

Removal of Polyethylene Glycol Mono-*p*-Nonylphenyl Ether and Dodecylbenzenesulfonate by Chloromethylated Polystyrene-Polyethylenepolyamines and -Polyethyleneimines

TATSUO TASHIRO, *Research Institute for Polymers and Textiles, 1-1-4,
Yatabe-Higashi, Tsukuba, Ibaraki Pref. 305, Japan*

Synopsis

The reactions of chloromethylated divinylbenzene crosslinked polystyrene (CMPS) with polyethylenepolyamines (PEPA), polyethyleneimines (PEI), 2-methyl-2-oxazoline (MeOZO), and the hydrolysis of CMPS-MeOZO reaction products were carried out. The abilities of these products for removing a nonionic surfactant, polyethylene glycol mono-*p*-nonylphenyl ether (NP, $n = 10$), solutes in water were investigated. Removal rates of NP by and the amounts of NP removed by CMPS-PEPA, -PEI, -MeOZO, and hydrolyzate of CMPS-MeOZO were compared. The adaptability of removal behavior of the products to the Freundlich's adsorption isotherm and the amounts of NP removed by unit masses of the products were investigated. The products also removed an anionic surfactant, sodium dodecylbenzene sulfonate (DBS), solutes in water. The mechanisms for removing NP and DBS were discussed.

INTRODUCTION

The author reported previously that polystyrene-polyoxyethylene block copolymers supported on activated alumina¹ and the reaction products of chloromethylated divinylbenzene crosslinked polystyrene (CMPS) with polyethylene glycol² have the ability to remove NP. The author further studied the reaction products of CMPS with polyethylenepolyamines (PEPAs) and polyethyleneimines (PEIs) as well as the reaction products of CMPS with 2-methyl-2-oxazoline (MeOZO) and their hydrolyzates. These products were found to remove NP and also an anionic surfactant, sodium dodecylbenzenesulfonate (DBS), solutes in water. This study deals with the preparation of these products and the removal behavior of the surfactants in water.

EXPERIMENTAL

Materials

CMPS [Polysciences Inc., 200-400 mesh beads, Lot No. 34126, Cl content; 2.63 meq/g (9.32%), divinylbenzene; 2.00 mol %], tetraethylenepentamine (TEP), pentaethylenhexamine (PEH) (Tokyo Kasei Co., technical grade), 2-methyl-2-oxazoline (MeOZO) (Aldrich Co., bp 109.5-110.5°C, 98%), NP, and DBS (Tokyo Kasei Co., extra pure) were commercially obtained. Po-

lyethyleneimines* were supplied by Nippon Shokubai Kagaku Kogyo Co. These reagents were used without further purification. Dioxane, benzene, and toluene were best grade reagents, which were used after drying and distillation. Dimethylsulfoxide (DMSO) and dimethylacetamide (DMAc) were best grade and used after drying with calcium hydride.

Reactions of CMPS with PEPA and PEI

The reactions were carried out as follows: 2 g of CMPS beads ($-\text{CH}_2\text{Cl}$ groups 0.00526 mol) were placed in a three-necked flask of 50 mL. Into this flask were put 10 mL of dioxane; the flask was stoppered and allowed to stand overnight to allow the beads to swell. After 9.5 g of PEH (0.0409 mol) and 10 mL of dioxane were added into the flask, the mixture was stirred for 113 h at 100°C.

When the reaction was completed, boiling water was added to the flask and the mixture was stirred for about 10 min at 100°C. The mixture was then filtered using a no. 2 glass filter, the reaction product was washed on the filter with boiling water, 1N HCl, 1N NaOH, and boiling water until excess alkali was removed, and finally with methyl alcohol. Furthermore, the product was extracted with tetrahydrofuran (THF) for 72 h, and dried *in vacuo* at 80°C [the yield and the elementary analysis values are shown at the line of CMPS-PEH(2) in Table I].

Reactions of CMPS with MeOZO and Hydrolyses of the Products³

Two grams of CMPS and 20 g of MeOZO (0.235 mol) were put into a 50 mL three-necked flask and left overnight. Then the mixture was stirred at 100°C for 24 h. The reaction mixture was filtered using a no. 2 glass filter. The product was treated as described above. The hydrolysis was carried out as follows: A mixture of the CMPS-MeOZO 3.70 g and 25 mL of water containing 6.00 g of NaOH was stirred in a three-necked flask for 50 h at 98°C. Post-treatment of the product was carried out similarly as described above [the yield etc. are shown at the lines of CMPS-MeOZO(2) and its hydrolyzate in Table II].

Removal of NP and DBS

In a 50-mL flask 0.250g of each reaction product was placed, and 50 mL of 50–250 ppm aqueous solution of NP or DBS was added. Blank solution which does not contain NP was similarly prepared. Other experimental operations, the methods for measuring absorbance, for determining residual concentration, and for the amount of NP removed were the same as described in the previous papers.^{1,2} An experiment for removing DBS solutes in water was operated similarly to that for NP. The removed amount was determined on the basis of the absorbance at 223 nm.

* PEIs used here are not completely linear, but branched molecules having primary, secondary, and tertiary amino nitrogens, whose ratio is $-\text{NH}_2$: $-\text{NH}-$: $>\text{N}-$ = 1:1:1. PEI 250 and 1000 have terminal groups of $-\text{OH}$.

TABLE I
 Reaction Conditions for the Preparation and Elementary Analysis Values of CMPS-PEPAs and -PEIs

Reaction product ^a	CMPS (g)	PEPA or PEI (g)	Solvent ^b (mL)	React. temp (°C)	React. time (h)	Yield (g)	Reacted CH ₂ Cl groups (mol %)	Combed. PEPA (mmol/g CMPS)	H (%)			C (%)			N (%)						
									f	c	f	c	f	c	f	c					
CMPS-TEP(1)	2.00	3.00	Dioxane 20	35	240	2.61	22.0	1.83	9.02	8.82	78.33	80.02	9.99	10.15	8.90	8.66	81.45	81.16	8.69	8.70	
	(2)	2.00	3.00	Dioxane 20	100	> 2.40	18.0	1.52	8.90	8.66	81.45	81.16	8.69	8.70	8.87	8.62	78.89	81.46	8.26	8.32	
	(4) ^c	3.00	4.47	Dioxane 20	100	51	4.15	17.0	1.42	8.87	8.62	78.89	81.46	8.26	8.32	8.91	8.64	80.78	81.31	8.39	8.51
	(6)	3.00	4.50	Benzene 25	80	144	> 3.70	17.5	1.46	8.91	8.64	80.78	81.31	8.39	8.51	8.65	8.53	80.02	81.97	7.60	7.62
	(7)	3.00	4.50	Benzene 25	75	132	> 3.82	15.3	1.28	8.65	8.53	80.02	81.97	7.60	7.62	8.87	8.67	80.36	81.01	8.91	8.89
	(8)	2.00	3.00	Benzene 20	40	240	2.46	18.5	1.54	8.87	8.67	80.36	81.01	8.91	8.89	8.52	8.62	77.19	81.46	8.24	8.32
	(9) ^c	2.50	6.22	DMSO 20	100	50	3.16	17.0	1.42	8.52	8.62	77.19	81.46	8.24	8.32	8.79	8.63	78.09	81.02	8.25	8.34
	CMPS-PEH(1)	2.00	3.70	DMAc 20	100	72	2.61	14.4	1.20	8.79	8.63	78.09	81.02	8.25	8.34	8.91	8.84	79.53	79.67	10.16	10.15
		(2)	2.00	9.50	Dioxane 20	113	2.70	18.5	1.54	8.91	8.84	79.53	79.67	10.16	10.15	8.94	8.76	79.74	80.91	8.53	8.62
(3)		2.00	3.66	B 15, DA 5	75	120	2.55	15.0	1.25	8.94	8.76	79.74	80.91	8.53	8.62	8.81	8.70	79.34	80.59	8.92	8.97
(4)		2.00	3.66	Toluene 20	80	96	2.55	15.8	1.32	8.81	8.70	79.34	80.59	8.92	8.97	9.08	9.00	79.21	80.55	8.96	9.08
(5)		2.00	3.66	Dioxane 20	50	240	2.54	16.0	1.33	9.08	9.00	79.21	80.55	8.96	9.08	9.32	8.78	78.77	80.07	9.57	9.65
(6)		2.00	3.66	Benzene 20	40	240	2.61	17.4	1.45	9.32	8.78	78.77	80.07	9.57	9.65	8.71	8.84	78.94	79.67	10.05	10.15
(7)		2.00	3.66	Benzene 20	40	360	2.77	18.5	1.54	8.71	8.84	78.94	79.67	10.05	10.15	8.62	8.87	75.15	79.40	10.37	10.47
(8)		2.00	6.10	Benzene 20	70	75	2.86	19.4	1.62	8.62	8.87	75.15	79.40	10.37	10.47	8.76	8.73	79.76	80.45	9.15	9.19
(9) ^c		2.50	7.64	DMSO 20	100	78	3.25	16.3	1.36	8.76	8.73	79.76	80.45	9.15	9.19	8.11	8.52	71.77	81.90	7.33	7.40
CMPS-PEI 250(1)	2.50	7.64	DO 10,DS 10	90	288	2.85	12.4	1.03	8.11	8.52	71.77	81.90	7.33	7.40	9.07	8.99	75.96	77.12	8.50	8.69	
	(2)	3.00	3.94	Benzene 20	80	144	4.00	24.6	2.05	9.07	8.99	75.96	77.12	8.50	8.69	8.67	8.69	79.86	79.60	6.73	6.76
	(300(2))	3.00	4.74	Benzene 20	80	104	4.19	14.5	1.21	8.94	8.83	79.90	79.57	9.91	9.92	8.72	8.76	79.21	79.97	9.16	9.36
CMPS-PEI 300(1)	2.00	4.74	DMAc 20	100	70	2.70	13.4	0.882	8.72	8.76	79.21	79.97	9.16	9.36	8.74	9.03	78.86	78.52	11.29	11.39	
	(300(3))	2.00	4.74	Benzene 20	40	240	2.73	17.5	1.46	8.74	9.03	78.86	78.52	11.29	11.39	9.02	9.13	76.35	76.89	11.93	12.05
	(600(1))	3.00	9.46	Benzene 25	80	120	4.69	10.3	0.859	9.02	9.13	76.35	76.89	11.93	12.05	9.33	9.12	75.96	76.91	11.70	11.90
CMPS-PEI 1000(1)	2.00	9.46	DO 10,DA 10	85	120	2.83	10.1	0.842	9.33	9.12	75.96	76.91	11.70	11.90	8.98	8.84	78.44	78.52	9.12	9.16	
	(2)	3.00	15.7	DMAc 20	100	72	3.87	4.8	0.400	8.98	8.84	78.44	78.52	9.12	9.16	8.97	8.87	78.25	76.72	9.22	9.16
	(1200(1))	3.00	18.9	DMAc 25	100	100	3.82	4.0	0.334	8.97	8.87	78.25	76.72	9.22	9.16	8.96	8.70	75.27	75.22	10.24	10.40
CMPS-PEI 1800(1)	2.00	18.9	TL 10,DA 10	85	240	2.71	4.3	0.359	8.96	8.70	75.27	75.22	10.24	10.40	9.37	9.06	77.20	77.03	11.35	11.33	
	(2)	2.00	28.4	Benzene 20	80	192	250	3.3	0.275	9.37	9.06	77.20	77.03	11.35	11.33						
	(1800(1))	2.00	28.4	Benzene 20	80	192	250	3.3	0.275	9.37	9.06	77.20	77.03	11.35	11.33						

(continued)

TABLE I
(continued from previous page)

Reaction product ^a	CMPS (g)	PEPA or PEI (g)	Solvent ^b (mL)	React. temp (°C)	React. time (h)	Yield (g)	Reacted CH ₂ Cl groups (mol %)	Combed. PEPA (mmol/g CMPS)	H (%)			C (%)			N (%)		
									f	c	f	c	f	c	f	c	
(2)	2.00	18.9	DMAc 20	100	139	> 2.32	1.9	0.158	8.88	8.60	80.88	80.59	7.61	7.62			
(3)	2.00	18.9	B 10, DA 10	85	230	2.48	2.2	0.183	9.12	8.71	79.40	79.73	8.54	8.52			

^a CMPS-TEP expresses the reaction product of CMPS with tetraethylenepentamine, PEH is pentaethylenhexamine, and PEI 250 is polyethylenimine having MW of about 250. PEI 250 and 1000 have terminal groups of OH. The PEIs used are not completely linear, but branched molecules having primary, secondary, tertiary amino nitrogens, whose ratio in $-\text{NH}_2$; $-\text{NH}-$; $> \text{N}-$ = 1:1:1.

^b DMSO and DS = dimethylsulfoxide, DMAc and DA = dimethylacetamide, B = benzene, DO = dioxane, and TL = toluene. B 15, DA 5 expresses a mixture of 15 mL of benzene and 5 mL of DMAc.

^c In these products the presence of chlorine was confirmed by the Beilstein test.

TABLE II
Elemental Analysis Values and Abilities to Remove NP by the Reaction Products of CMPS with MeOZO and Their Hydrolyzates

Reaction product	CMPS (g)	MeOZO (g)	React. temp. (°C)	React. time (h)	Yield (g)	H (%)	C (%)	N (%)	Removal from solution of			
									50 ppm ^a		250 ppm ^a	
									Residual concn (ppm)	Removed amount (mg/g)	Residual concn (ppm)	Removed amount (mg/g)
CMPS-MeOZO(2)	2.00	20.0	100	24	3.87	8.19	67.19	9.65	—	—	—	—
Its hydrolyzate	3.70	—	98	50	3.21	9.06	73.22	10.50	3.9	9.2	40.5	41.5
CMPS-MeOZO(3)	2.00	20.0	100	25	3.55	8.23	73.35	7.44	5.0	9.0	—	—
Its hydrolyzate	2.60	—	98	48	2.31	8.72	76.80	7.85	2.4	9.5	41.3 ^b	41.7 ^b

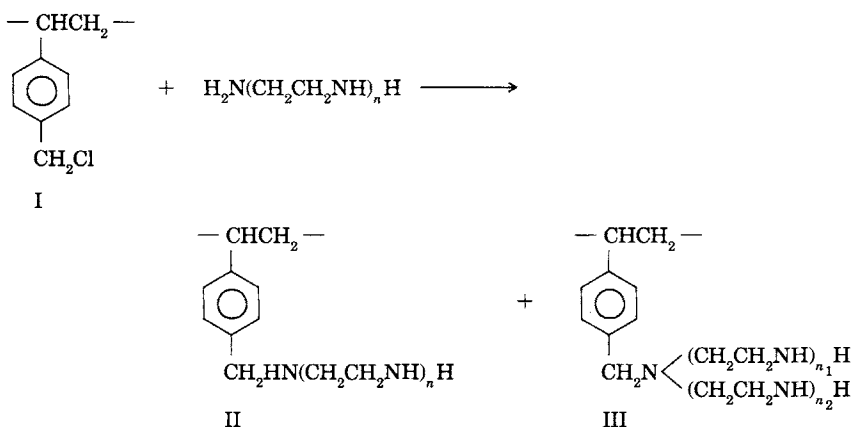
^a These were determined on 3rd day after the beginning of the removal test at 25°C.

^b Same as ^a except on the 5th day.

RESULTS AND DISCUSSION

The Reactions of CMPS with PEPA and PEI

The reactions of CMPS with PEPA give polymers in which chloromethylstyrene parts in CMPS were converted into a few vinylaminobenzyl polyethylenepolyamines (II and III). The amount of III,



however, seems to be small compared with the amount of II. The reactions of CMPS with PEI yield similar polymers in which the chloromethylstyrene unit parts converted into a few vinylbenzylamino-polyethyleneimines.

The reactions of CMPS with TEP, PEH, and several PEIs with different MWs were carried out using dioxane, benzene, toluene, DMSO, and DMAc as solvent. Table I lists the reaction conditions, yields, and the elementary analysis values.

As observed in the elementary analysis values of the reaction products of CMPS with PEG [poly(ethylene glycol)]-Na,² those products obtained here also did not agree with the elemental contents of the products which were yielded by reaction of all $\text{---CH}_2\text{---Cl}$ groups of CMPS with PEPA or PEI. No chlorine was detected by the Beilstein reaction except in four products. Accordingly, $\text{---CH}_2\text{Cl}$ groups, which did not react with PEPA or PEI, seemed to be hydrolyzed during the reaction and the post-treatment of the reaction mixture and gave $\text{---CH}_2\text{OH}$ groups. With this view, the components of CMPS are 31.54, 66.46, and 2.00 mol % of chloromethylstyrene, styrene, and divinylbenzene units, respectively. The amounts of reacted $\text{---CH}_2\text{Cl}$ groups, the molar numbers of combined PEPA or PEI, and the calcd values of H, C, and N contents of the products were determined from the found elementary analysis values as described in the earlier paper² (Table I). In these calculations mol % of reacted $\text{---CH}_2\text{Cl}$ groups with PEPA or PEI (x) was determined so that the calculated elemental contents might agree with the found ones and $(31.54 - x)$ mol % was defined as the amount of hydroxymethylstyrene unit yielded by hydrolysis of $\text{---CH}_2\text{Cl}$ groups during the reaction and the post treatment. Although the elementary analysis values of most products were in approximate agreement with the calculated elemental contents, the found C % of some products were about

4–2% different from the calculated ones [CMPS-TEP(4), (9) and -PEH(1), (8), (10)]. Since TEP and PEH are of technical grade, they may contain impurities.

Egawa and Saeki⁴ have carried out the reactions of CMPS with diethylenetriamine, triethylenetetramine, and TEP. Gózdź and Kolarz⁵ have also done the reactions of CMPS with mono-, di-, trimethylamine, 2-hydroxyethylamine, and others. However, they have not reported the elementary analysis values of the reaction products. Accordingly, it is not clear whether or not the values of the products which were synthesized by them have been in agreement with the calculated elemental contents.

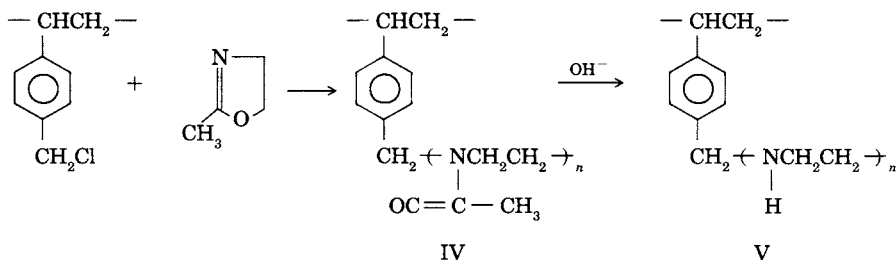
Solvents suitable for the reactions were studied from the amounts of reacted $-\text{CH}_2\text{Cl}$ groups with PEPA or PEI. Dioxane and benzene allowed the beads to swell, but did not dissolve much PEPA and PEI. In the initial stages of the reactions, although the reagents seemed to be dissolved or dispersed by the solvents, the beads formed soft sticky lumps by stirring with these reagents as the reaction time progressed. When the reactions were continued, the reagents seemed to react with the beads. In the reactions of CMPS with TEP and PEH, when dioxane or benzene was used, the amounts of reacted $-\text{CH}_2\text{Cl}$ groups with these reagents was above 17%. However, since the reactions proceeded in such state as described above, the reproducibility of the amount of $-\text{CH}_2\text{Cl}$ groups with these reagents was small (see Table I).

DMAc and DMSO dissolved PEPA and PEI, but their abilities to allow the beads to swell were smaller than those of dioxane and benzene. The amount of reacted $-\text{CH}_2\text{Cl}$ groups with PE-PA or PEI was smaller when DMSO or DMAc were used as solvents than in that of dioxane or benzene. A possible explanation for this fact is that the abilities of DMSO and DMAc to allow the beads to swell are smaller than those of dioxane and benzene.

The reactivity of PEI decreased with an increase in its MW. In the case of the reactions of PEI 1200 (PEI having MW of 1200) and of PEI 1800, despite a longer reaction time, the amount of reacted $-\text{CH}_2\text{Cl}$ groups with the PEIs were 4.0–4.3 mol % (Table I).

The Reaction of CMPS with MeOZO and the Hydrolysis of the Reaction Product

The reaction and hydrolysis proceed as shown in Scheme 2³:



Scheme 2

Table II shows the reaction conditions, the yields, and the elementary analysis values. Although the reaction was carried out twice under almost identical conditions, as the yields and the elementary analysis values show, the reproducibility was not good. Saegusa et al.³ have carried out these reactions in sealed tubes and obtained good reproducibility.

The Rates and the Amounts in the Removal of NP

Figure 1 illustrates a few examples of the decrease in the residual concentrations in the removal of NP by the products. Molar numbers of combined PEH groups in 1 g of CMPS-PEH(2) and (8) are 1.20 and 1.25 mmol/g, respectively. Their removal rates are nearly equal. On the other hand, molar numbers of combined PEI 600 groups in 1 g of CMPS-PEI 600(1) and (2) are 0.592 and 0.614 mmol/g prod, respectively. Despite that, the removal rate of -PEI 600(1) is greater than that of -PEI 600(2). Although the amount of combined PEI 1200 groups in 1 g of -PEI 1200(1) and (2) are not very different, the difference between both removal rates is great.

The molar numbers of combined PEH groups in 1 g of CMPS-PEH(2) and (8) are greater than those of -PEI 600(1) and (2). However, the removal rates of -PEI 600(1) and (2) are nearly equal or greater than those of -PEH(2) and (8). The removal rate of the reaction product with PEPA or PEI having large MW is greater when the molar numbers of combined groups are approximately equal. This tendency was also observed in the removal behavior of CMPS-PEG.²

In general, it took more than 4 days to reach equilibrium in the removal of NP by each product. Especially, in the case of CMPS-PEI ≥ 1000 , their removal rates were smaller than those of CM-PS-PEI ≤ 600 in consequence of the small molar number of combined groups in each 1 g.

Table III lists the amount of NP removed. In the removal by CMPS-PEI ≤ 600 from 50 ppm solution, when the number of repeating unit or MW of PEPA or PEI and PEG are nearly equal, even if the molar numbers of combined PEPA or PEI were smaller than those of combined PEG groups,

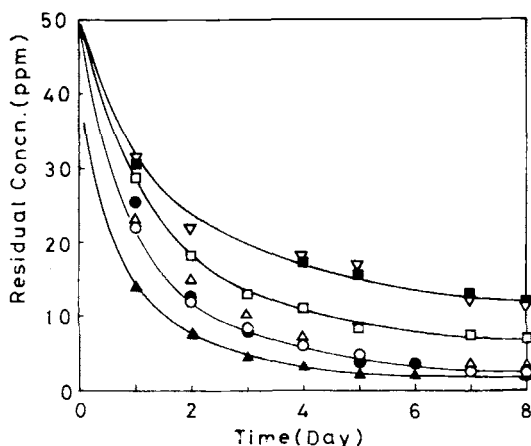


Fig. 1. The changes in NP concentrations with the lapse of time: (●) CMPS-PEH(2); (○) -PEH(8); (▲) -PEI 600(1); (△) PEI 600(2); (▽) -PEI 1000(1); (■) -PEI 1200(1); (□) -PEI 1200(2)

TABLE III
The Amounts of NP Removed from the Solutions of Initial Concentrations of 50 and 250 ppm

Reaction product	Combines groups (mmole/g prod?)	Removal from 50 ppm ^a			Removal from 250 ppm ^b		
		Residual concn (ppm)	Removed Amount		Residual concn (ppm)	Removed Amount	
			(mg/g prod)	(mmol/mmol group)		(mg/g prod)	(mmol/mmol group)
CMPS-TEP(1)	1.45	2.7	9.5	0.0099	17.5	46.5	0.0485
-TEP(2)	1.24	5.7	8.9	0.0109	87.3	32.5	0.0396
-TEP(4)	1.19	3.1	9.4	0.0119	36.7	42.8	0.0396
-TEP(6)	1.21	4.0	9.2	0.0114	57.0	38.6	0.0487
-TEP(7)	1.09	6.3	8.7	0.0121	47.5	40.5	0.0562
-TEP(8)	1.27	18.0	6.4	0.0076	110	28.0	0.0334
-TEP(9)	1.19	27.6	4.5	0.0057	212	7.5	0.0095
CMPS-PEH(1)	0.993	21.8	5.7	0.0087	117	14.5	0.0221
-PEH(2)	1.20	2.8	9.5	0.0145	13.0	47.4	0.0593
-PEH(3)	1.03	21.8	5.7	0.0084	159	18.2	0.0267
-PEH(4)	1.07	21.2	5.7	0.0080	139	22.0	0.0311
-PEH(5)	1.09	15.9	6.8	0.0094	80	34.0	0.0476
-PEH(6)	1.15	12.6	7.5	0.0099	66	36.7	0.0484
-PEH(7)	1.18	8.5	8.3	0.0107	37.6	42.5	0.546
-PEH(8)	1.25	2.5	9.5	0.0115	13.7	47.2	0.0573
-PEH(9)	1.09	25.3	4.9	0.0068	169	16.1	0.0224
-PEH(10)	0.881	18.5	6.3	0.0108	154	19.2	0.0330
CMPS-PEI 250(1)	1.39	6.5	8.7	0.0948	41.5	41.7	0.0455
-PEI 250(2)	1.11	28.5	4.3	0.0659	187	12.6	0.0172
CMPS-PEI 300(1)	0.936	6.3	8.7	0.0131	28.2	44.4	0.0719
-PEI 300(2)	0.882	10.8	7.9	0.0135	59.1	38.2	0.0656
-PEI 300(3)	1.07	6.5	8.7	0.0123	21.5	45.7	0.0647
CMPS-PEI 600(1)	0.592	1.9	9.6	0.0245	9.3	48.1	0.123
-PEI 600(2)	0.614	3.6	9.3	0.0229	15.9	46.8	0.115
CMPS-PEI 1000(1)	0.298	12.5	7.5	0.0381	31.7	31.7	0.161
CMPS-PEI 1200(1)	0.248	13.0	7.4	0.0452	108	28.3	0.171
-PEI 1200(2)	0.261	7.6	8.5	0.0493	41.7	41.7	0.242
CMPS-PEI 1800(1)	0.191	12.6	7.5	0.0595	74.8	35.0	0.277
-PEI 1800(2)	0.128	33.6	3.3	0.0390			
-PEI 1800(3)	0.143	24.1	5.2	0.0550	187	12.6	0.133

^a Determined on 7th day after the beginning of the removal test at 25°C.

^b Same as ^a except on the 14th day.

the removed amounts were greater in CMPS-PEPA or -PEI than in CMPS-PEG, but the removal rates were nearly equal or smaller in CMPS-PEPA or -PEI. In the removal by CMPS-PEG 1000-1500 and -PEI 1000-1800 having groups of 0.25-0.29 mmol/g, the removal rates and removed amounts were greater in CMPS-PEG than in -PEI.

Several CMPS-PEH samples were prepared under different conditions. When the solvent was different, even if the molar numbers of combined PEH groups in each 1 g were nearly equal, it was observed that the amount of NP removed varied. The CMPS-PEH prepared in dioxane or benzene removed a greater amount of NP than those in toluene, DMSO, or DMAc [Table III, -PEH(5) > (9), and -PEH(5) > (4)]. Therefore, dioxane and benzene are better solvents for obtaining products with great removal ability.

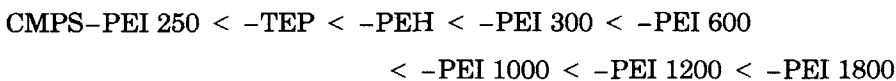
On the other hand, even if products prepared in the same solvent had nearly equal molar numbers of combined groups, it was observed that part of the NP removed was appreciably different [Table III, -PEH(2), (7), and (8)]. This can be attributed to the preparation procedure. Generally, the products prepared and allowed to react at high temperature for a long time removed relatively large amounts of NP.

While CMPS-TEP(1) was prepared at 35°C, the amount of combined groups and of removed NP were fairly large. It is necessary to establish a method to prepare products with good reproducibility in the molar number of combined groups and removal ability.

The Effect of Molar Number of Combined Groups on the Amount Removed

The amounts removed (mmol/g prod) from the solutions of the initial concentrations of 50 and 250 ppm were divided by the molar numbers of combined groups which existed in 1 g of each of the products. These quotients correspond to the molar numbers of NP removed by 1 mol of combined PEPA or PEI groups (Table III). Figure 2 shows correlation between both. The plots of CMPS-TEP and -PEH do not correlate. This may be due to the differences in solvents used. Generally, however, the removed amount (mmol/mmol group) increases with a decrease in the molar number of combined groups.

The magnitude order of the removed amount is as follows:



The combined PEPA and PEI groups are more effective for removing NP in water in groups having larger atomic group weights. Since the product, whose removed amount per unit mass (mg/g) is large, it can be concluded that CMPS-TEP(1), -PEH(2), (8), and -PEI 600(1), (2) are good removal agents (Table III).

While MW of PEI 250 is greater than those of TEP (189.3) and PEH (232.4), the removed amount (mol/mol group) of CMPS-PEI 250 is smaller than those of CMPS-TEP and -PEH. One of the reasons for this is that

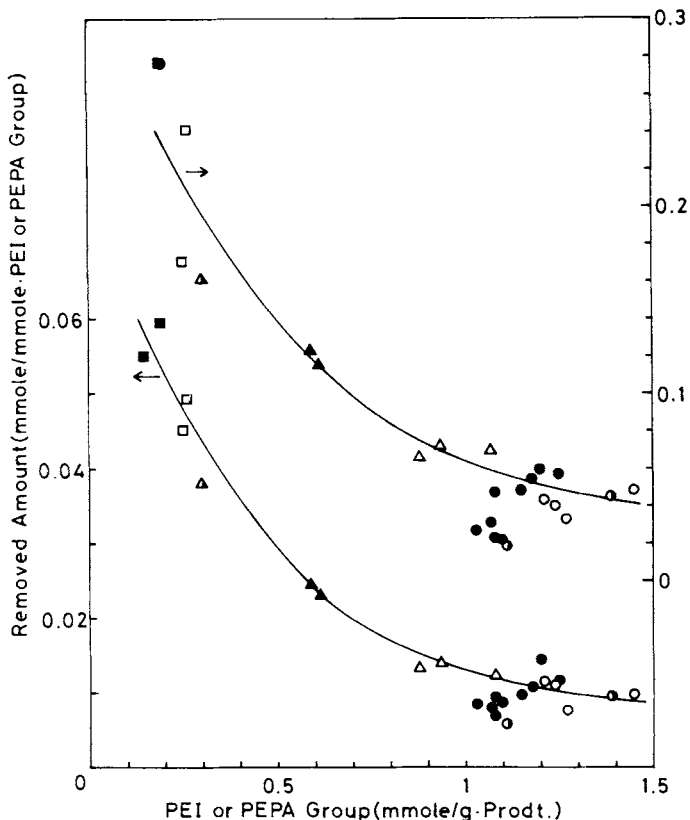


Fig. 2. Plots of the amounts of NP removed by CMPS-PEPAs and -PEIs vs. molar numbers of combined PEPA and PEI groups with CMPS: (○) CMPS-TEP; (●) -PEH; (○) -PEI 250; (△) -PEI 300; (▲) -PEI 600; (△) -PEI 1000; (□) -PEI 1200; (■) -PEI 1800.

the terminal groups of PEI 250* are not $-NH_2$, but $-OH$. As described before, oxyethylene units of PEG and PEPA or PEI and the molar number of combined groups are approximately equal, the amount of NP removed by CMPS-PEG is smaller than those of CMPS-PEPA and -PEI.

The removed amounts of several CMPS-PEPA and -PEI were determined from the initial concentrations of 500, 1000, and 1500 ppm (Table IV). The order of magnitude of the removed amount (mg/g) was CMPS-PEH(2) > -PEI 600(2) \geq -PEI 600(1) > -PEI 300(3) > -PEI 300(1) > -TEP(6) > -TEP(4). The amounts removed by CMPS-PEH(2), -PEI 600(2), and (1) were greater than those by CMPS-PEG.² However, the removal rate was greater in CMPS-PEG (especially, in -PEG 1000 and 1500) than in CMPS-PEPA and -PEI. When this fact is taken into account, it cannot be immediately concluded which is better CMPS-PEPA and -PEI or CMPS-PEG. The amount removed by CMPS-PEH(2) was the largest of all the products prepared. That removed by CMPS-TEP(1) was also large (Table III). However, since there is a problem of reproducibility in the preparations of CMPS-TEP and -PEI, CMPS-PEI 600 with more molar number of groups than 0.06 mmol/g. By carrying out the reaction in dioxane or benzene at high temperature (in a sealed flask) for a long period of time an improved removal agent is obtained.

TABLE IV
The Amounts of NP Removed from the Solution of Initial Concentrations of 500, 1000, and 1500 ppm^a

Reaction product	Molar number of combined PEG groups (mmol/g prod)	Removed amount								
		From 500 ppm soln			From 1000 ppm soln			From 1500 ppm soln		
		(mg/g prod)	(mmol/g prod)	(mmol/mmol PEG group)	(mg/g prod)	(mmol/g prod)	(mmol/mmol PEG group)	(mg/g prod)	(mmol/g prod)	(mmol/mmol PEG group)
CMPS-TEP(4)	1.19	56	0.0843	0.0708	64	0.0962	0.0809	71	0.107	0.0896
(6)	1.21	57	0.0856	0.0708	85	0.129	0.107	95	0.144	0.119
-PEH(2)	1.20	93	0.141	0.117	158	0.239	0.199	205	0.310	0.259
-PEI 300(1)	0.936	83	0.126	0.134	83	0.126	0.134	115	0.174	0.186
(3)	1.07	67	0.101	0.0947	109	0.165	0.154	142	0.215	0.201
-PEI 600(1)	0.592	91	0.138	0.233	150	0.277	0.383	172	0.260	0.400
(2)	0.614	92	0.140	0.151	0.228	0.372	0.175	0.265	0.431	

^a Temp 25°C, product 0.100 g in 20 mL of NP solution. Determined on 14th day after the beginning of the removal.

Removal of NP by CMPS-MeOZO and Its Hydrolyzate

IV and V showed relatively good abilities to remove NP. Although the polymerization degrees and the molar numbers of grafted chains are not clear, as judged from the nitrogen contents, the degrees and the molar numbers seem to be small. When the nitrogen content in the removed amounts are compared IV and V are better than CMPS-PEI in the removal ability. The removal rates of IV and V were nearly equal to that of CMPS-PEI 600(1). However, when IV and V were put in water (25°C), despite extraction with methyl alcohol for 72 h, as the day went by, certain components (perhaps MeOZO and its homopolymer) were eluted into the water. Even after IV and V were subsequently extracted with THF for 48 h, the elution amounts hardly decreased. Therefore, these are their limitations as removal agents. A post-treatment to prevent the elution has to be established.

The Effect of Initial Concentration on Removed Amount

The removal from the initial concentrations of 50, 100, 150, 200, and 250 ppm were carried out at 25°C, and the residual concentrations and the removed amounts were determined at the time (12-14th day after beginning of the removal) when the residual concentrations were essentially constant. The plots of both values in logarithmic scales showed linear correlations (Fig. 3). The behavior of these products for removing NP conformed to Freundlich's adsorption isotherm. The slopes ($1/n$) of these lines and the logarithms of the amounts of removal at the equilibrium concentration 1 ppm ($\log K$) were shown (Table V). The values of $1/n$ of CMPS-PEPA and -PEI ≤ 600 were 0.68-0.74, which were approximately equal in spite of different MW of PEPA and PEI and smaller than those of CMPS-PEG analogues (0.98-1.05).²

Since removal rates of CMPS-PEI ≥ 1000 were small, in the removal from the initial concentrations of 150 ppm or more the residual concentrations

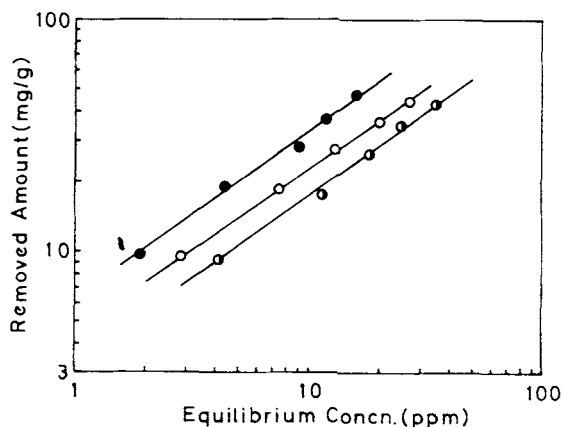


Fig. 3. The adaptability to the Freundlich's adsorption isotherm to the removal of NP by CMPS-PEH and -PEI: (○) CMPS-PEH(8); (○) -PEI 250(1); (●) -PEI 600(1)

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

Reaction product	$1/n$	$\log K$
CMPS-TEP(2)	0.72	0.45
CMPS-PEH(2)	0.69	0.82
CMPS-PEH(7)	0.74	0.47
CMPS-PEH(8)	0.69	0.66
CMPS-PEI 250(1)	0.73	0.50
CMPS-PEI 300(2)	0.71	0.32
CMPS-PEI 600(1)	0.73	0.79

decreased even after 14th day from beginning of the removal. Therefore, the adaptability of this isotherm to CMPS-PEI ≥ 1000 was not studied.

Removal of DBS

CMPS-PEPA and -PEI removed DBS solutes in water. Figure 4 illustrates the plots of the removed amounts vs. time. CMPS-PEH(2) and (8) which had molar numbers of combined PEH groups of 1.20 and 1.25 mmol/g, respectively, removed about 46–47 mg/g for 1 day. The molar number of combined PEH groups in -PEH(6) is 1.15 mmol/g and smaller than those in -PEH(2) and (8). Therefore, it is reasonable that the rate of -PEH(6) for removing DBS is smaller than that for -PEH(2) and (8).

Although the preparation conditions and the molar numbers of PEH groups of -PEH(6) and (7) (1.18 mmol/g) are not very different, the removal rate of -PEH(6) is about twice as great as that of (7). Furthermore, the molar numbers of combined PEH groups in -PEH(4) and (5) are approximately equal (1.07 and 1.09 mmol/g, respectively), but the removal rate of -PEH(4) is about twice as great as that of -PEH(5). As observed in the removal of NP, the reproducibility was also small in the removal of DBS.

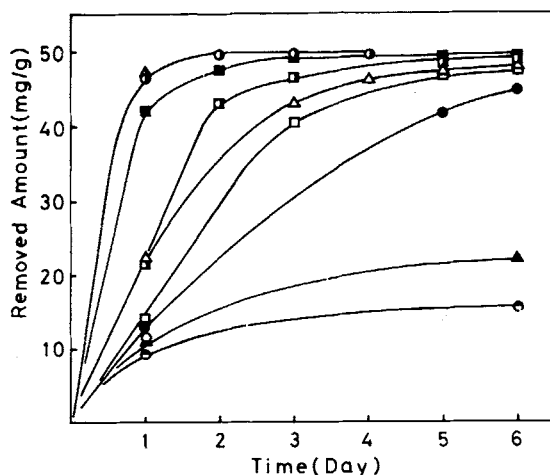


Fig. 4. Plots of the amounts of DBS removed by CMPS-PEHs vs. time at 25°C: (○) CMPS-PEH(1); (○) (2); (●) (3); (□) (4); (□) (5); (■) (6); (△) (7); (△) (8); (▲) (9); (○) (10).

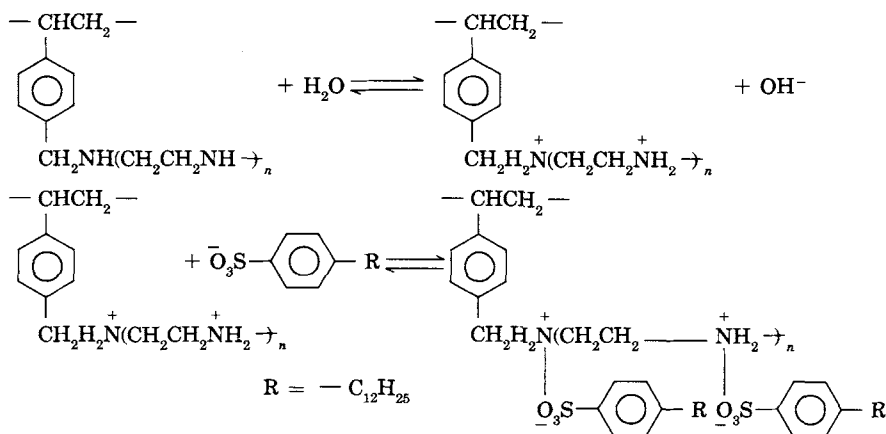
The molar number of PEH groups in -PEH(9) is nearly equal to that in -PEH(4), but the removed amount of the former is much smaller than that of the latter. This is ascribable to use of DMSO in the preparation of -PEH(4).

The amount of DBS removed by CMPS-PEPA and -PEI were determined (Table VI). The removal rate and amount by each product were greater than those in the removal of NP. The removal rate is large, and each of the products was removed until the residual concentration was several ppm for 1 day.

Removal Manners of NP and DBS by CMPS-PEPA and -PEI

Generally, polymers which are composed of hydrophobic and hydrophilic parts can bind some organic compounds by interaction between the hydrophobic parts of the polymers and those of the organic compounds.⁶⁻⁸ The removal mechanism of NP solutes in water by CMPS-PEPA or -PEI, similar to that by CMPS-PEG,² involves bonding between some types of sites which must be formed by the hydrophobic parts of CMPS-PEPA or -PEI and the hydrophobic parts of the NP solutes.

The removal of DBS by CMPS-PEPA or -PEI can be considered as follows: Strong and weak basic anion exchange resins adsorb (or remove) DBS effectively.⁹⁻¹¹ The methods for removal by CMPS-PEPA and -PEI are similar to that by weak basic resins. Since amino nitrogens in CMPS-PEPA and -PEI are protonated in water to yield cationic amines, it can be considered that they combine with DBS by electrostatic complexation of the cationic amines with DBS anions:



Scheme 3

Branched PEI and its acylated products bond methyl orange, and the bound amounts increase with increases in the hydrophobicities of the acyl groups. In bonding of pH 7, as the polymers are protonated markedly, the bonding of methyl orange solutes with negative charges to the polymers take place by both hydrophobic and electrostatic interactions between them.¹¹ Accordingly, the removal of DBS by CMPS-PEPA and -PEI seems

TABLE VI
The Amounts of DBS Removed from the Solutions of Initial Concentrations of 50 and 250 ppm^a

Reaction product	Combined groups (mmol/g prod)	Removal from 50 ppm ^a			Removal from 250 ppm ^a		
		Residual concn (ppm)	(mg/g prod)	(mmol/mmol group)	Residual concn (ppmP)	(mg/g prod)	(mmol/mmol group)
CMPS-TEP(6)	1.21	5.2	9.0	0.0229	33.1 ^b	43.4 ^b	0.110 ^b
CMPS-PEH(2)	1.20	3.3	9.3	0.0238	18.5	46.3	0.119
CMPS-PEH(8)	1.25	3.0	9.4	0.0243	16.3	46.	0.121
CMPS-PEI 250(1)	1.39	1.5	9.7	0.0214	13.5	47.3	0.105
CMPS-PEI 300(1)	0.936	1.5	9.7	0.0318	30.9	43.8	0.144
CMPS-PEI 600(2)	0.614	4.4	9.1	0.0445	21.8	45.6	0.228
CMPS-PEI 1000(1)	0.298	9.5	0.0980	46.0 ^b	40.8 ^b	0.421 ^b	
CMPS-PEI 1200(2)	0.261	3.1	9.4	0.110	28.5	44.3	0.522
CMPS-PEI 1800(1)	0.191	3.0	9.4	0.151	48.6 ^c	40.3 ^c	0.648 ^c

^a The amounts (mmol/g prod) of removed DBS were obtained by dividing the amounts (mg/g prod) by the atomic group weight (325.4) of DBS anion.

^b Measured on 1st day, ^c2nd day, and ^d4th day after the beginning of the removal at 25°C.

to proceed by both mechanisms of the electrostatic and hydrophobic interactions.

Although CMPS-PEG² also removed DBS, the removed amount was much smaller than the amount of NP removed. For example, CMPS-PEG 400(1) and -PEG 1000(1) removed 3.0 and 3.4 mg/g, respectively, for 7 days from the initial concentration of 50 ppm at 25°C. This fact supports the foregoing speculation that CMPS-PEPA and -PEI also bond DBS by the hydrophobic interaction. One of the causes that the rates for removing DBS by these products are larger than those of NP seems to be ascribable to the fact that the two interactions act for removing DBS, especially, the electrostatic interaction.

SUMMARY

The reactions of CMPS with PEPA, PEI, MeOZO, and the hydrolysis of CMPS-MeOZO were carried out. Only a part of —CH₂Cl groups reacted in these reactions. The amount of reacted PEI decreased with an increase in its MW. These reaction products removed NP solutes in water. Although removal rates for NP were generally small, CMPS-PEI 600 was better than —PEI ≥ 1000 for removal rate and removed amount. The behavior for removing NP by CMPS-PEPA and -PEI conformed to Freundlich's adsorption isotherm ($1/n = 0.69-0.74$). CMPS-PEPA and -PEI also removed DBS solutes in water, and the removal rates and removed amounts were larger than those for NP. The removals of NP and DBS by these products seem to proceed by hydrophobic and electrostatic interactions, respectively.

It is necessary to solve problems associated with the small reproducibility of the amount of reacted —CH₂Cl groups with PEPA or PEI, the removed amount, the slow removal rate, and the large amounts of some components eluted from CMPS-MeOZO and its hydrolyzate. The removal rate increases by stirring the solution in the batch system, and also by use of the continuous system which flows the solution through a column packed with the product.

When CMPS-PEPA or -PEI to which NP solutes had been bound in water were placed in methyl or ethyl alcohol, the NP were eluted from them. therefore, these products can be used repeatedly as agents for removing NP solutes in water.

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