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RESEARCH ARTICLE

INVESTIGATION OF NEW COOLING PAINTS ACTUATED ON HOT DAYS WITHOUT ELECTRICAL ENERGY AND LABORS

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ABSTRACT

I New cooling paints were developed by exploiting the vaporization heat of water. These systems were constructed with *N*-isopropylacrylamide (NIPAAm) and butyl acrylate (BA). The homopolymer of NIPAAm is insoluble in water above ca. 32°C (hydrophobic), whereas it dissolves in water below the stated temperature (hydrophilic); therefore, application of the temperature responsive polymer on the outside of a house is difficult on cool and rainy days. By copolymerization of NIPAAm with a coating component of BA which is widely used for various commercial paints, water resistance was gained in this system. When the copolymer was applied to the wall of a model house, water molecules were adsorbed on the material from air during the night (below ca. 30°C) and the temperature of the room decreased if the outside temperature exceeded the temperature. The coating material could cool the room on hot days without using any electrical energy or labors, therefore this system can relieve the burden of energy consumption by air conditioners.

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INTRODUCTION

Global warming and the heat island phenomenon are serious problems in this period. An enormous amount of energy is used to cool rooms using air conditioners, especially in the summer. People often use water to cool the atmosphere by sprinkling lanes and gardens. Recently, wall- and roof-greening projects have been successfully applied to reduce the consumption of electrical energy during the summer. However, labors and electrical energy are required to perform work and for plant growth, e.g., water has to be pumped up to roofs and sprinkled using electrical energy or human activity. 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, the energy required to keep rooms cool can be reduced.

We previously proposed a new cooling system consisting of temperature responsive polymer of poly (*N*-isopropylacrylamide), abbreviated as P (NIPAAm), with a C₂H₄-inserted mesoporous silica (Suzue *et al.*, 2014). This material undergoes hydrophobic/hydrophilic switching at around 30°C. The system absorbs water molecules from the air during the night and water is desorbed when the temperature rises above the aforementioned temperature. Based on this effect, the temperature in a box is successfully decreased by ca. 4°C relative to that outside the building. This system can cool rooms on hot days without using any electrical or labors. In addition, P(NIPAAm) adsorbed in the mesoporous silica is hardly desorbed into water at temperatures below 32°C, since P(NIPAAm) can be anchored into the porous materials. P(NIPAAm) is well known as having a lower critical solution temperature (LCST) at ca. 32°C in aqueous solution (Heskins *et al.*, 1968). The polymer can dissolve in water below the LCST but becomes insoluble above this temperature. This property is exploited in drug delivery (B. P. Timko *et al.* 2014; Qian *et al.*, 2013; Wang *et al.*, 2011; Hoffman *et al.* 1986; Hruby *et al.*, 2009; Saitoh *et al.*, 1999), separation (Kimhi *et al.*, 2002; Sassi *et al.*, 1996; Castellanos

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et al., 2007; Tokuyama *et al.*, 2007; Fujinaga *et al.*, 1997; O'Shea *et al.*, 2010), thermo responsive self-assembling micelles (Hofmann *et al.*, 2009), catalysts (Hamamoto, 2012), etc. This property change is proposed to occur via the coil-to-globule transition of P(NIPAAm). At temperatures below the LCST, the polymer adopts a coiled conformation and solvent molecules can link the side chains of P(NIPAAm); in contrast, the polymers condense together in solution above the LCST (Stillinger 1980; Sun *et al.*, 2008; Crassous *et al.*, 2008 Mackiewicz *et al.*, 2014; Speřác'ek *et al.*, 2014; Ishida *et al.*, 2007; Ishida *et al.*, 2007). In solid-state P (NIPAAm), similar behavior to that in solution has been reported: The polymer swollen in a small amount of water shows a phase transition at a temperature close to the LCST (Suzue *et al.*, 2014; Badiger *et al.*, 1991). Solid-state NMR measurements show that the motions of P(NIPAAm) molecules grafted on cotton fabric surfaces are restricted above the LCST (Yang *et al.*, 2012; H. Yang *et al.*, 2013). 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 (Tao *et al.*, 2009). Wall formation is reduced in the composite comprising the polymer with C₂H₄-inserted mesoporous silica due to absorption of water molecules. As described above, we can obtain cooling systems using only temperature and humidity changes without the use of electrical and labors (Suzue *et al.*, 2014). Based on the report, this system can apply to large areas of high temperature and humidity. For more universal application of the cooling system, e.g. trains, cars, buildings, etc., we can propose a cooling paint in which P(NIPAAm) is included.

Butylacrylate (BA) is a component of painting materials that is widely used for various commercial coating materials. Copolymers of BA and NIPAAm with propyl acrylic acid are currently applied to therapeutic protein delivery in vivo (Garbern *et al.*, 2011; Joshi *et al.*, 2013). However, the application of copolymers of NIPAAm and BA to cooling systems is rarely reported. In this study, we investigate new cooling paints based on NIPAAm with BA (the chemical structures are displayed in Fig. 1 and an image of this system is illustrated in Fig. 2). Since the copolymers of NIPAAm-co-BA can paint on several materials, the pasts can cool rooms of house, train, cars, etc. on hot days without electrical energy or labors. This system can apply in wide areas of the world, especially in East and Southeast Asia.

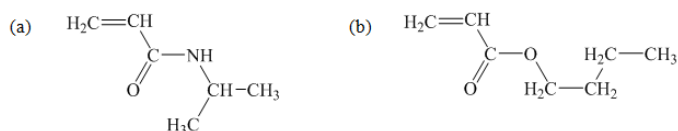


Fig. 1. Chemical structures of (a) *N*-isopropylacrylamide (NIPAAm) and (b) butyl acrylate (BA).

Experimental

A homopolymer of NIPAAm was prepared by free-radical polymerization: 5.0 g of *N*-isopropylacrylamide (NIPAAm) (Wako Junyaku Co.) and 84 mg of α,α -azobisisobutyronitrile (AIBN) (Kanto Kagaku Co.) were dissolved in 20 mL of ethanol under N₂ gas atmosphere.



Fig. 2. Graphical abstract of this study. Water molecules are adsorbed on NIPAAm-co-BA in night and desorbed on hot daytime. By the vaporization heat of water, rooms can be cooled. This system can actuate without any electric energy and or labors

After stirring for 30 min at room temperature, the flask was heated at 60°C for 2.5 h. Hydroquinone was added to the ethanol solution to stop the polymerization. The solution was slowly dropped into diethyl ether and solid P(NIPAAm) was obtained. After filtration, the residue was dried under reduced pressure (the monomer and unreacted reagents can be dissolved in ether). The other homopolymer of BA was prepared by the similar procedures. Copolymers of NIPAAm and BA (NIPAAm-co-BA) were obtained by the following process: NIPAAm and BA (the monomer ratios before starting copolymerization are listed in Table 1) were dissolved in 56.6 mL of *tert*-butanol and radical polymerization was started by adding 0.136 g of AIBN. After keeping the temperature of the solution at 60°C for 20 h, the copolymers diluted in *tert*-butanol were obtained.

Table 1. The mole ratios of NIPAAm and BA

(NIPAAm : BA)	NIPAAm / g	BA / mL
(1.00 : 0) [P(NIPAAm)]	5.64	0.00
(0.95 : 0.05)	5.37	0.36
(0.93 : 0.07)	5.09	0.50
(0.89 : 0.11)	4.81	0.75
(0.80 : 0.20)	4.52	1.42
(0.70 : 0.30)	3.96	2.13
(0 : 1.00) [PBA]	0.00	7.12

¹H NMR spectra of the samples dissolved in deuterium-substituted CDCl₃ were recorded at a Larmor frequency of 600.13 MHz, respectively, using a Bruker Avance 600 spectrometer (14.10 T). ¹H NMR chemical shifts (CSs) were calibrated using an impurity peak of CHCl₃ ($\delta = 7.26$ ppm) in CDCl₃ as an internal standard. Differential scanning calorimetry (DSC) data were obtained using a Shimadzu DSC-60 calorimeter using Al₂O₃ as a reference sample.

The samples were heated from ca. 273 K at a rate of 3 K min⁻¹. The cooling effects of P(NIPAAm) and the copolymers were estimated based on the following measurements: a coating material termed Sararof (Ohashi Chemical Industries LTD.) was painted on two glass-bottles with an outer diameter of 40 mm and height of 120 mm and P(NIPAAm) powder was sprinkled on one (the other was only painted with Sararof). In addition, a mixture of P(NIPAAm) and Sararof was coated onto another glass-bottle. These three bottles and the reference on which nothing was coated were set outside of a building as shown in Fig. 3.

The temperatures in the glass bottles were continuously recorded using data loggers of Sato Keiryu SK-L210T instrument. Similar procedures were applied for the copolymers of NIPAAm and BA to estimate the cooling effects.



Fig. 3. Photograph of apparatus used for measuring temperatures in glass bottles outdoors

RESULTS AND DISCUSSION

Cooling Effect of P(NIPAAm)

In order to estimate the cooling effect of P(NIPAAm), an admixture (1.0 g of polymer with 10.0 g of Sararof; abbreviated as In-Sara) was coated on the outer surface of a glass bottle. After drying under ambient conditions for 1 d, the glass bottle was placed outdoors. Another bottle was treated with 10.0 g of Sararof only and this bottle was also set on the same apparatus as displayed in Fig. 3. The temperature dependence of the cooling effects obtained for the In-Sara sample is shown in Fig. 4. This result suggests that P(NIPAAm) has little cooling effect; in fact, the temperature was found to increase when the polymer was mixed into the Sararof coating material. Since it is reported that P(NIPAAm) shows a cooling effect in mesoporous materials (A. Suzue *et al.*, 2014), this slight effect may be because most of the P(NIPAAm) polymer was covered with the paint components of Sararof and little of the polymer could interact with water molecules in the air, i.e. there is a little P(NIPAAm) on the surface of coating material. In order to demonstrate this model, the following manipulation was carried out: 10.0 g of Sararof was applied to the outer surface of another glass bottle; before drying the paint component, 1.0 g of P(NIPAAm) powder was uniformly sprinkled on the paint component (abbreviated to On-Sara).

That is, On-Sara was constructed by forming a heterogeneous layer (inner and outer layers were formed by Sararof and P(NIPAAm), respectively); in contrast, In-Sara comprised a homogeneous layer in which Sararof and P(NIPAAm) were uniformly mixed. The bottle coated with On-Sara was set outside of a building along with another vessel coated with Sararof, i.e., a similar combination was prepared for comparison with the aforementioned evaluation (In-Sara). The temperature changes observed in these bottles are displayed in Fig. 5.

This figure shows that the temperature inside the bottle coated with On-Sara was reduced relative to the internal temperature of the bottle coated with only Sararof (negative temperature differences mean that the internal temperature of the On-Sara specimen is lower than that of the reference) when the outer temperature was increased to above ca. 30°C. Conversely, the temperature difference became slightly positive when the outer temperature was reduced to below 30°C (evening and night period). In addition, this tendency was reproducibly observed day after the day as demonstrated in Fig. 5. These results suggest that On-Sara adsorbs water molecules in the evening and night period and desorbs them during the hot daytime. Thus, P(NIPAAm) shows cooling effects without the input of electrical energy or labors.

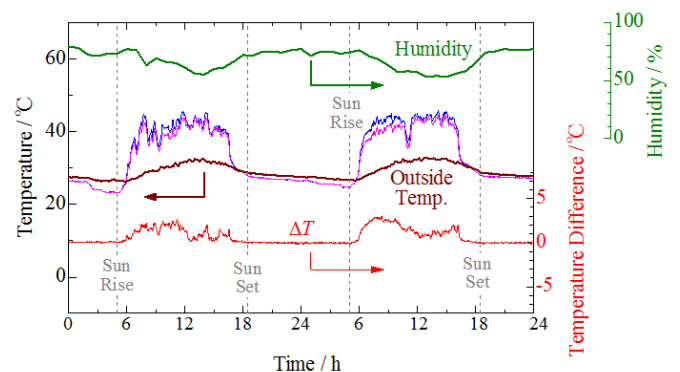


Fig. 4. Temperature changes observed in glass vessels coated with a mixture of P(NIPAAm) and Sararof (In-Sara). Inside temperatures of the bottles treated with Sararof (reference) and with the sample are represented by purple and blue curves, respectively. Temperature difference (ΔT) between the sample and reference is displayed as red curves. Temperature and humidity of outer environment are shown by brown and green curves. In this figure, sunrise and sunset times are shown by gray dotted lines

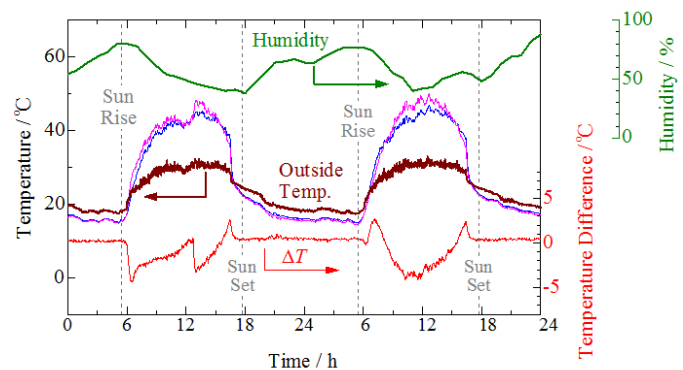


Fig. 5. Temperature changes in glass vessels coated with P(NIPAAm) (On-Sara). Temperatures of Sararof (reference) and sample are shown by purple and blue solid-lines, respectively. Temperature difference (ΔT) between sample and reference is displayed by red curves. Temperature and humidity of outer environment are shown by brown and green curves. In this figure, sunrise and sunset times are shown by gray dotted lines

In order to detect phase transition of In-Sara and On-Sara, DSC measurements were carried out. DSC thermo grams for original P(NIPAAm), Sara roof, In-Sara, On-Sara, and water are shown in Fig. 6. For this analysis, the materials without

water were exposed to saturated aqueous vapor at room temperature before the DSC measurements.

In this Figure, the decreasing baselines over wide temperature ranges are thought to be caused by vaporization of water adsorbed on the sample faces. The data in this figure support the postulate that the cooling effect of On-Sara observed in the outside measurement is linked to phase transition of P(NIPAAm). In addition, a small peak was detected in the DSC profile of In-Sara. Based on these results, it can be proposed that P(NIPAAm) localized on the sample surfaces contributes to the cooling effect rather than P(NIPAAm) localized in the inner region of the material; and P(NIPAAm) chains can be moved on the surface of On-Sara at the coil-globule transition temperature, conversely, Sararroof matrixes on the surface of In-Sara restrict motions of P(NIPAAm) chains at the temperature. As described in this section, the On-Sara system can repeatedly cool a room; however, there is one drawback: this system can be dissolved in water at low temperature. In actuality, the surface of the coating materials on the glass bottle of On-Sara was easily peeled off after outdoors measurements. Therefore, we investigated new cooling paints using copolymers of NIPAA as described in the following sections.

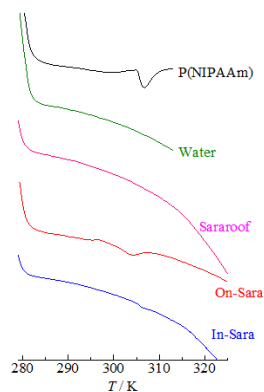


Fig. 7. DSC thermograms of P(NIPAAm) (black), water (green), Sararroof (purple), On-Sara (red), and In-Sara (blue). In this figure, the variation appearing at around 280 K is due to instrument noise

Copolymer of NIPAAm with BA (NIPAAm-co-BA)

In order to investigate cooling paints, copolymers of NIPAAm and BA were prepared in various ratios (BA is widely used as a main component of paints). Comparison of the ^1H NMR spectra of BA (monomer), PBA (homopolymer of BA), NIPAAm, P(NIPAAm), and the copolymers in CDCl_3 solvent confirmed the successful polymerization. The NMR spectra are shown in Fig. 7. In the NMR spectra of the chemical products, the signals at 5-7 ppm attributed to the H atoms in the $\text{CH}_2=\text{CHR}$ groups of the monomers ($\text{R} = \text{COOC}_4\text{H}_9$; (BA), $\text{CONH-CH}(\text{CH}_3)_2$; (NIPAAm)) were disappeared, and new signals due to $-\text{CH}_2-\text{CHR}-$ were appeared at 1-3 ppm region as the polymerization proceeded. In addition, broad signals were recorded at 1.7-2.4 ppm for NIPAAm-co-BA. This range corresponds to the main chains of PBA and P(NIPAAm). In contrast, the sharp line-widths in the sub-chains of the polymers were detected in the copolymer. The result of the broad signals in the main chains of the copolymers can be explained that there are some patterns, e.g. $-\text{BA-BA-BA-}$, $-\text{NIPAAm-BA-BA-}$, $-\text{NIPAAm-NIPAAm-BA-}$, etc., therefore it

can be concluded that the copolymers were successfully obtained. Using ^1H NMR spectra, the apparent polymerization rates were additionally estimated. The monomer peaks declined with increasing reaction time as shown in Fig. 8. Based on this measurement, a reaction rate of $2.45 \times 10^{-2} \text{ mol s}^{-1}$ was obtained for NIPAAm and BA, respectively.

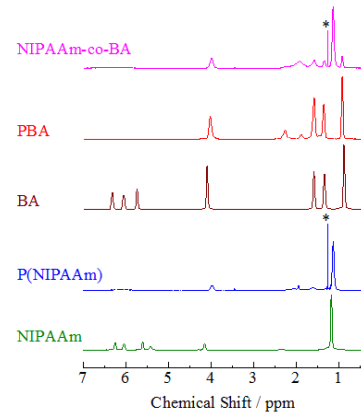


Fig. 7. ^1H NMR spectra of NIPAAm, P(NIPAAm), BA, PBA, and NIPAAm-co-BA in CDCl_3 solution. Here, * denotes peaks of the solvent ($t\text{-BuOH}$)

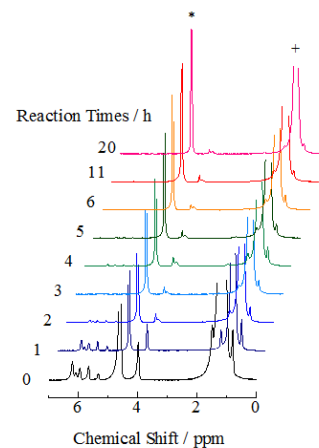


Fig. 8. Reaction-time dependence of ^1H NMR signals observed during copolymerization of NIPAAm and BA with mole ratio of 0.50:0.50. Here, * and + denote peaks of DMSO and $t\text{-BuOH}$, respectively

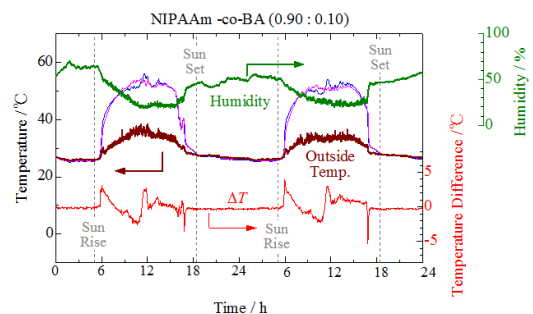


Fig. 9. Temperature changes observed in glass vessels coated with the NIPAAm-co-BA copolymer having a mole ratio of 0.90:0.10.

The temperatures of the reference and sample are shown by purple and blue lines, respectively. Temperature difference (ΔT) between sample and reference is displayed as red curves. Temperature and humidity of outer environment are shown by brown and green curves. In this figure, sunrise and sunset times are shown by gray dotted lines

In order to monitor the cooling effects of NIPAAm-co-BA, the copolymer of 1.0 g with a mole ratio of 0.90:0.10 was coated onto the outer surface of a glass bottle. The vessels were set in the same apparatus presented in Fig. 3 with another glass container on which nothing was coated (reference). The temperature changes in the glass bottle and the difference ($\Delta T = \text{reference} - \text{sample}$) are plotted in Fig. 9. Here, spike signals in ΔT were recorded at ca. 6 and 17 o'clock. These peaks can be considered as the difference in the heat capacity of the copolymer versus the reference. Negative ΔT values were obtained from 10 to 13 o'clock, i.e., NIPAAm-co-BA showed the cooling effect. However, a positive ΔT was observed at ca. 13 o'clock and $\Delta T \sim 0$ was obtained after this time on both days, although the outer temperature remained above 30°C. The P(NIPAAm) homopolymer (On-Sara) can cool the inner temperature of the vessel for a long time-period as demonstrated in Fig. 5; therefore, it can be deduced that a small amount of water molecules is adsorbed on the surface of NIPAAm-co-BA.

In order to confirm the cooling effect of NIPAAm-co-BA, the weight changes of the copolymer were observed as a function of time (t) at 38°C (the temperature is seemed to be much higher than the hydrophobic/hydrophilic switch-temperature of PNIPAAm and room temperatures, however ^1H NMR measurements reveal that the whole polymers can't be condensed in aqua solution at ca. 32°C and the condensation is continued until ca. 36°C (Suzu *et al.*, 2014). Therefore the measurement was carried out at 38°C.). Before this observation, the copolymers were exposed to water vapor at room temperature. The weight ratios defined by the following relation were plotted versus t as shown in Fig. 10.

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

The ratio decreased gradually with t at a constant temperature of 38°C (humidity of ca. 50%). This weight reduction is the result of vaporization of water molecules from the copolymer. After the first cycle of measurements, the same sample was again exposed to water vapor at room temperature (ca. 20°C) and then reheated at 38°C (the second cycle). The copolymer weight at the beginning and end of the second cycle was similar to the values in the first cycle. Therefore, it was revealed that water molecules are repeatedly absorbed on and removed from the copolymer. Based on these results, it can be considered that the cooling effect was actuated until 13 o'clock in the outdoors' experiment. Since a short operating time was recorded in the outdoors' measurement of the copolymer compared with that reported for P(NIPAAm) adsorbed on mesoporous materials (A. Suzue *et al.* 2014) and the On-Sara (Fig. 5) specimen, DSC measurements were performed after exposure of the copolymers to water vapor at room temperature. The DSC curves obtained for NIPAAm-co-BA are displayed in Fig. 11. These thermograms show that the intensity of the endothermic peak was reduced and the signal-width became broad with increasing BA ratios in the copolymer. In addition, the peak maximum shifted to low temperature with increasing BA ratios. The former results (broad line-breadth) suggest that the switch temperature is distributed over the copolymer. In the case of P(NIPAAm) homopolymer, all of the NIPAAm components are located in the same chemical environment (excepting the terminals of the

polymer); therefore, the homopolymer shows a unique switch temperature. In contrast, NIPAAm can take many chemical environments in a copolymer, e.g., -BA-NIPAAm-BA-, -BA-NIPAAm-NIPAAm-BA-, -BA-NIPAAm-NIPAAm-NIPAAm-BA-, etc. Therefore, the switch temperature can be considered to be distributed over wide temperature range as compared with the homopolymer. For the later result (decreasing average value of switch-temperature), the hydrophobic character of BA is thought to influence the switch-temperature. It is reported that P(NIPAAm) assumes globular and coiled conformations in aqueous solution at low and high temperatures, respectively. Water molecules can link to the hydrophilic part of -CO-NH- and prevent aggregation of the hydrophobic regions in NIPAAm at low temperatures (Stillinger 1980; Sun *et al.*, 2008; Crassous 2008; Mackiewicz 2014; Speřvácěk *et al.*, 2014; Ishida *et al.*, 2007; Ishida *et al.*, 2007). In the copolymer, it can be considered that increasing the BA components promotes aggregation of the hydrophobic regions in NIPAAm and BA, and the copolymer has low transition temperatures. The present DSC results suggest that the average switch-temperature of the copolymer of NIPAAm-co-BA (0.90:0.10), which was employed for the outdoor measurement (results are presented in Fig. 10), was ca. 20°C. Therefore, if the ambient temperature were to fall below 20°C on a summer night, more water molecules would be adsorbed on the coating materials and cooling effects would be observed in the afternoon, as shown in Fig. 9. In order to evaluate the water resistance, a wall was coated with the copolymer. After drying, the wall was washed with D_2O (NMR solvent). However, no flow of the coating materials (NIPAAm and BA and the copolymer) was observed in ^1H NMR spectra. Therefore, it can be concluded that the copolymer showed water resistance.

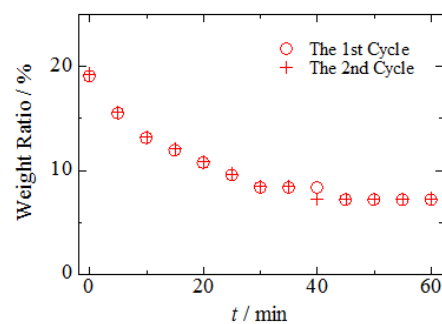


Fig. 10. Weight ratios of NIPAAm-co-BA with a mole ratio of 0.90:0.10, observed in the first () and second (+) cycles at 38°C as a function of time

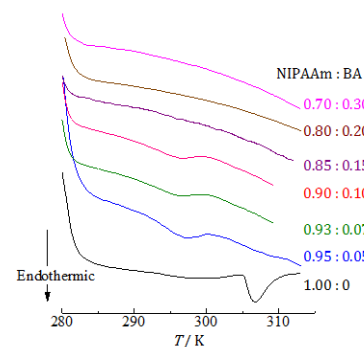


Fig. 11. DSC thermograms of NIPAAm-co-BA. Values described in this figure are mole ratios

Conclusion

We showed that NIPAAm can apply to paints by copolymerization with coating materials and the cooling paints using the vaporization heat of water can be investigated. The NIPAAm-co-BA material showed water resistant below 30°C, although the original P(NIPAAm) polymer dissolves in water at these temperatures. In addition, NIPAAm-co-BA retained hydrophobic/hydrophilic switching character. This system can be widely applied to buildings, trains, cars, etc. Since this paint absorbs water molecules from the air during the night (if it is below the switching temperature), this system can be actuated using only temperature changes, without the use of electrical energy and labors. This system depends on climate, therefore it can be applied in wide areas, especially Southeast Asia, where it is high temperature and humidity, and in addition, urban population is increased and they use an enormous amount of energy in future.

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