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Synthesis of P(NIPAM-co-Am)/Mesoporous Silica Composites and Their Temperature-Responsive Anion Exchange

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Abstract

The purpose of this study is to examine the structure and the temperature-responsive anion exchange property of amino-functionalized mesoporous silica coated with temperature-responsive copolymer, poly(*N*-isopropylacrylamide-co-acrylamide) (P(NIPAM-co-Am)). For this purpose, the composites which contained 0, 10, or 20 wt% of Am were synthesized. From the TG results, it was found that the amounts of copolymer immobilized on the mesoporous silica were 1.6 - 2.6 wt%. XRD patterns revealed that the structures of composites were hexagonal and almost the same as that of original mesoporous silica without polymer. At low temperature the methyl orange (MO) anions adsorbed and desorbed reversibly with changing pH of the solution, while at high temperature the MO anions did not. This temperature, at which the amount of adsorbed MO anions changed considerably, shifted to the higher temperature side with increasing the amount of added Am.

Keywords

Mesoporous Silica, Temperature-Responsive Anion Exchanger, *N*-Isopropylacrylamide, Acrylamide, Transition Temperature

1. Introduction

Materials composed of stimuli-responsive polymer and mesoporous silica have been synthesized widely [1]-[11]. Such composites are expected to be used as a carrier for drug delivery system (DDS), a column packing agent for stimuli-responsive chromatography, and so on. We also synthesized the amino-functionalized mesoporous

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silica coated with poly (*N*-isopropylacrylamide) (PNIPAM) and studied their temperature dependence of the amount of anion exchange [12]-[15]. The mesoporous silica is effective for the adsorption of large molecules such as amino acids, proteins, and sugars, because it has large uniform pores (about 3 nm) and large specific surface area (about 700 m^2/g). On the other hand, PNIPAM, which is one of the thermosensitive polymers, is well-known to swell due to the hydration of polymer below its lower critical solution temperature (LCST, about 32˚C) and shrink due to the dehydration above the LCST. In our previous studies [12] [13], we showed that the synthesized composites had the following characteristics. Below the LCST of the polymer, the methyl orange (MO) anions could be adsorbed and desorbed reversibly depending on the pH of the aqueous solution. Above the LCST, on the other hand, the MO anions could not be adsorbed and desorbed independent of the pH of the aqueous solution. These phenomena were considered to be due to the change in the surface property of the synthesized composite with the change in the solution temperature. That is, the MO anions could easily penetrate through the PNIPAM layer because of the hydrophilic property of the PNIPAM on the external surface of the composite below the LCST, while the MO anions could hardly penetrate through the PNIPAM layer because of the hydrophobic property of the PNIPAM above the LCST.

In this way, the PNIPAM on the external surface of mesoporous silica is considered to play a role of gate for the pore. Next purpose of this study is to control the temperature at which the anion exchange property of the composite changed suddenly. Hereafter, this temperature is referred to as a transition temperature. Previously, we reported that the transition temperature shifted to the higher temperature side by the addition of a crosslinking agent, *N*, *N*'-methylenebisacrylamide (BIS), to the NIPAM monomer solution and then the synthesis of BIS-crosslinked PNIPAM [14]. However, the transition temperature increased only by 5˚C, though 10 wt% of BIS was added. In order to shift the transition temperature of the composite to the much higher temperature, the copolymer of NIPAM and acrylamide (Am) was immobilized on the mesoporous silica in this study. Wu *et al*. described that the LCST increased in the copolymerization of PNIPAM and a monomer with high hydrophilicity such as acrylamide, while the LCST decreased in the copolymerization of PNIPAM and a monomer with high hydrophobicity such as butyl methacrylate [16]. However, the transition temperature of the mesoporous silica covered with the P(NIPAM-co-Am) copolymer has not been clarified yet. In this study, the influence of the addition of the Am on the structure and the transition temperature of the prepared composites was examined.

2. Experimental

2.1. Synthesis of P(NIPAM-co-Am)/Amino-Functionalized Mesoporous Silica Composite

Figure 1 shows the procedure for the synthesis of P(NIPAM-co-Am)/mesoporous silica composites.

The amino-functionalized silica/surfactant mesophase was prepared according to the method reported by Grun *et al*. [17]. A surfactant, hexadecyl trimethyl ammonium bromide (2.4 g) ($[CH_3(CH_2)_{15}N(CH_3)_3]Br$, CTMABr, Nacalai tesque) was dissolved in a mixture of 120 ml of distilled water and 9.5 ml of 28 wt% ammonia solution at 80˚C. After the solution containing surfactant was cooled to room temperature, a mixture of 9.9 ml of tetraethylorthosilicate (TEOS, Nacalai tesque), as a source of silica, and 0.5 ml of 3-aminopropyl triethoxysilane (APTES, Nacalai tesque), providing a functional group having anion-exchange ability, was slowly added to the solution containing surfactant under stirring at room temperature for 1 h. Then, the resulting precipitate was filtered, washed with distilled water, and dried at 60˚C for 24 h. In this way, an amino-functionalized silica/surfactant mesophase was prepared.

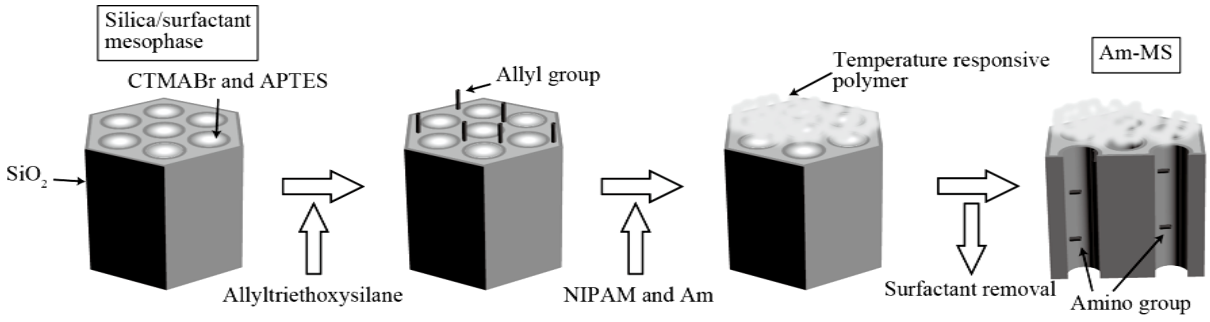

Figure 1. Schematic illustration of synthesis of mesoporous silica coated with P(NIPAM-co-Am) copolymer.

The second step is to immobilize allyl groups on the external surface of the mesophase for anchoring of the copolymer. After 4 g of the amino-functionalized silica/surfactant mesophase was added into a mixture of 120 ml of toluene (Nacalai tesque) and 1 ml of allyltriethoxysilane (Shin-Etsu Chemical), the suspension was refluxed at 200˚C for 4 h. Then, the suspension was filtered, washed with ethanol, and dried at 60˚C for 24 h.

The third step is to copolymerize the NIPAM and Am in the presence of amino-functionalized silica/surfactant mesophase with allyl groups (1 g). A mixture of NIPAM and Am monomers (total weight is 0.5 g) was dissolved in 30 ml of distilled water. The mixed ratio of Am was set to 0, 10, and 20 wt%. The polymerization was carried out at 30˚C for 4.5 h with stirring under a nitrogen atmosphere, after 3 ml of ammonium persulfate (APS) aqueous solution (concentration: 20 mg/ml), as a radical polymerization initiator, was added into the suspension by using micro syringe. The resultant product was filtered, washed with distilled water, and dried at 60˚C for 24 h.

Finally, the surfactant was removed from the mesophase by acidic solvent extraction. The sample was added to a mixed solution of 3.5 ml of concentrated hydrochloric acid (35% conc.) and 150 ml of ethanol. The suspension was heated at reflux (200˚C) for 2 h, and then the resulting precipitate was filtered, washed with ethanol, and dried at 60˚C for 24 h. Hereafter, the samples with 0, 10, 20 wt% of Am were designated as Am0-MS, Am10-MS, and Am20-MS, respectively. As a reference sample, the mesoporous silica without temperature-responsive polymer was also prepared and referred to as MS.

2.2. Characterization of Composites

X-ray diffraction patterns were collected using a Rigaku Ultima IV diffractometer with CuKα radiation source with a scan speed 2.000˚/min from 2θ = 1.500˚ to 10.000˚. The divergence slit was 1.0˚, the receiving slit was 0.30 mm, and the sampling width was 0.020˚. Nitrogen adsorption measurements were performed at 77 K on a BEL Japan BELSORP mini II. The specific surface area was calculated by BET analysis in the relative pressure ranging from 0.1 to 0.3. The pore size distribution was calculated by BJH method. Before the measurement, the samples were pre-treated at 150˚C for 4 h under vacuum. TG measurements were carried out using a Shimadzu TGA-50 in 40 ml/min of air flow at a heating rate of 10˚C/min up to 1000˚C.

2.3. Ion Exchange of Methyl Orange Anions

The synthesized composites were used in the ion-exchange experiments. After 0.1 g of sample was added to 100 ppm of methyl orange (MO) aqueous solution (100 ml), the suspension was stirred magnetically at a speed of 1000 rpm. At first, the temperature of the aqueous solution was set to 25˚C. The pH of the solution was adjusted 8.6 - 9.0 by the addition of NH_3 aqueous solution (28 wt%) to desorb MO anions from the composite. Then, the temperature of the aqueous solution increased to the desired temperature between 25˚C and 55˚C, and the pH of the solution was adjusted to 2.8 - 3.3 by the addition of 4 M of hydrochloric acid. Sampling was repeated in every 30 min and the concentration of MO anions in the supernatant liquid was analyzed with a UV-Vis spectrometer (JASCO V-630) at 510 nm. The amount of MO anions adsorbed on adsorbent was calculated by the mass balance before and after adsorption.

3. Results and Discussion

3.1. Characterization of Products

The XRD patterns for MS, Am0-MS, Am10-MS, and Am20-MS are shown in **Figure 2**. In the MS sample, the appearance of three diffraction peaks that can be attributed to a hexagonal lattice is typical of MCM-41 type mesoporous silica. The peak intensity decreased slightly and the d spacing of (100) reflection, d_{100}, increased from 41.7 to 42.9 Å with the amount of Am addition. **Figure 3** shows the nitrogen adsorption-desorption isotherms for MS, Am0-MS, Am10-MS, and Am20-MS. All the samples were found to have mesopores because these isotherms exhibited the characteristic type-IV adsorption-desorption patterns. The BET specific surface areas for MS, Am0-MS, Am10-MS, and Am20-MS were 810, 890, 870, and 840 m^2/g, respectively, which indicates that the copolymer did not exist in the mesopore. As shown in **Figure 4**, the average pore diameters determined by BJH analysis were 2.7 nm independent of the presence of polymer. In this way, little change in the structural properties such as the silica framework, the specific surface area and the pore size distribution was observed, indicating that the immobilization of copolymer hardly affected the structure of mesoporous silica.

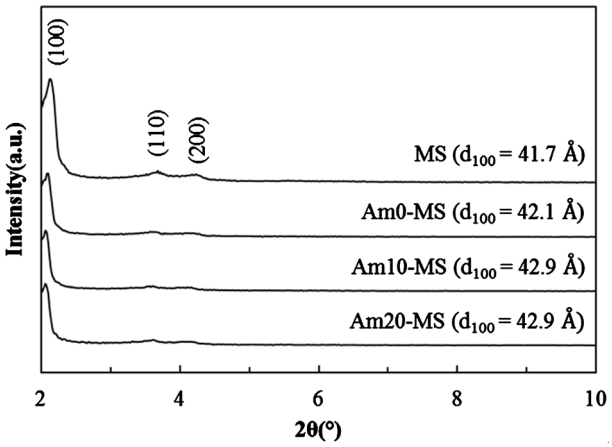

Figure 2. XRD patterns of MS, Am0-MS, Am10-MS, and Am20-MS samples.

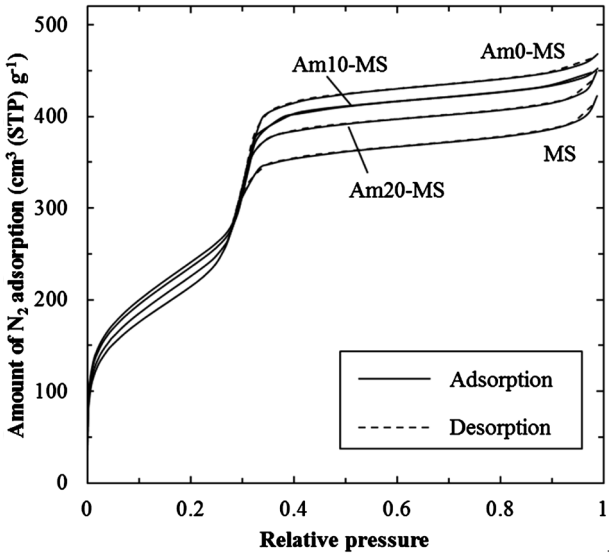

Figure 3. Nitrogen adsorption-desorption isotherms of MS, Am0-MS, Am10-MS, and Am20-MS samples.

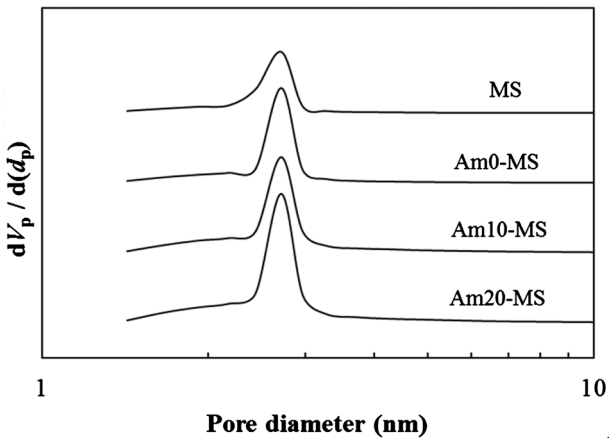

Figure 4. Pore size distributions of MS, Am0-MS, Am10-MS, and Am20-MS samples.

The thermogravimetric curves for MS, Am0-MS, Am10-MS, and Am20-MS were shown in **Figure 5**. In order to remove the adsorbed water from the composites, the samples were dried at 100˚C prior to the TG measurement. In the case of MS, the decrease in the weight was 12.2 wt% up to 1000˚C, which corresponds to the decomposition of aminopropyl groups inside the pore, the allyl groups on the external surface of the mesoporous silica, and the hydroxyl groups present on the surface of mesoporous silica [18]. Thus, the amount of PNIPAM or P(NIPAM-co-Am) immobilized on the mesoporous silica can be estimated from the difference in weight between MS and composites at 1000˚C. As the result, the amount of immobilized PNIPAM or P(NIPAM-co-Am) was 1.6 - 2.6 wt%, which was rather a low value. This is because two radical reaction occurred simultaneously: one was the polymerization of the NIPAM or Am monomer, and the other was the immobilization of PNIPAM or P(NIPAM-co-Am) on the external surface of the mesoporous silica.

In the previous study [19], the amino groups present in the MS prepared by the same method as this study was estimated to be 0.87 wt% from the elemental analysis. Thus, the amount of the amino groups was calculated at 0.62 mmol/g-SiO_2. Because the specific surface area for MS sample was 810 m^2/g, the occupied surface area per one amino group was about 220 $Å^2$/amino group (=(810 m^2/g)/(0.62 mmol/g)), indicating that the amino group was distributed sparsely.

3.2. Temperature Dependence on the Amount of Adsorbed Methyl Orange (MO) Anions

The results of adsorption-desorption experiments of MO anions for MS, Am0-MS, Am10-MS, and Am20-MS are shown in **Figure 6**. The result of MS in **Figure 6(a)** was almost the same that in the previous study [12]: the MO anions adsorbed and desorbed reversibly and repeatedly with changing the pH of the solution at 25 and 35˚C. Describing the results in detail, the amount of the adsorbed MO anions was about 0.25 mmol/g in the low pH region, while the amount of the adsorbed MO anions was about 0.018 mmol/g in the high pH region. This adsorption-desorption behavior for MS sample is typical for the anion exchanger.

Unlike to the case of MS sample, the amount of adsorbed MO anions for Am0-MS shown in **Figure 6(b)** depended on the solution temperature. At 25˚C and 30˚C, the amount of the adsorbed MO anions was about 0.26 mmol/g in the low pH region, while the amount of the adsorbed MO anions was about 0.024 mmol/g in the high pH region, indicating that the adsorption-desorption behavior at low temperature was almost the same as the case of MS. On the other hand, the amount of the adsorbed MO anions was almost constant at 0.02 - 0.03 mmol/g independent of the pH of the aqueous solution. This suggests that the PNIPAM exist near the entrances of mesopores. In other words, the dehydrated and shrunken PNIPAM prevents the MO anions from entering into and leaving the mesopores above the LCST of the PNIPAM. Similar tendency was seen in the cases of Am10-MS and Am20-MS, as shown in **Figure 6(c)** and **Figure 6(d)**, respectively. However, the transition temperature for Am10-MS and Am20-MS were different from that for Am0-MS.

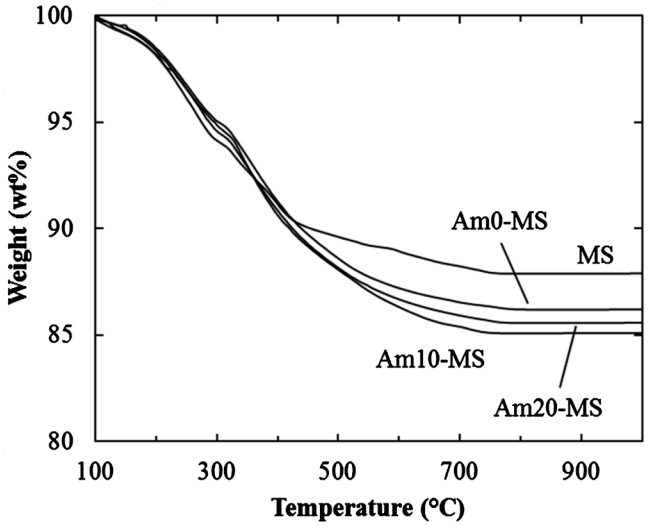

Figure 5. Thermogravimetric curves of MS, Am0-MS, Am10-MS, and Am20-MS samples.

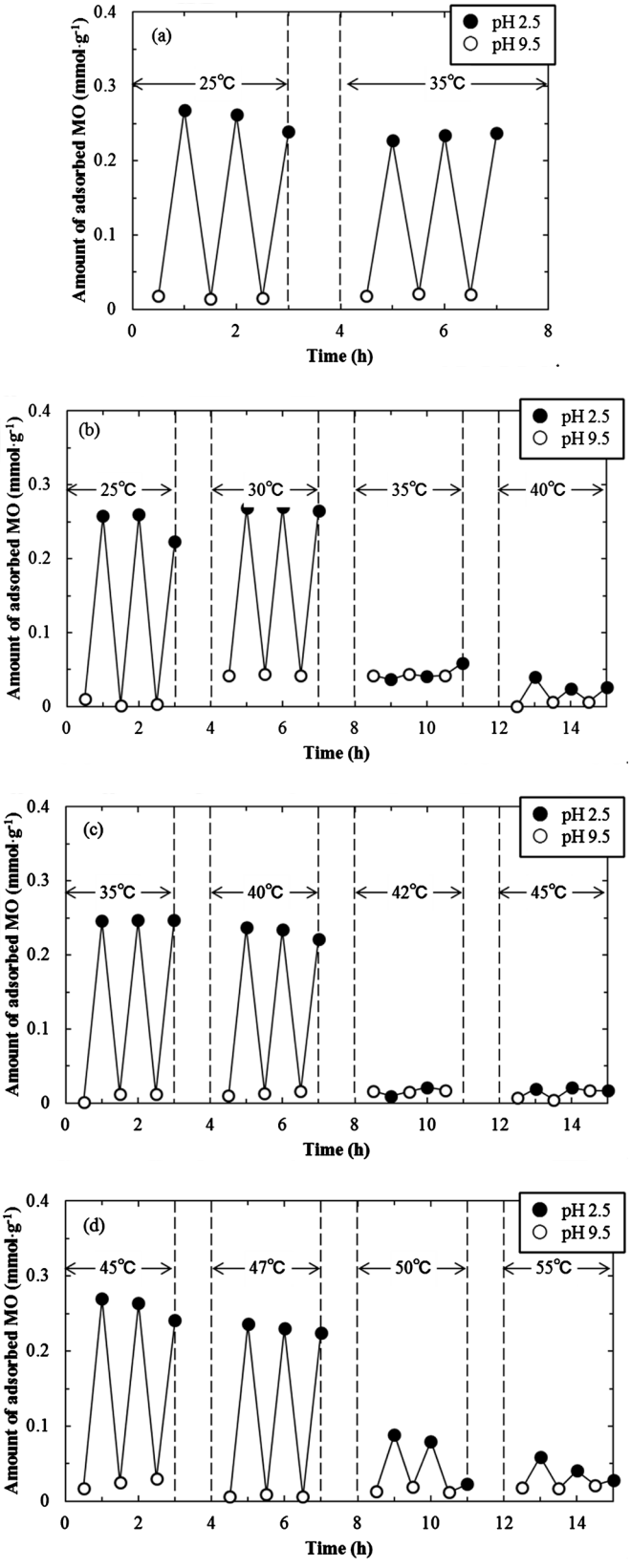

Figure 6. Change in the amount of adsorbed MO ions at various temperatures for (a) MS, (b) Am0-MS, (c) Am10-MS, and (d) Am20-MS samples.

Figure 7 shows the average amount of adsorbed MO anions at low pH against the solution temperature. In this figure, the temperature at which the amount of adsorbed MO anions changed suddenly was the transition temperature. It was found that the transition temperatures for Am0-MS, Am10-MS, and Am20-MS were 30˚C - 35˚C, 40˚C - 42˚C, and 47˚C - 50˚C, respectively. That is, the transition temperature shifted to the higher temperature side with increasing the amount of added Am. **Table 1** shows the comparison of transition temperature between the bulk polymer [16] and the polymer immobilized on the mesoporous silica. The transition temperature for Am0-MS was almost the same as that for bulk PNIPAM, while the transition temperatures for Am10-MS and Am20-MS were higher than those for bulk copolymer by about 5˚C. This would be because the hydration and dehydration behavior is restricted by the immobilization of copolymer on the surface of mesoporous silica.

The relation between the amount of the added Am monomer (mol%) and the transition temperature is shown in **Figure 8**. In this figure, the previous results which were obtained in the case of the addition of crosslinking agent, BIS, are also plotted. Both results were plotted on the same straight line and there was a tendency that the transition temperature increased linearly with increasing the amount of additives such as BIS and Am. It is very interesting to be able to control the transition temperature by only the amount of additives. However, in the case of BIS, it was difficult to add more than 10 wt% of BIS, because the three-dimensional network was formed. On the other hand, the amount of added Am can increase further, so that the transition temperature is expected to shift to the much higher temperature side.

4. Conclusion

In this study, the amino-functionalized mesoporous silicas coated with P(NIPAM-co-Am) were synthesized. Even if the amount of added Am increased up to 20 wt%, the structure of composite maintained a hexagonal structure. There was no influence on the porous property of the mesoporous silica, because the amount of immobilized polymer was very small at 1.6 - 2.6 wt%. The transition temperatures for Am0-MS, Am10-MS, and Am20-MS were 30˚C - 35˚C, 40˚C - 42˚C, and 47˚C - 50˚C, respectively, and it was found that the transition temperature of the composite shifted to the higher temperature side with increasing the amount of added Am.

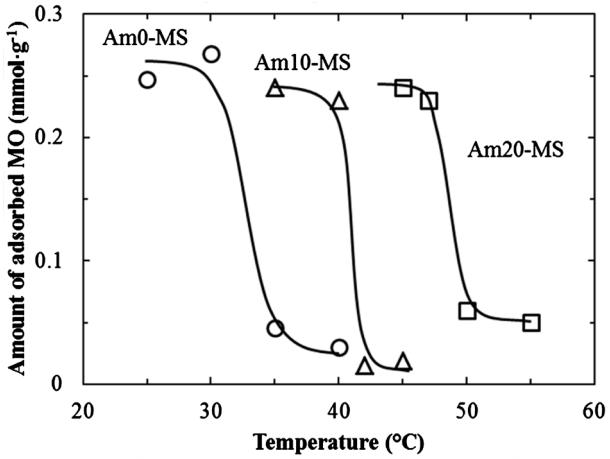

Figure 7. The solution temperature dependence of average amount of adsorbed MO ions in the low pH region for Am0-MS, Am10-MS, and Am20-MS samples.

Table 1. Transition temperature for the composite (this study) and the bulk polymer [16].

Sample	Composite	Bulk polymer
Am0-MS	30˚C - 35˚C	32.5˚C
Am10-MS	40˚C - 42˚C	38.7˚C
Am20-MS	47˚C - 50˚C	45.4˚C

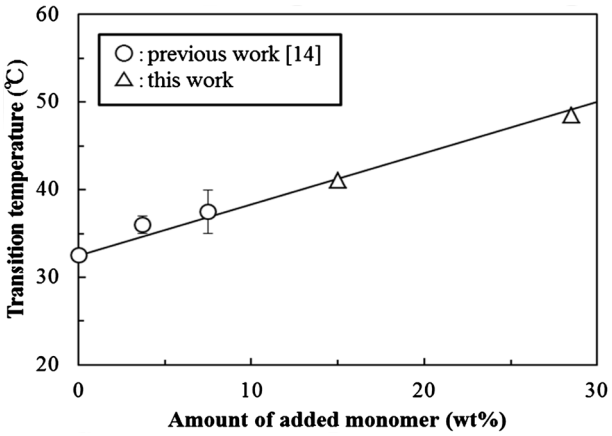

Figure 8. Relationship between the amount of added additives such as Am (this work) and BIS [14] and transition temperature.

Acknowledgements

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