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GRAFTING OF POLYMERS ONTO ACTIVATED CARBON SURFACE: GRAFT POLYMERIZATION OF VINYL MONOMERS INITIATED BY AZO GROUPS THAT WERE INTRODUCED ONTO THE SURFACE

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ABSTRACT

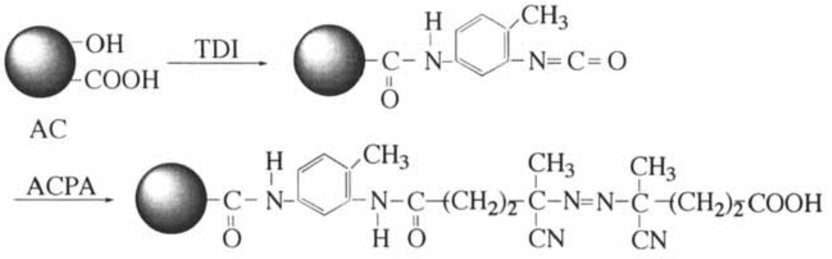
We examined the grafting of polymers onto an activated carbon powder surface by polymerization that was initiated by azo groups that were introduced onto the surface as well as the effects of grafted polymers on the adsorption of acetic acid. The introduction of azo groups onto the surface was achieved by the following methods: (1) a reaction of 4,4'-azobis(4-cyano-pentanoic acid) (ACPA) with surface isocyanate groups that were introduced beforehand by treatment with tolylene 2,4-diisocyanate (AC-Azo **1**) and (2) the direct condensation of ACPA with surface phenolic hydroxyl groups by using *N,N'*-dicyclohexylcarbodiimide (AC-Azo **2**). The radical polymerizations of styrene, methyl methacrylate, *N,N*-diethylacrylamide (DEAM), and *N*-isopropylacrylamide (NIPAM), were successfully initiated by the azo groups on the surface and the corresponding polymers were grafted onto the surface. There was a significant decrease in the adsorption of the acetic acid of the activated carbons when polymers were grafted onto them, particularly in regards to the grafting of hydrophobic polymers. On the other hand, a decrease in the adsorbability of the polyDEAM-grafted and polyNIPAM-grafted activated carbon was barely observed. In addition, polyDEAM-grafted and polyNIPAM-grafted activated carbons showed temperature-dependent adsorption of acetic acid: the adsorbability of these activated carbon decreased above lower critical solution temperature of these polymers, which is about 32°C.

INTRODUCTION

The dispersibility in solvents and compatibility in polymer matrices can be improved significantly by the surface grafting of polymers onto powder, for example, carbon black and silica [1-3]. In addition, the grafting of polymers onto powder surfaces enables us to give various functions, such as photosensitivity, bioactivity, crosslinking ability, and amphiphilic properties, to the powder surface [1-3].

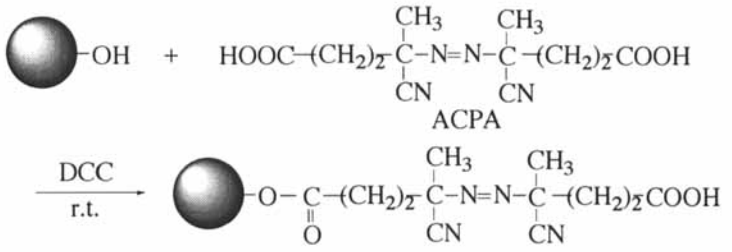
In a previous paper, we examined the grafting of various polymers onto the surface of carbon black [4-7], ultrafine silica [8-10], and organic pigment [11, 12]. For example, we noted that azo and peroxyester groups were successfully introduced onto carbon black surfaces and the radical graft polymerization of vinyl monomers was initiated by surface radicals that were formed by the decomposition of azo and peroxyester groups to give the corresponding polymer-grafted carbon black [4, 5]. In addition, the cationic and anionic graft polymerization was initiated by acylium perchlorate [6] and alkali metal carboxylate groups [7] that had been introduced onto the carbon black surfaces, respectively. In these polymerization systems, effective grafting occurred and the polymer-grafted carbon black with a large amount of grafting was obtained, because the grafted polymers were propagated from the surface: the amount of grafting exceeded 100% in the anionic grafting system [7].

The introduction of these initiating groups onto the carbon black surfaces was achieved by the conversion of the carboxyl and the phenolic hydroxyl groups that were present on the carbon black surfaces. Therefore, it is possible to introduce these initiating groups onto carbon fiber [13-15] and carbon whisker surface [16-18] and to initiate the graft polymerization by means of these initiating groups.



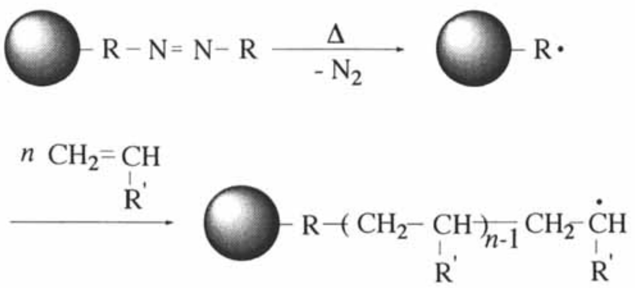
AC-Azo 1

(1)



AC-Azo 2

(2)



(3)

On the other hand, activated carbon is one of the most adsorbent materials that can be used in water [19, 20]. It is well known that activated carbon also has carboxyl and phenolic hydroxyl groups. However, to date, research about the surface modification of activated carbons by the grafting of polymers has not been done.

In this paper, we investigated the introduction of azo groups onto activated carbon powder surfaces (Equations 1 and 2) and the radical graft polymerization of vinyl monomers that were initiated by azo groups (Equation 3). Furthermore, the adsorbing properties of the polymer-grafted activated carbons were compared with that of those that had not been subjected to radical graft polymerization.

TABLE 1. Functional Group Content of Activated Carbon

Particle size (μm)	COOH (mmol/g)	OH (mmol/g)	CO (mmol/g)
20	0.10	0.14	0.67

EXPERIMENTAL

Activated Carbon Powder

The activated carbon powder was obtained from Kanto Chemical Co., Japan. The properties of the activated carbons are shown in Table 1. The amount of carboxyl, phenolic hydroxyl and quinoic oxygen groups was determined by the use of sodium bicarbonate [21], 2,2-diphenyl-1-picrylhydrazyl [22], and sodium borohydride [23], respectively. The activated carbon was dried *in vacuo* at 110°C before use.

Reagents

Methyl methacrylate (MMA) (Kanto Chemical Co., Inc.) was washed with a 10% aqueous solution of sodium bisulfate, a 5% aqueous solution of sodium hydroxide, and a 20% aqueous solution of sodium chloride. It was first dried over sodium sulfate and then over calcium hydride and was distilled twice under reduced pressure. The styrene was washed with a 10% aqueous solution of sodium hydroxide, followed by water, dried over barium oxide, and distilled twice under reduced pressure. *N,N*-Diethylacrylamide (DEAM) and *N*-isopropylacrylamide (NIPAM) were obtained from Kojin Co. Ltd., Japan. DEAM was distilled under reduced pressure before use and NIPAM was recrystallized from acetone.

Dimethyl sulfoxide (DMSO) was dried over calcium hydride and was distilled under reduced pressure. Tetrahydrofuran (THF) was refluxed over sodium and distilled. Acetic acid and tolylene 2,4-diisocyanate (TDI) were distilled before use. 4,4'-Azobis(4-cyanopentanoic acid) (ACPA) (Wako Pure Chemical Ind. Ltd., Japan) was recrystallized from methanol. *N,N'*-Dicyclohexylcarbodiimide (DCC) was used without further purification. Other solvents and reagents were purified by generally used procedures.

Introduction of Azo Groups onto Activated Carbon Surface

The preparation of activated carbons that contained azo groups, AC-Azo **1** and AC-Azo **2**, was done with the following methods:

Preparation of AC-Azo 1

Azo groups were introduced onto an activated carbon surface by the reaction of ACPA with isocyanate groups on the surface, which were introduced onto the surface by the reaction of carboxyl and phenolic hydroxyl groups on the surface with TDI. A typical example is as follows: 3.0 g of activated carbon, 60.0 mL of DMSO, 1.0 mL of TDI, and α-picoline as a catalyst were charged into a 100 mL flask. The mixture was stirred for 4 hours with a magnetic stirrer at 60°C under dry nitrogen. The resulting mixture was cooled to room temperature. Then, 4.0 g of ACPA was added into the flask and the reaction was continued with stirring for 12 hours at 25°C. After the reaction, the resulting activated carbon was repeatedly washed with methanol and dried *in vacuo* at room temperature.

Preparation of AC-Azo 2

Azo groups were introduced onto the activated carbon surface by the direct condensation of phenolic hydroxyl groups on the surface with ACPA in the presence of DCC as a condensing agent. A typical example is as follows: 5.0 g of activated carbon, 2.0 g of ACPA, 50.0 mL of THF, and 1.0 g of DCC were charged into a 100 mL flask. The mixture was stirred with a magnetic stirrer under nitrogen at 25°C for 8 hours. After the reaction, the resulting activated carbon was filtered, washed with methanol and then DMSO repeatedly and was dried *in vacuo* at room temperature.

These treated activated carbons were stored in the dark below 0°C.

Graft Polymerization

0.20 g of AC-Azo and 10.0 mL of vinyl monomer were charged into a glass ampule. The ampule was cooled by liquid nitrogen, thawed three times, and sealed *in vacuo*. The sealed ampule was heated at 70°C by shaking. After a certain time, the product was poured into a large excess of precipitant: the precipitant for polyMMA and polystyrene, polyDEAM, and polyNIPAM were methanol, hexane, and hot water, respectively. The precipitate was filtered and dried *in vacuo* at 60°C. The conversion was calculated by the following equation:

$$\text{Conversion (\%)} = (A/B) \times 100$$

A = Precipitate (g) - Activated carbon charged (g)

B = Monomer charged (g)

Percentage of Grafting and Grafting Efficiency

To isolate the polymer grafted activated carbon from the reaction product, the product was dispersed in THF and the dispersion was centrifuged at 10^4 rpm until the activated carbon was completely precipitated. The activated carbon was extracted with THF by using a Soxhlet apparatus until no more polymer could be extracted with the refluxing solvent. The grafting percentage and grafting efficiency were determined by the following equations.

Grafting (%) = $(A/B) \times 100$
Grafting efficiency (%) = $(A/C) \times 100$
A = Polymer grafted (g)
B = Activated carbon (g)
C = Total amount of polymer formed (g)

The weight of the polymer that had been grafted onto the surface was determined from the weight increase of the activated carbon after graft polymerization had occurred.

Adsorption of Acetic Acid by Activated Carbon

0.100 g of activated carbon and 10.0 mL of acetic acid aqueous solution were charged into a test tube and the mixture was stirred at 20°C with a magnetic stirrer. After 2 hours, the activated carbon was filtered and 2.0 mL of the filtrate was titrated by a 0.005N aqueous solution of sodium hydroxide using phenolphthalein as an indicator.

Determination of Azo Groups by DSC

The introduction of azo groups onto the activated carbon was confirmed by the exothermic peak of the DSC curve that was based on the decomposition of the azo groups. A Shimadzu differential scanning calorimeter (DSC-50) was used for DSC.

RESULTS AND DISCUSSION

Introduction of Azo Groups onto Activated Carbon Surface

In a previous paper, we noted that azo groups could be successfully introduced onto carbon black [4] and carbon whisker surfaces [16] by an ACPA reaction with isocyanate groups, which were introduced by a reaction of surface carboxyl and phenolic hydroxyl groups with TDI. On the other hand, surface

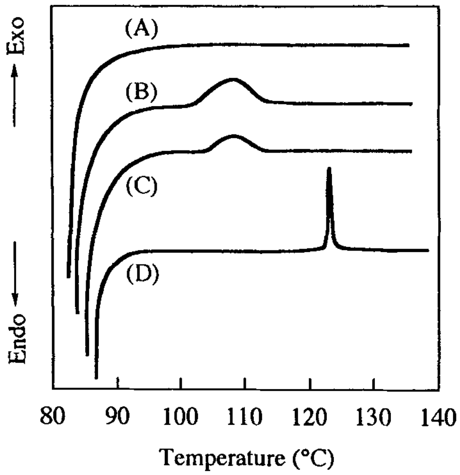


Figure 1. DSC thermograms of (A) untreated activated carbon, (B) AC-Azo **1**, (C) AC-Azo **2**, and (D) ACPA. 5°C; under nitrogen.

phenolic hydroxyl and carboxyl groups on carbon black readily reacted with functional polymers that had carboxyl and phenolic hydroxyl groups in the presence of condensing agents such as DCC to give polymer-grafted carbon black [24].

Therefore, in this paper we are examining the introduction of azo groups onto the activated carbon surface by the use of the following two methods: (1) a reaction of ACPA with isocyanate groups on the surface, which were introduced onto the surface by the reaction of carboxyl and phenolic hydroxyl groups on the surface with TDI, as is shown in Equations 1 and (2) the direct condensation of phenolic hydroxyl groups on the surface with ACPA in the presence of DCC as a condensing agent as is shown in Equation 2. The activated carbon with azo groups that were prepared with methods (1) and (2) were abbreviated as AC-Azo **1** and AC-Azo **2**, respectively.

The DSC thermograms of the untreated, AC-Azo **1**, AC-Azo **2**, and ACPA were shown in Figure 1. Untreated activated carbon has no exothermic peak, but those of AC-Azo **1** and AC-Azo **2** do. This clearly gives evidence for the introduction of azo groups onto the surface by the methods (1) and (2). The azo group content of the AC-Azo **1** and AC-Azo **2** (which were determined from the exothermic peak area) was 0.03 mmol/g, and 0.01 mmol/g, respectively.

The azo group content of AC-Azo **1** was higher than that of AC-Azo **2**. This may be due to the fact that in the case of AC-Azo **2**, the reaction sites on the

TABLE 2. Polymerization of Styrene Initiated by Azo Groups That Had Been Introduced Onto Activated Carbon

AC	Conversion (%)	Grafting (%)	Grafting Efficiency (%)
None	1.8	–	–
Untreated	0	–	–
AC-Azo **1**	1.6	13.5	18.6
AC-Azo **2**	14.9	14.8	2.2

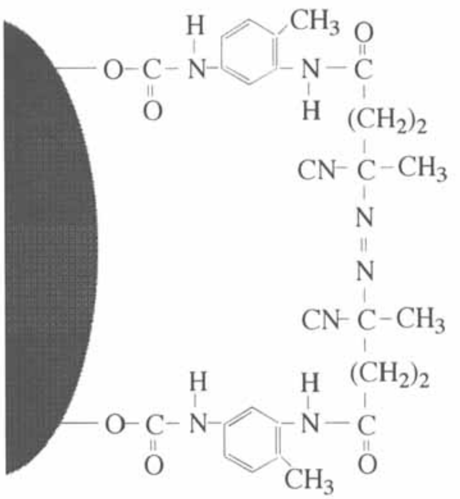
AC, 0.20 g; monomer, 10.0 mL; 70 °C; 8 h.

activated carbon for the introduction of the azo groups were limited to the phenolic hydroxyl groups.

Graft Polymerization Initiated by Surface Azo Groups on Activated Carbon

We have reported that the radical polymerization of vinyl monomers is initiated by surface azo groups on carbon black and carbon fiber and the corresponding polymers are grafted onto these surfaces [4, 13]. In this paper, we performed the polymerization of styrene in the presence of AC-Azo **1** and AC-Azo **2** at 70°C and we examined the initiating activities of the azo groups on the surface. The results are shown in Table 2. The thermal polymerization of the styrene occurred even in the absence of initiators, although the rate of the polymerization was small. In the presence of untreated activated carbon, the polymerization was completely inhibited and the grafting of polystyrene onto the surface barely progressed. The polymerization of styrene, however, was successfully initiated by AC-Azo **1** and AC-Azo **2** to give polystyrene-grafted activated carbon.

These results indicate that, in the presence of AC-Azo **1** and AC-Azo **2**, polymerization is initiated by the radicals that are formed by the decomposition of surface azo groups and the grafted polystyrene chains are propagated from the activated carbon surface. The polymerization rate of styrene that was initiated by AC-Azo **2** was considerably larger than that by AC-Azo **1**, but the percentage of polystyrene grafting by AC-Azo **1** was almost equal to that by AC-Azo **2**. It is significant that the grafting efficiency in the polymerization that was initiated by AC-Azo **1** was higher than that by AC-Azo **2**. This indicates that the formation of



(4)

ungrafted polymer predominantly occurred during the polymerization that was initiated by AC-Azo **2**.

We expected to find two types of ACPA immobilization on the activated carbon surfaces: (1) where only one carboxyl group of ACPA reacts with surface functional groups (as is shown in Equations. 1 and 2) and (2) where both carboxyl groups of ACPA react with surface functional groups, as is shown in Equation 4. Activated carbon that has type-1 azo groups produces both surface and fragment radicals due to the decomposition of azo groups, but type-2 azo groups do not produce fragment radicals. Surface radicals start the graft polymerization, but fragment radicals produce ungrafted polymers.

Therefore, the content of type-1 azo groups of AC-Azo **1** is larger than that of AC-Azo **2**, because of higher reactivity of the isocyanate groups. This is the reason why the grafting efficiency of AC-Azo **1** is higher than that of AC-Azo **2**.

Effect of Polymerization Time on the Grafting from Activated Carbon

Figures 2 and 3 show the relationship between polymerization time and conversion (or percentage of grafting) in the polymerization of DEAM initiated by AC-Azo **1** and in the polymerization of styrene initiated by AC-Azo **2**, respectively.

As shown in Figures 2 and 3, the conversion of DEAM and styrene increased linearly with the progress of the polymerization; the polymerization rate of DEAM is much larger than that of styrene. The polyDEAM and polystyrene grafting onto the surface increased during the initial stage of the polymerization, but stopped increasing after about 30 minutes and 2 hours had passed, respectively.

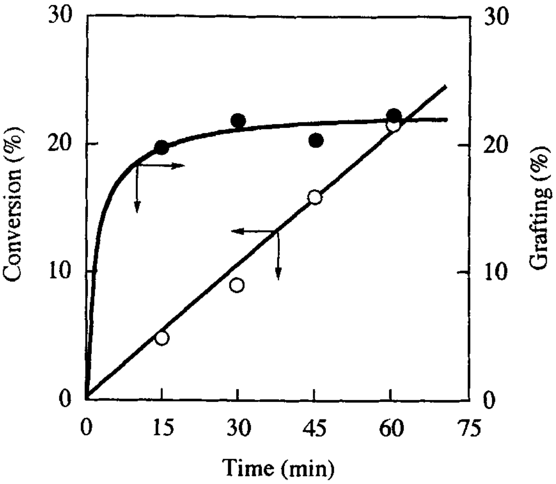


Figure 2. Graft polymerization of DEAM initiated by AC-Azo **1**. AC-Azo **1**, 0.20 g; DEAM, 10.0 mL; 70°C.

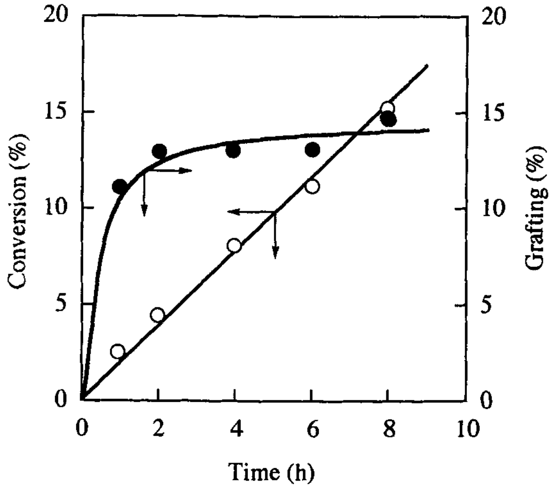


Figure 3. Graft polymerization of styrene initiated by AC-Azo **2**. AC-Azo **2**, 0.20 g; styrene, 10.0 mL; 70°C.

This may be caused by the fact that the surfaces of the activated carbon were blocked by grafted polymers during the progress of polymerization.

Grafting of Several Polymers onto Activated Carbon Surface

Graft polymerization of various vinyl monomers initiated by AC-Azo **1** and AC-Azo **2** was performed. The results are summarized in Table 3. We found that

TABLE 3. Polymerization of Vinyl Monomers Initiated by Azo Groups That Had Been Introduced Onto Activated Carbon[a]

AC	Monomer	Time (h)	Conversion (%)	Grafting (%)
AC-Azo **1**	St	8	1.6	13.5
	MMA	8	3.5	24.7
	DEAM	0.5	8.7	21.7
	NIPAM[b]	4	14.2	25.4
AC-Azo **2**	St	8	14.9	14.8
	MMA	1	8.8	16.9
	DEAM	0.2	21.4	10.0
	NIPAM[b]	2	32.0	11.3

[a] AC, 0.20 g; monomer, 10.0 mL; 70 °C.

[b] AC, 0.20 g; NIPAM, 5.0 g; THF, 5.0 mL; 70°C.

the azo groups that were introduced onto the activated carbon were able to initiate the radical polymerization of various vinyl monomers to give the corresponding polymer-grafted activated carbons.

Acetic Acid Adsorption Ability by Polymer-Grafted Activated Carbon

Table 4 shows the adsorption ability of untreated and polymer-grafted activated carbon that was obtained from the polymerization that was initiated by AC-Azo **1** and AC-Azo **2**. It became clear that the adsorbability of the activated carbon decreased drastically due to the grafting of the polymers. This may be due to the fact that the surface of the activated carbon was blocked by the hydrophobic polymer chains (such as polystyrene and polyMMA) which had been grafted onto the surface.

Figures 4 and 5 show the adsorption isotherm of the acetic acid in the presence of polyDEAM and polyNIPAM-grafted activated carbon, respectively, which were obtained from polymerization in the presence of AC-Azo **2**.

It is significant that the adsorbability of amphiphilic polyDEAAM-grafted activated carbon that was obtained in the presence of AC-Azo **1** also decreased considerably (Table 4), but that obtained in the presence of AC-Azo **2** decreased only significantly. This indicates that the surface of AC-Azo **1** was blocked by

TABLE 4. Adsorption of Acetic Acid by Polymer-Grafted Activated Carbon

AC	Grafted polymer	Acetic acid adsorbed (mg/g)
Untreated	None	15.3
AC-Azo **1**	Polystyrene	2.4
	PolyMMA	2.3
	PolyDEAM	7.2
	PolyNIPAM	8.1
AC-Azo **2**	Polystyrene	10.8
	PolyMMA	7.6
	PolyDEAM	15.7
	PolyNIPAM	17.0

Equilibrium concentration, 4.0×10^{-3} mol/L; 20°C; 2 h.

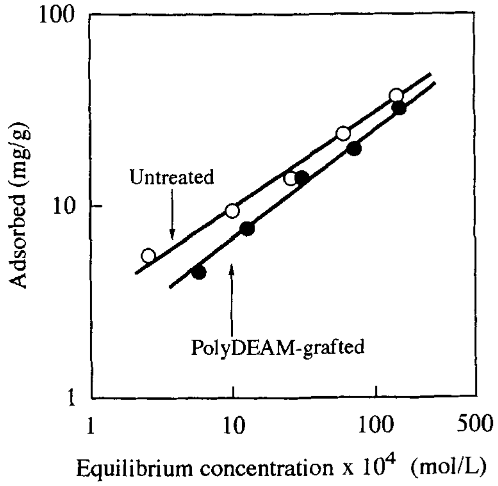


Figure 4. Adsorption isotherm of acetic acid by PolyDEAM-grafted activated carbon (grafting=20.6%) obtained from graft polymerization by use of AC-Azo **2**. 20°C; 2 hours.

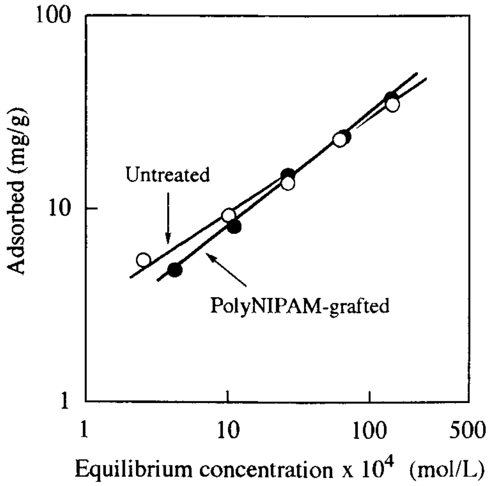


Figure 5. Adsorption isotherm of acetic acid by PolyNIPAM-grafted activated carbon (grafting=11.3%) obtained from graft polymerization with the use of AC-Azo **2**. 20°C; 2 hours.

treatment with TDI because of the higher reactivity of TDI. The grafted amphiphilic polymers on the activated carbon did not interfere significantly with the adsorption of acetic acid.

Effects of Temperature on the Adsorption of Acetic Acid by PolyDEAM and PolyNIPAM-Grafted Activated Carbon

It is reported that polyDEAM and polyNIPAM are soluble in water below its lower critical soluble temperature (LCST), about 32°C, but is insoluble in water above that temperature [25, 26]. Yoshinaga *et al*. found that polyNIPAM-grafted silica was dispersed in water below the LCST, but was precipitated above the temperature [27].

The dispersion of polyDEAM and polyNIPAM-grafted activated carbon in water also shows the same tendency; they were dispersed in water below the LCST, but were precipitated above the temperature. This is because the activated carbon surface is hydrophilic below the LCST, but is hydrophobic above the temperature.

Therefore, we believed that the adsorption of acetic acid by polyDEAM and polyNIPAM-grafted activated carbon is temperature-dependent. The effects of temperature on the adsorption of acetic acid by the above types activated carbon are shown in Figures 6 and 7, respectively. The former was obtained from the polymerization using AC-Azo **1** and the latter by using AC-Azo **2**.

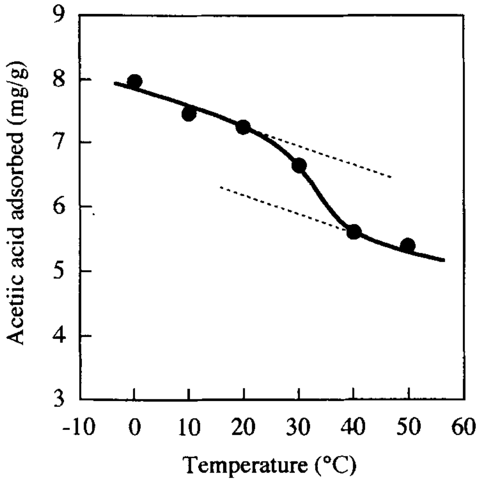


Figure 6. Effects of temperature on the adsorption of acetic acid by the polyDEAM-grafted activated carbon (grafting=20.6%) that was obtained from the graft polymerization by use of AC-Azo **1**. Equilibrium concentration, 4.0x10^{-3} mol/L; 2 hours.

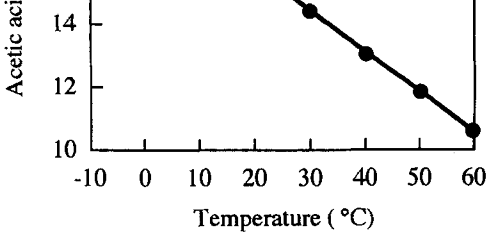


Figure 7. Effects of temperature on the adsorption of acetic acid by the polyNIPAM-grafted activated carbon (grafting=11.3%) that was obtained from the graft polymerization with the use of AC-Azo **2**. Equilibrium concentration, 4.0x10^{-3} mol/L; 2 hours.

It is clear that the adsorbability of acetic acid on polyDEAM-grafted and polyNIPAM-grafted activated carbon decreased above the LCST. This may be because the surfaces of these polymer-grafted activated carbon changes from hydrophilic to hydrophobic above the LCST.

CONCLUSIONS

The radical polymerization of vinyl monomers was initiated by azo groups that had been introduced onto activated carbon surface and the corresponding polymers were successfully grafted onto these surfaces.

The adsorbability of acetic acid by activated carbon decreased considerably due to the grafting of hydrophobic polymers such as polystyrene and polyMMA.

No significant decrease in the adsorbability of polyDEAM and polyNIPAM-grafted activated carbon that had been obtained from the graft polymerization that used AC-Azo **2** was detected.

PolyDEAM and polyNIPAM-grafted activated carbon exhibited temperature-dependent adsorption of acetic acid.

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