVA	-VA-*
CH_2	4.64295	1.55645	2.12565
CH	7.64515	5.23085	5.59515
CH_3	1.82705	1.84895	2.21622

* CS values of VA in a NIPAAm-NIPAAm-VA-NIPAAm-NIPAAm model

where an isotropic shielding-tensor of TMS was simulated by the same process as described above. We adopted the CS values at the center block of the homopolymer models. The results of the ^{13}C NMR CS simulation are summarized in Table 2. In this table, CS values estimated for VA in a NIPAAm-NIPAAm-VA-NIPAAm-NIPAAm model were also displayed. This model corresponds to a copolymer of NIPAAm-co-VA treated in this study, because ^{13}C NMR measurements was performed for the copolymer (VA:NIPAAm = 10:90). ^{13}C NMR spectra observed in VA, PVA, NIPAAm, P(NIPAAm), and NIPAAm-co-VA dissolved in CDCl$_3$ solution are shown in Fig. 3. Comparing the spectra of PVA and VA with our DFT simulation, the C atom signal of $-\underline{C}H_2-CH(OCOCH_3)-$ detected at ca. 39 ppm guaranteed that PVA was successfully prepared in our synthesis condition. In addition, the signal of $-\underline{C}H_2-CH(OCOCH_3)-$ recorded at ca. 39 ppm was reduced and a new line was observed at ca. 31 ppm in the spectrum of
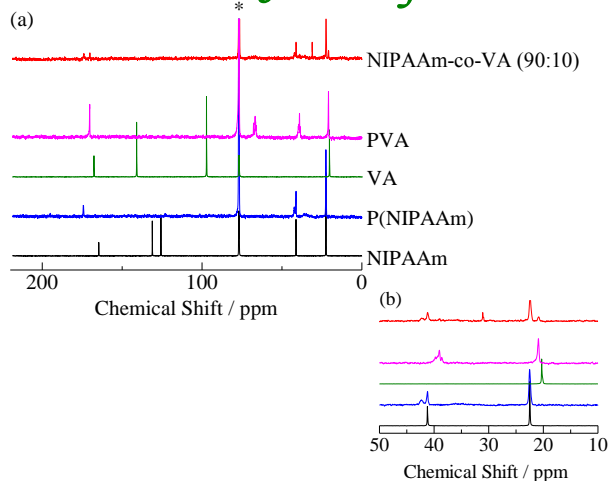
Figure 3: ^{13}C NMR spectra of NIPAAm, P(NIPAAm), VA, PVA, and VA-co-NIPAAm in CDCl$_3$ solution. (a) Whole and (b) enlarged signals. Here, * denotes a ^{13}C signal of
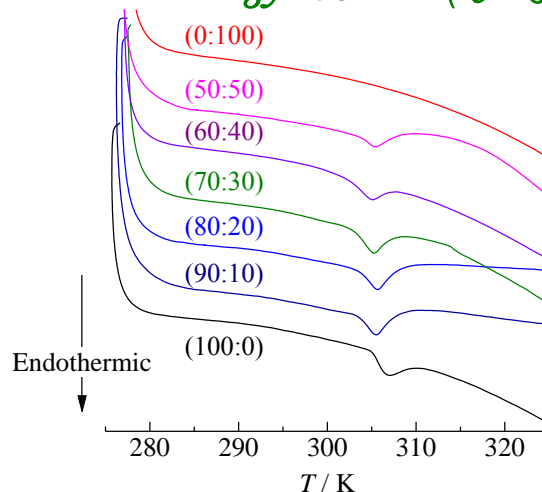

Figure 4: DSC thermograms of NIPAAm-co-VA. Values in parentheses are the ratios of NIPAAm and VA. The ratios of (0:100) and (100:0) corresponding to the homopolymers of PVA and P(NIPAAm), respectively.

Hydrophilic/hydrophobic switch-temperatures

It is reported that hydrophilic/hydrophobic switch-temperatures are decreased with increasing BA concentration in NIPAAm-co-BA, but in contrast, are increased with DMAAm ratios in NIPAAm-co-DMAAm [3]. In this study, we observed VA ratio dependencies of the switch temperatures in NIPAAm-co-VA. DSC thermograms observed in NIPAAm-co-VA with various VA ratios are displayed in Fig. 4. This figure shows that (i) NIPAAm-co-VA also has a switch temperature of around 30 °C, although PVA showed no transition; and (ii) the temperature is independent of the VA ratios in NIPAAm-co-VA; and in addition, (iii) the DSC peak widths are constant. In NIPAAm-co-BA, it is reported that the line-breadth is increased with BA ratios and the signal cannot be detected with a BA ratio of 15 mol% [3]. It can be considered that this disappearance between NIPAAm-co-VA and NIPAAm-co-BA is caused by an affinity difference of BA and VA with NIPAAm in each copolymer. In order to estimate the difference between BA and VA, measurements of reaction rate were performed. Both NIPAAm (0.50 g) and VA (0.38 g) were dissolved into *t*-BuOH (10 mL), and Phen (0.50 g) was added into the solution. Here, Phen is the internal reference to estimate amounts of VA and NIPAAm monomers in the reaction solution. Before this copolymerization, it was confirmed that Phen hardly reacted with AIBN (the polymerization initiator), VA, NIPAAm, hydroquinone (HQ; terminator for radical polymerizations) in *t*-BuOH by use of ^{1}H NMR measurements; and in addition, ^{1}H NMR signals of Phen were detected in the range of 7.5-9.5 ppm where the peaks of VA, NIPAAm, and the

copolymer weren't detected. After AIBN (0.015 g) was added into the bottle, the temperature in the flask was kept at 65 °C. We took out a small amount of the reaction solution from the container and dropped it into an NMR tube with DMSO-*d*6 and HQ solution. The ^{1}H NMR spectra obtained at each time are shown in Fig. 5. These areas were normalized by the peak area of Phen. The same measurements were repeated three times and averaged signal-areas of VA and NIPAAm monomers were plotted as a function of reaction time (*t*). The results displayed in Fig. 6(a) show this reaction is a first-order reaction. The reaction rates estimated by the slopes are listed in Table 3. The same procedures were applied to copolymerization of NIPAAm with BA, alternating VA to BA, of 0.57 g. The time dependencies of remaining monomer ratio were demonstrated in Fig. 6(b). In order to compare the reaction rates, homopolymerization of NIPAAm was performed by adding NIPAAm (1.00 g) and Phen (0.50 g) into *t*-BuOH (10 mL). The slope and reaction rate obtained in P(NIPAAm) are displayed in Fig. 6(c) and Table 3, respectively.

Table 3: Reducing rates (mol min^{-1}) of NIPAAm, VA, and BA monomers.

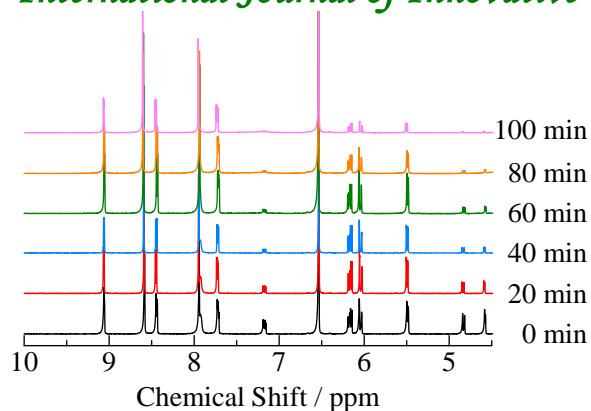|	NIPAAm	VA or BA
NIPAAm-co-VA	1.97±0.08	5.08±0.30
NIPAAm-co-BA	2.99±0.03	2.05±0.03
P(NIPAAm)	3.70±0.05	-

Figure 5. Reaction-time dependence of ^{1}H NMR signals observed during the copolymerization of NIPAAm and VA with a mole ratio of 50:50. Here, the signals recorded in a range of 7.5-9.3 ppm are inner reference of 1,10-phenanthroline (Phen). The spectral intensities are normalized by the signals of Phen. Values shown on right side of each spectrum are reaction times.
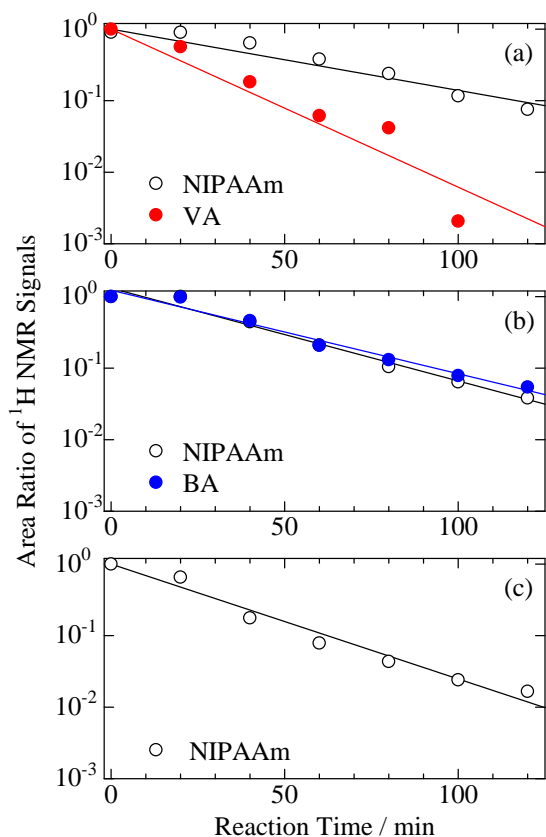
slopes of NIPAAm and VA were different to NIPAAm-co-VA, although similar gradients were obtained in NIPAAm-co-BA. Since the slopes show the reaction rates of the monomers, it can be considered that NIPAAm and BA are uniformly polymerized: -BA-NIPAAm-BA-NIPAAm-BA-NIPAAm-. In contrast, the slope of VA is larger than that of NIPAAm in NIPAAm-co-VA. This fact suggests that heterogeneous polymerization occurred in the reaction: a VA monomer prefers polymerizing with another VA, rather than NIPAAm, in the initial period of the reaction. Based on this result, we can determine a copolymerization model (Fig. 7). This model can explain why the hydrophilic/hydrophobic switch temperature is hardly dependent on the VA ratio in NIPAAm-co-VA, whereas in NIPAAm-co-BA, it depends on the BA ratio. Since polymerization is uniformly developed in NIPAAm-co-BA, NIPAAm can take many chemical environments in a copolymer, e.g. -BA-NIPAAm-BA-, -BA-NIPAAm-NIPAAm, -NIPAAm-NIPAAm-NIPAAm-, etc. Therefore, the switch-temperature can be strongly dependent on the BA ratio. In contrast, the copolymerization with VA progresses heterogeneously, therefore NIPAAm-co-VA can be considered to have NIPAAm and VA blocks, and the switch-temperature is hardly dependent on the VA ratio.
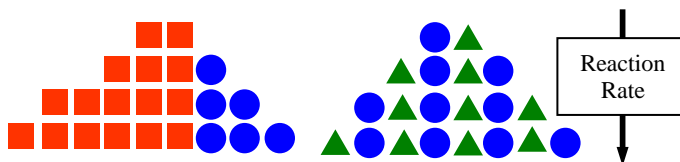

Figure 7: Copolymerization models of NIPAAm-co-VA and NIPAAm-co-BA constructed from the results of Fig. 6. In this model, the symbols red square, blue circle, and green triangle, denote the monomers of VA, NIPAAm, and BA, respectively.

Figure 6: Reaction time dependencies of ^{1}H NMR spectra areas observed in monomers of NIPAAm (○), VA (●), and BA (●) in copolymerization of (a) NIPAAm and VA, (b) NIPAAm and BA, and (c) homopolymerization of P(NIPAAm).

Based on the reaction rates shown in Fig. 6 and Table 3, the

Cooling Effect

In order to demonstrate the cooling effects of NIPAAm-co-VA, the copolymers with NIPAAm:VA = 90:10 were coated onto the outer surface of glass bottles and set up in an apparatus as displayed in Fig. 2. The temperature changes and difference (ΔT) values observed in the inside of the containers are plotted in Fig. 8. Here, it was fine weather on the first day, however, it was cloudy for a short period at around 15:00 h on the second day. Therefore, the temperatures in the bottles and the atmosphere were drastically decreased on the second day, this accounts for the spiked signals in the ΔT values. The ΔT signals recorded at ca. 6:00 h (Sunrise) and 18:00 h (Sunset) can be considered in terms of the difference between the heat capacity of the copolymer and reference. In this figure, the inner temperature of the bottle coated with the copolymer was lower than that of the reference (negative ΔT values were recorded), if the outer temperature was above ca. 30 °C: the cooling effect was obtained in the coating material of NIPAAm-co-VA. In addition, the cooling effect was detected again on the second day. In order to confirm this cooling effect, weight changes of NIPAAm-co-VA were measured as a function of time (t) at 38 °C. Before this measurement, the copolymers were exposed to water vapor at room temperature. The weight ratios, as defined by the following equation, were plotted versus t, as shown in Fig. 9.

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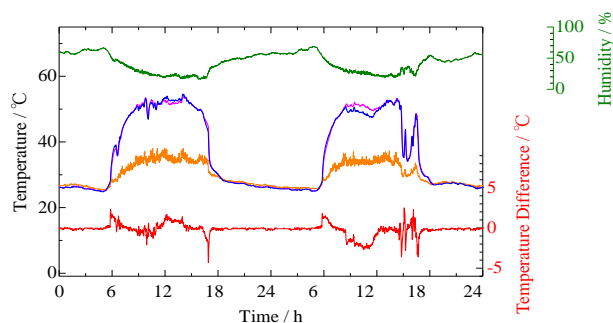

Figure 8: Temperature changes in glass bottles coated with the copolymer of NIPAAm-co-VA. Temperatures of the outer environment, reference, and sample are shown by orange, purple, and blue lines, respectively. The temperature difference between the sample and reference (red line) and humidity (green line) are displayed.

The ratio was gradually reduced with t at the constant temperature of 38 °C. This weight change is the result of vaporization of water molecules from the copolymer. After

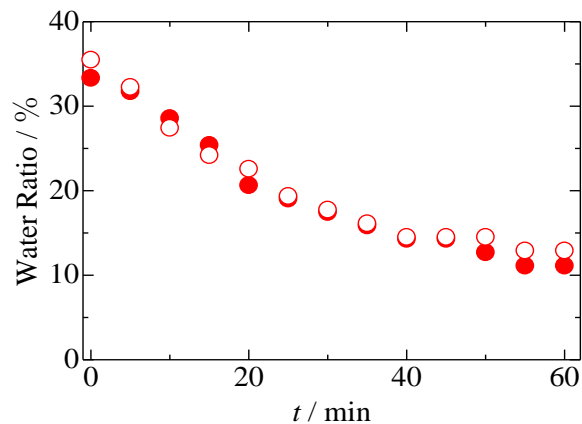the first cycle of measurements, the same sample was again

Figure 9: Weight ratios of NIPAAm-co-VA observed in the first (●) and second (○) cycles at 38 °C as a function of time.

exposed to water vapor at room temperature, and then reheated (the second cycle). The copolymer weight at the beginning and end of the second cycle was similar to those recorded in the first cycle, as demonstrated in Fig. 9. Therefore, it was revealed that water molecules can be repeatedly absorbed onto and removed from the copolymer. Therefore, it can be concluded that this paint material can cool rooms in hot days without requiring any electrical or human energy. In this copolymer, it is suggested that a small amount of water molecules are adsorbed on and removed from the copolymer, therefore the cooling effect is short-lived. However, we can show that cooling materials are obtained when a copolymer of NIPAAm with one chemical component is obtained. To carry out investigations of the cooling paints, it is important that the hydrophobic/hydrophilic switch-temperature is largely independent of the copolymer agents.

Conclusions

We describe a new cooling paint composed of NIPAAm-co-VA that exploits the vaporization heat of water. The copolymer can adsorb water molecules from air if the external temperature decreases to below ca. 30 °C, and desorb water molecules from the copolymer when the ambient temperature increases to above the switch-temperature. The copolymer of NIPAAm-co-VA retains a hydrophobic/hydrophilic switch-temperature of ca. 30 °C with increasing VA ratios, although the switch-temperature is decreased with BA ratios in the copolymer NIPAAm-co-BA [3]. These different behaviors can be explained by homogeneous and heterogeneous polymerization methods: VA monomers prefer polymerizing with other VA molecules, rather than NIPAAm monomers, in the reaction solution.

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This inhomogeneous copolymerization results in VA and NIPAAm blocks in the copolymer. Conversely, a BA monomer can randomly react with NIPAAm or another BA, and therefore form copolymers in which BA and NIPAAm are uniformly distributed. Since the NIPAAm-co-VA copolymer can activate at around 30 °C with various VA ratios, this system can be applied to the investigation of cooling materials, which do not require the use of electrical or human energy.

Acknowledgements

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