Removal of Nonionic Surfactant by Systems Based on Polystyrene–Polyoxyethylene Block Copolymers

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Synopsis

Three polystyrene (PS)–polyoxyethylene (POE) block copolymers were synthesized: S-114 and S-123 as copolymers of POE–PS–POE type, and S-61-10 as that of ─(─PS─X─POE─X─)ₙ─ type. Although the copolymers themselves did not remove nonionic surfactant, polyethylene glycol mono-*p*-nonylphenyl ether (NP, $n = 10$), in water, the copolymers, which were supported on activated alumina, removed the surfactant. The removal rates of NP by the copolymers supported on the alumina were compared. The effect of initial concentration of NP and the effect of the amount of supported copolymer on the amount of NP removed were studied. The Freuindlich adsorption isotherm was observed between the residual concentration of NP and the amount of NP removed. In the three copolymers supported on the alumina, the amount of removal per unit mass was the greatest for the S-61-10.

INTRODUCTION

Metal ions and ionic organic substances, which are expressed as COD, can be removed by ion exchange resins,[1,2] but it is difficult to remove nonionic organic substances, especially nonionic surfactants, dyestuffs, oily substances, and phenol and its derivatives by use of ion exchange resins. Therefore, it is necessary to use adsorbents in order to remove them.

Many reports have been published on syntheses of high molecular compounds which remove ionic organic compounds in water. However, a few studies have been carried out on syntheses of the compounds which remove nonionic organic compounds in water. Recently, studies on binding of polymer systems based on polystyrene with organic solutes in water have been reported. For example, Sinta et al.[3,4] studied binding of organic solutes to poly(vinylbenzo crown ether)s in water, and Kobayashi et al.,[5-7] binding of amphiphilic polymer consisting of sugar and styrene derivative with organic solutes in water.

Furthermore, Fujita et al.[8] have reported separation of alkali and alkaline-earth cations by using noncyclic polyoxyethylene derivatives synthesized from chloromethylated crosslinked polystyrene and polyoxyethylene derivatives, and Yanagida et al.,[9,10] binding of acyclic oligooxyethylene derivatives with the metallic cations.

It seems, however, that studies on binding of polystyrene derivatives with nonionic surfactants have not been carried out yet. Although Shimura and

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Lin[11,12] have investigated the syntheses of polystyrene (PS)–polyoxyethylene (POE) block copolymers, studies have not been done on their utilization. Therefore, in this study, it was investigated whether or not these copolymers remove polyethylene glycol mono-p-nonylphenyl ether (NP) (nonionic surfactant) in water. When the copolymers were used alone for the removal of NP, although they did not remove it, hybrid type materials, which supported the copolymers on activated alumina, did. This paper describes the abilities of the hybrid type materials to remove NP solutes in water.

EXPERIMENTAL

Materials

All reagents and solvents used for syntheses of the copolymers were either best grade or reagent grade, and purified by means of the same procedure as that described in the previous paper.[11]

Activated alumina used was Aluminium Oxide W 200 acid (for column chromatography, activity grade Super 1) (ICN Pharmaceuticals GmbH and Co., West Germany). This was employed without further purification.

Polyethylene glycol mono-p-nonyl phenyl ether ($n = 10$) (Tokyo Kasei Industry Co., Ltd.) was used without further purification.
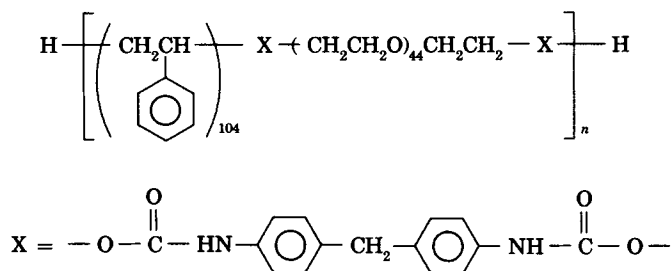
Preparation of α,ω-Dihydroxyl Polystyrene S-61[11]

In a 1-L flask was placed 0.5 g of lithium which was heated in vacuo for 30 min. After cooling the flask, 600 mL of tetrahydrofuran was distilled in from previously prepared Na–naphthalene–THF complex. Biphenyl, 3.10 g (0.020 mol), was introduced from a dropping funnel by the aid of a heating lamp. A bluish-green color developed rapidly in the mixture, and the solution was swirled for about 6 h at room temperature. Without exposing to air and through a #3 glass filter, the initiator solution was transferred to another flask equipped with break sealed dropping funnels delivering 21.5 g styrene and 13.0 g ethylene oxide. The initiator solution was cooled to $-20°C$, rapidly swirled by a magnetic stirrer, and the styrene and ethylene oxide added successively over an interval of a few minutes. The resulting polymer solution was allowed to stand for 1 h, acidified by addition of 1:1 aqueous HCl solution, and precipitated in methanol. The obtained polymer was purified by reprecipitation from its benzene solution. End group analysis by phenyl isocyanate method[13] showed 0.28% N. M_n by VPO in benzene was 10,800.

Preparation of —⟨—PS—X—POE—X—⟩ₙ— Type Block Copolymer S-61-10[11]
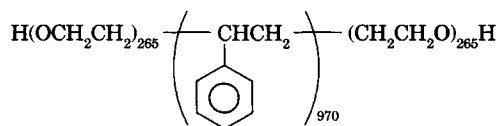
Fifteen grams of α,ω-dihydroxyl polystyrene S-61 dried for 3 h at 10^{-3} mm Hg and 100°C and 0.021 g triethylene diamine as a catalyst were dissolved in dry benzene 50 mL. After adding 2.05 eq (0.710 g) 4,4′-diphenylmethane diisocyanate in 5 mL of benzene, the mixture was flushed with nitrogen, sealed in a bottle, and allowed to stand for 9 h at 20°C. An equiv-

alent amount of polyethylene glycol (M_n 1960, 2.72 g) in 50 mL of benzene was then added, and the total volume was made up to 120 mL. After 96 h at 50°C with occasional shaking, the reaction mixture in a nitrogen atmosphere was poured into methanol and purified by repeated reprecipitations from benzene solution with methyl alcohol. The idealized chemical structure of the copolymer obtained here is as follows:
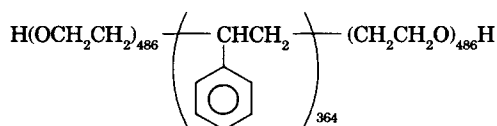
$$H \left[\left(CH_2CH \right)_{104} X \left(CH_2CH_2O \right)_{44} CH_2CH_2 - X \right]_n H$$

$$X = -O - \overset{O}{\overset{\|}{C}} - HN - \langle \bigcirc \rangle - CH_2 - \langle \bigcirc \rangle - NH - \overset{O}{\overset{\|}{C}} - O -$$

Preparation of POE–PS–POE Type Block Copolymer S-114 and S-123

POE–PS–POE copolymer was prepared by adding ethylene oxide to polystyryl dianion initiated in Cs–naphthalene–THF in a similar manner as in the preparation of α,ω-dihydroxyl polystyrene. The polymer solution obtained was precipitated in petroleum ether. The use of Cs (or K) countercation is preferable, and a longer reaction time of a day or two was necessary for the chain growth of ethylene oxide molecules.[12] The molecular weight (120,000) as determined with high-speed membrane osmometer (37°C toluene and a Sartorius UCF membrane) and elementary analysis (C : 84.82%, H : 8.13%) showed that the average strucure for S-114 was

$$H(OCH_2CH_2)_{265} \left(CHCH_2 \right)_{970} (CH_2CH_2O)_{265}H$$

Similarly, the average structure for S-123 was given as

$$H(OCH_2CH_2)_{486} \left(CHCH_2 \right)_{364} (CH_2CH_2O)_{486}H$$

Preparation of Copolymer–Alumina Hybrid Materials

A method to support the synthesized copolymer on the alumina is as follows: After 0.10–0.50 g of the synthesized copolymer was dissolved in 10 mL of benzene, to this solution was added 10 g of the alumina, and then this mixture was well shaken. After the copolymer was allowed to impregnate onto the alumina by standing the mixture for 2 h with occational

shaking, the benzene was evaporated at room temperature or below 50°C. After the remained copolymer–alumina hybrid material was heated for 1 h at 130°C, it was washed with boiling water by decantation in order to remove very fine powders of the copolymer–alumina hybrid material, of the copolymer, and of the alumina, which were present as components of muddiness in the water, and to remove components which are easy to elute from the hybrid material. Although this operation was repeated several times, the absorbance of the decanted water at 223 nm was still observed a very little. The washed copolymer–alumina hybrid material was heated again for 1 h at 130°C. Thus the PS–POE block copolymers supported on alumina, i.e., copolymer–alumina hybrid material [hereinafter abbreviated as copolymer(s)/alumina] was obtained. The amount (%) of copolymer supported on alumina was determined by gravimetric analysis.

Removal Test of NP in Water

In 100-mL Erlenmeyer flasks 0.500 g of the copolymer/alumina was put, and then there was poured 100 mL of aqueous solution of 50–250 ppm concentration of NP ($n = 10$):

$$C_9H_{19}$$

$$O(CH_2CH_2O)_nH$$

NP
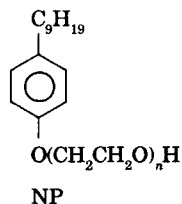
$n = 10 \quad MW = 660.86$

The flasks were stoppered, placed in a thermostatted bath of an operation temperature, and allowed to stand until the concentration of NP decreased scarcely with lapse of time.

The concentration of NP was determined as follows: A part of supernatant liquid in the flask was pipetted out, and the residual concentration of NP was determined by measuring absorbance of the liquid at 223 nm using a Shimadzu UV-VIS Recording Spectrophtometer UV 240. Very small amounts of copolymers eluted from the copolymers/alumina were observed in the blank tests which 0.500 g of the copolymers/alumina were placed in 100 mL of distilled water without addition of NP. Therefore, the blank test was also carried out at the same time, and the residual concentrations of NP were determined the differences between the absorbances of the test solutions and those of the blank tests. The removal amount (mg/g copolymer/alumina) was calculated from the difference between the initial and the residual concentration. The measured supernatant liquid was brought back to the flask.

RESULTS AND DISCUSSION

Removal Rate

The abilities of the copolymers and the activated alumina themselves to remove NP were examined first. S-114, which was pulverized into 50–80-
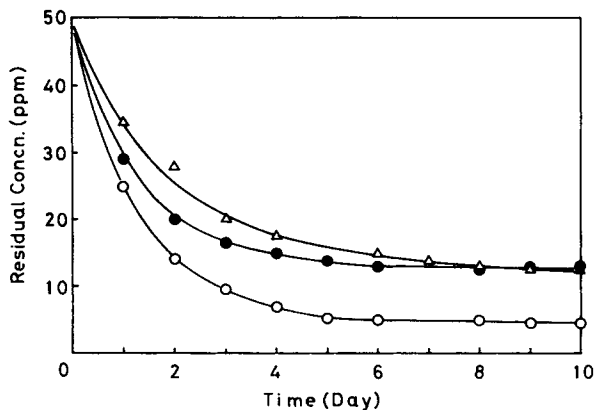
Fig. 1.   Decreases of the residual concentrations in the removal of NP by the PS–POE block copolymers/alumina at 25°C: (△) S-114 (the amount of supported S-114 2.8%), (●) S-123 (2.6%); (○) S-61-10 (2.6%).

mesh granules, was insoluble, was not swollen in water, and did not remove at all the NP in water. The alumina itself behaved similarly.

One-half grams of the copolymers/alumina having the amounts of supported S-114, S-123, and S-61-10 of 2.8%, 2.6%, and 2.6%, respectively, were placed in 100 mL of the initial concentration of 50 ppm of NP. Figure 1 illustrates the decrease in the residual concentration with lapse of time. Since the rate at which these copolymers/alumina removed NP were small, it took more than 5 days to arrive at removal equilibrium. The removal rate of S-61-10 supported on the alumina (S-61-10/alumina) was greater than those of the other two. Since the amounts of supported copolymers of the three copolymers/alumina were approximately equal, this might be attributable to the difference among the chemical structure (composition and MW) of the copolymers, i.e., S-61-10 has 4,4′-diphenylmethane diurethane bonds in the segmented copolymer.

As described earlier, the blank tests showed the elutions of the copolymers into the water. For example, in the case of the copolymers/alumina used here, the absorbances at 223 nm was from first to 10th day after the beginning of the tests at 25°C as follows: S-114, 0.000–0.003; S-123, 0.000–0.003; S-61-10, 0.033–0.042 (in this connection, the absorbance of 10 ppm of NP at 223 nm is 0.150). The large removal rate and amount of S-61-10/alumina are discussed later.

Although the removal rate of S-123/alumina was greater in the initial stage of removal than that of S-114/alumina, the removed amount was approximately equal at the removal equilibrium.

Effect of Initial Concentration on Removal Amount

Each 0.500 g of the three copolymers/alumina was placed in a 100 mL of aqueous solution of 25, 50, 75, 150, 200, and 250 ppm concentration of NP. These were allowed to stand in a thermostatted bath until the residual concentrations were essentially constant. Figure 2 shows the plots of the removed amounts vs. the equilibrium residual concentrations in logarithmic scales. These plots gave linear relationships. It was observed that the re-
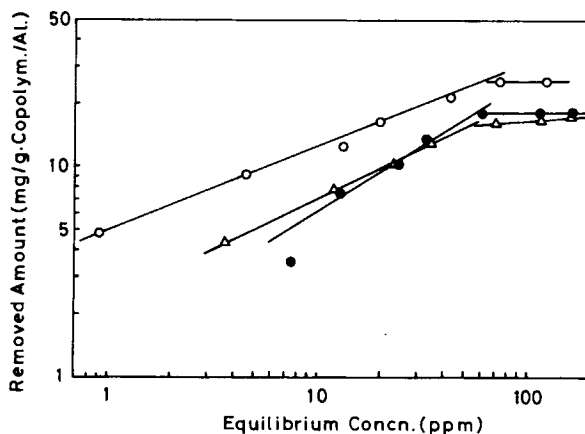
Fig. 2. The Freundlich adsorption isotherm in the removal of NP by the copolymers/alumina at 25°C: (△) S-114 (the amount of supported S-114 2.8%); (●) S-123 (2.6%); (○) S-61-10 (2.6%).

moval behavior of these copolymers/alumina conformed to the Freundlich adsorption isotherm[14]:

$$\log Q = \frac{1}{n} \log C + \log K$$

where Q = adsorption amount (mg/g adsorbent) at the equilibrium state, C = the equilibrium concentration, and n and K are constants. The amount removed by the three copolymers/alumina were constant in the removal from the larger initial concentration than 150 ppm.

The slopes $(1/n)$ of the lines and the logarithm of the removed amounts at the equilibrium concentration of 1 ppm ($\log K$) were calculated and listed in Table I. The removal equilibrium concentration and the removal equilibrium amount were measured on S-114/alumina having different supported amounts. Figure 3 illustrates the plots of them. The each plot showed a linear correlation with slope in the removal from the smaller initial concentration than 150 ppm. In the region above the concentration (150 ppm) the three slopes were nearly zero, and, even if the initial concentrations are allowed to increase, the amounts removed by the three copolymers/alumina are essentially constant under these conditions. The values of the $1/n$ and $\log K$ of the lines were calculated and listed in Table II.

TABLE I
The Constants of the Freundlich Adsorption Isotherm (25°C)

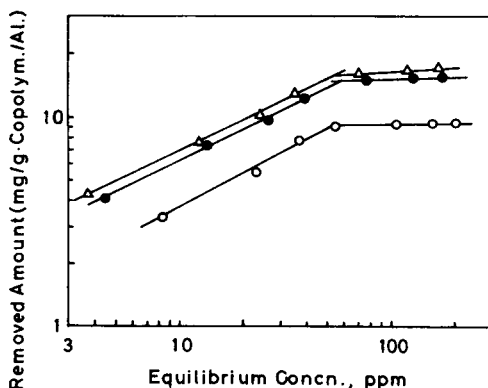| Supported copolymer	Supported amount (%)	$1/n$	$\log K$
S-114	2.8	0.48	0.36
S-123	2.6	0.58	0.22
S-61-10	2.6	0.38	0.70

Fig. 3. The Freundlich adsorption isotherm in the removal of NP by S-114/alumina at 25°C: (△) the amount of supported S-114 2.8%; (●) 3.5%; (○) 1.6%.

The slopes were about 0.51 ± 0.03, which were approximately equal. The effect of the amount of the supported copolymer on the slope was minor. Comparison of the removal equilibrium amount of S-114/alumina having the 2.8% S-114 with that having 3.5% S-114 showed that the former was larger than the latter (Fig. 3).

In order to confirm this fact in more detail, removal tests from the initial concentration of 50 ppm were carried out on the three copolymers/alumina having several different supported amounts, whose removal equilibrium concentrations and removal equilibrium amounts were determined (Table III). Figure 4 illustrates plots of the supported amounts vs. the removed amounts. In the cases of S-61-10 and S-114/alumina, although the removed amounts (mg/g copolymer/alumina) increase with increases in the supported amounts, they decrease with further increase in those. In the case of S-123/alumina, it can be said that the removal behavior is similar to that of S-114/alumina, because the plots of the two copolymers/alumina are on the same curve. The removed amount was the greatest at the supported copolymer of 2.5–3.5%.

The removed amounts (mg/g copolymer/alumina) were converted into those per 1 g of the copolymer (mg/g copolymer), which were listed in Table III. The plots of the removed amounts (mg/g copolymer) vs. the amounts of supported copolymer showed that the removed amounts decreased with increases in the supported amounts. In the cases of S-114 and S-123/alumina, the plots were on the same line. The removed amount was greater

TABLE II
The Constants of the Freundlich Adsorption Isotherm (25°C) : The Effect of the Amount of the Supported Copolymer

Supported copolymer	Supported amount (%)	$1/n$	$\log K$
S-114	1.6	0.54	0.02
S-114	2.8	0.48	0.36
S-114	3.5	0.50	0.29

TABLE III
The Amount of NP Removed by the PS-POE Block Copolymers Supported on Alumina[a]

Supported copolymer	Supported amount (%)	Removal from 50 ppm solution			Removal from 200 ppm solution		
		Equilibrium concn (ppm)	Removed amount (mg/g copolymer/ alumina)	Removed amount (mg/g copolymer)	Equilibrium concn (ppm)	Removed amount (mg/g copolymer/ alumina)	Removed amount (mg/g copolymer)
S-114	1.6	23.0	5.4	338	153	9.4	588
	2.8	12.5	7.5	268	114	17.2	614
	3.5	13.5	7.3	209	123	15.4	440
S-123	2.2	15.5	6.9	314	134	13.3	605
	2.6	13.0	7.4	285	111	17.8	684
S-61-10	1.1	16.0	6.8	618	133	13.5	1227
	1.5	10.5	7.9	527	108	18.4	1227
	2.0	7.0	8.6	430	98	20.3	1015
	2.6	4.5	9.1	350	74	24.3	973
	3.7	3.4	9.3	251	71	25.9	700
	4.9	6.8	8.6	176	90	21.9	447

[a] In 100 mL 50 and 200 ppm aqueous solutions of NP 0.500 g of the copolymers/alumina were placed and allowed to stand at 25°C. These values are those measured at the state which the residual concentrations of NP decreased scarcely.
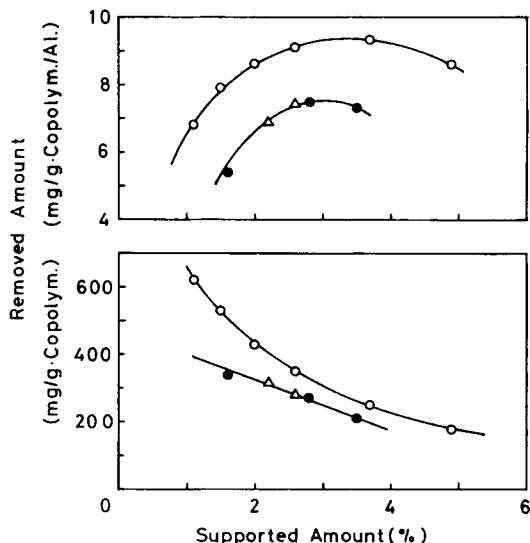
Fig. 4. Plots of the removed amounts vs. the amounts of supported copolymers in the removal of NP by the copolymers/alumina at 25°C. Initial concentration 50 ppm–100 mL; the copolymers/alumina 0.500 g: (△) S-114; (●) S-123, (○) S-61-10/alumina.

in S-61-10/alumina than in S-114 and S-123/alumina, when the supported amount was equal.

The removal test was carried out at an initial concentration of 200 ppm. The removed amounts were also listed in Table III. These are the maximum values of the copolymers/alumina having the respective amount of supported copolymer. Figure 5 shows the relationship between the removal equilibrium amounts and the supported amounts of copolymers. In the case of S-61-10/alumina, the amount removed (mg/g copolymer/alumina) was greatest for 2.5–3.5% supported copolymer. On the other hand, the amounts removed (mg/g copolymer) decreased linearly with an increase in the supported copolymer amount, and were 970–700 mg in the region of supported copolymer amounts of 2.5–3.5 %. It can be said that the values are fairly large. In the cases of S-114 and S-123/alumina, the tests did not give such good data as observed in the tests from the initial concentration of 50 ppm.

When the amounts of the supported copolymers were increased more than certain amounts, the removal equilibrium amounts decreased. This fact is attributable to the following points: When more than a certain amount of copolymer is supported on alumina; (1) the pores of the supported alumina are clogged with the polymer, and, consequently, their surface area is decreased; and also (2) since a copolymer layer on the alumina become thicker and NP become difficult to diffuse into inner of the layer, only the surface and the layer near it participate in the removal of NP. Accordingly, it can be considered that the removed amount does not increase directly with an increase in the amount of supported copolymer. This explanation is reasonable from the fact that S-114 granules of 50–80 mesh did not remove at all NP in water.

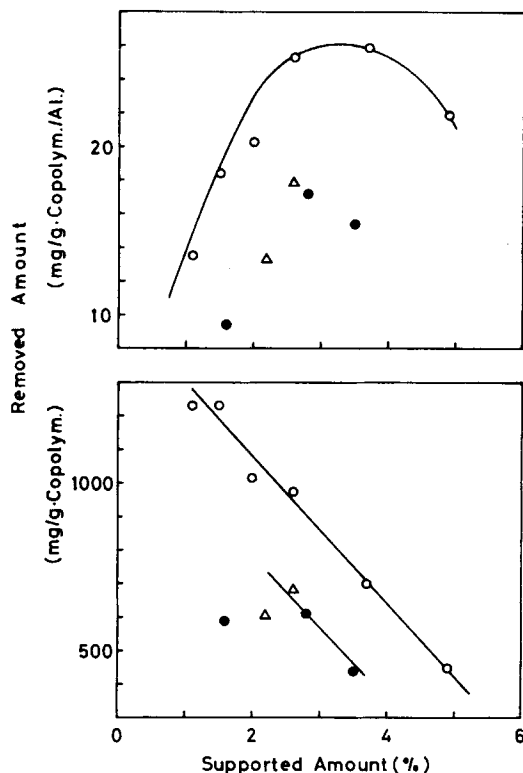Judging from the relationship between the amounts of removed NP and

Fig. 5. Plots of the removed amounts vs. the amounts of the supported copolymers in the removal of NP by the copolymers/alumina at 25°C. Initial concentration 200 ppm–100 mL; the copolymers/alumina 0.500 g: (△) S-114; (●) S-123; (○) S-61-10.

the amounts of the supported copolymer, the removal behaviors of S-114 and S-123/alumina are similar. The difference of the chemical structure between S-114 and S-123 is polymerization degree alone. Accordingly, it is suggested that this extent of difference of the polymerization degree does not influence on the removal ability.

The amount of NP removed by S-61-10/alumina was greatest of the three copolymers/alumina. What is this fact caused by? Since, in the blank tests, the absorbance at 223 nm was largest for S-61-10/alumina, in order to examine whether this was caused by its hydrophilic property, hygroscopicities of the three copolymers were measured. S-114 and S-123 were pulverized into 50–100 mesh granules. Since S-61-10, however, was broad fibrous and its block, and could not be pulverized, it was tested without pulverization. After about 1 g of each were dried *in vacuo* at 100°C until constant weights were reached, they stood for 10 days under saturated vapor pressure at room temperature (19–21°C). The amounts of moisture absorbed by the copolymers after 5 and 10 days are as follows, respectively: S-114, 4.92%, 5.77%; S-123, 23.56%, 39.11%; S-61-10, 1.58%, 1.78%. Even if it was taken into consideration that S-61-10 was not pulverized, the amount of moisture absorbed by S-61-10 was smallest.

The values of (the polymerization degree of POE)/(that of PS) are as follows: S-123 = 2.67, S-114 = 0.55, S-61-10 = 0.43. The order of magnitude of the amounts of moisture absorbed by the copolymers seems to be able to be explained by the ratios of (the polymerization degree of POE)/(that of PS).

The absorbance at 223 nm was largest for S-61-10/alumina in the blank tests. This was contrary to the results of the moisture absorption tests. The elutions of the polymers from the copolymers/alumina are related to interaction between the copolymers and the alumina. Therefore, the fact that the absorbance of S-61-10/alumina is largest seems to be not always incompatible with the fact that the amount of moisture absorbed by S-61-10 itself is smallest.

Since the amount of moisture absorbed by S-61-10 was smallest, it cannot be said that the hydrophilic property is large. Therefore, the greatest amount of removal by S-61-10/alumina seems to be not attributable to its hydrophilic property.

It is generally said that some of polymers, which are composed of hydrophilic and hydrophobic parts, can bind some of organic compounds, which are composed of hydrophilic and hydrophobic parts, to themselves and the bindings take place between the hydrophobic parts of both.[2,5-7,15] Since the removal mechanism of the copolymers/alumina is not clear, we cannot at present clarify the reason why the amount of NP removed by and the removal rate of the S-61-10/alumina was greatest of the three copolymers/alumina. If the removal mechanism of NP by the copolymers/alumina is similar to that described above, the reason may be attributable to an increase of hydrophobic part by introduction of 4,4'-diphenylmethane diurethane groups into the PS–POE block copolymer, to a decrease of hydrophilic property by a decrease of the ratio of (the polymerization degree of POE)/(that of PS), and to their interaction.

Then, when the copolymers/alumina, which bound with NP in water, were put in methyl or ethyl alcohol, the NP can be eluted from them. Therefore, these copolymers/alumina can be used repeatedly as adsorbents for NP in water.

SUMMARY

The three PS–POE block copolymers were allowed to support on the alumina. These copolymers/alumina removed NP in water. Although the polymerization degrees of S-114 and S-123 are different, a difference of the removal ability was not observed between the both copolymers/alumina. The removal ability of S-61-10/alumina was larger than those of S-114 and S-123/alumina. The removal behaviors of these copolymers/alumina obeyed the Freundlich adsorption isotherm. The slopes of the lines were 0.58–0.38 at 25°C. When the amounts of supported copolymers were 2.5–3.5%, the amounts removed by 1 g of each of the three copolymers/alumina were greatest. When the amounts of NP removed by 1 g of each of the three copolymers/alumina were expressed in the amounts (mg/g copolymer), they decreased with increases in the amounts of the supported copolymers.

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