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Graft Copolymerization of 2-Methyl-2-oxazoline onto Chloromethylated Polystyrene and Hydrolysis of Graft Copolymer to a Chelating Resin of Poly(styrene-*g*-ethylenimine)

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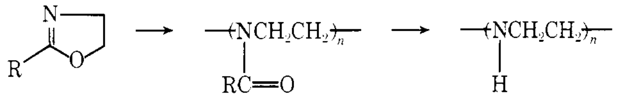
Received March 31, 1975

ABSTRACT: Poly(styrene-*g*-MeOZO) (**4**) consisting of polystyrene backbone and poly(*N*-acetylethylenimine) branches was prepared by the polymerization of 2-methyl-2-oxazoline (MeOZO) initiated by chloromethylated polystyrene (PSt–CH_2Cl). PSt–CH_2Cl used were noncross-linked and cross-linked, macroporous bead polymers. The polymerization rate of MeOZO by PSt–CH_2Cl was enhanced by the addition of KI due to the change of the nature of propagating species through the halogen exchange reaction. The graft copolymer **4** was hydrolyzed with alkali to prepare poly(styrene-*g*-ethylenimine) (**5**). The extent of hydrolysis of **4** to **5** reached 87.7%. Thus, it became possible to prepare **5** having long, linear polyethylenimine branches (n in **5** $\leq$ 16.62). Preparation of such graft copolymer could not be accomplished by the graft polymerization of ethylenimine (EI) by PSt–CH_2Cl due to the chain transfer. The reaction of cross-linked PSt–CH_2Cl with polyEI produced graft copolymer having a very low content of polyEI. Poly(styrene-*g*-ethylenimine) prepared in the present study was found to be quite effective for the absorption of heavy metal ions such as Cu^{2+}, Hg^{2+}, and Cd^{2+}.

Recently we succeeded in the preparation of crystalline polyethylenimine (**3**) by the polymerization of 2-oxazoline (**1a**) and the subsequent hydrolysis of the product polymer poly(*N*-formylethylenimine) (**2a**).[1,2] Poly(*N*-acetylethylenimine) (**2b**), the polymer of 2-methyl-2-oxazoline (**1b**) (MeOZO), has been known to be hydrolyzed by alkaline with difficulty.[3] But we found recently that **2b** was hydrolyzed up to about 90% under strong alkaline conditions.[4] Furthermore, we have observed that MeOZO (**1b**) was polymerized by methyl iodide[5,6] and benzyl chloride.[7]

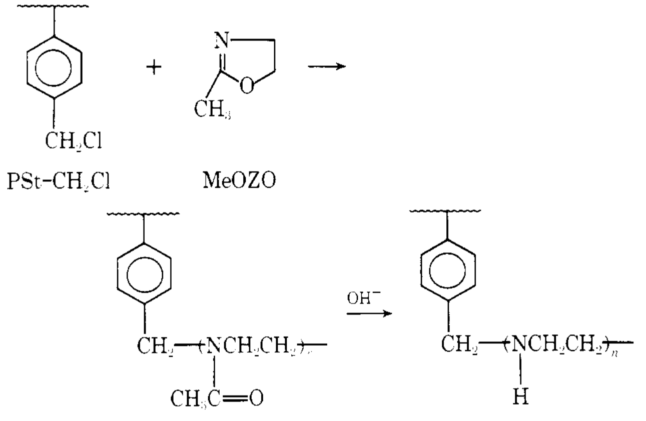


1a, R = H
b, R = CH_3

2a, R = H
b, R = CH_3

3

These findings prompted us to prepare poly(styrene-*g*-ethylenimine) (**5**) by the polymerization of MeOZO with chloromethylated polystyrene (PSt–CH_2Cl) and the subsequent alkaline hydrolysis of the product copolymer **4**. Polyethylenimine is known to be a good chelating agent for various metal ions; however, its complexes with metal ions are usually soluble in water. For the purpose of the removal of heavy metal ions, it is desirable to prepare chelating agents whose metal complexes are readily separated from the aqueous phase. The present paper describes the preparation of **4** and **5** and the chelating properties of **5** with Cu^{2+}, Hg^{2+}, and Cd^{2+}.



PSt-CH_2Cl MeOZO

4 5

Results and Discussion

Preparation of Poly(styrene-*g*-MeOZO). Samples of the backbone polymers of PSt–CH_2Cl were cross-linked as well as noncross-linked ones.

Noncross-linked Graft Copolymers. The MeOZO polymerization by PSt–CH_2Cl ($\bar{M}_n$ = 1.7 × 10^4) was carried out in various solvents. As the reaction proceeded, the system solidified because of the reduced solubility of graft copolymer in the polymerization solvent. The solvent effect is illustrated in Table I. It was reported that aprotic polar solvents with high dielectric constants such as DMF were suitable for the polymerization of 2-oxazoline.[1] The same tendency was observed in the graft polymerization. All the polymer products prepared in C_6H_5CN, $C_6H_5NO_2$, and $C_6H_5OCH_3$ were soluble in methanol. Polystyrene is insoluble in methanol whereas polyMeOZO is very soluble in it. So, the solubility of the product indicates the formation of graft copolymer. The graft copolymer prepared in DMF was not soluble anymore. This is probably due to the occurrence of cross-linking during polymerization. Actually, gelation was observed by heating independently a DMF solution of PSt–CH_2Cl at 110° for 17 hr. Therefore, DMF is not suitable for the preparation of the soluble graft copolymer. Good results were obtained with C_6H_5CN as the polymerization solvent (Table II).

Cross-Linked Graft Copolymers. In the case of bead

Table I
Solvent Effect in the Graft Polymerization of MeOZO onto PSt-CH$_2$Cl

Solvent	$[I]_0$,[a] mol/l.	$[MeOZO]_0$, mol/l.	$[MeOZO]_0/[I]_0$	Temp, °C	Time, hr	Conversion,[b] %	Solubility of copolymer in MeOH
C_6H_5CN	0.12	3.90	32.5	110	20	72	Soluble
$C_6H_5NO_2$	0.08	2.24	28.0	110	16	65	Soluble
$C_6H_5OCH_3$	0.10	1.73	17.3	110	110	99	Soluble
DMF	0.13	2.18	21.6	110	60	99	Insoluble
p-Dioxane	0.11	1.28	11.4	110	80	15	
Acetone	0.09	2.50	28.5	80	65	0	

[a] Concentration of the CH$_2$Cl group in the starting PSt-CH$_2$Cl. [b] Determined by NMR.

Table II
Graft Polymerization of MeOZO onto PSt-CH$_2$Cl at 110° for 20 hr

							MeOZO unit in the product polymer, mmol/g		Polymerized MeOZO, mol/ CH$_2$Cl, mol		
No.	PSt–CH$_2$Cl,[a] g	MeOZO, g	C_6H_5CN, ml	Yield, g	Conversion, %	N (%)[b] in the product polymer	A[c]	B[d]	A[c]	B[d]	C[e]
S-1	0.41	1.96	2	1.44	52.6			8.41		15.1	17.3
S-1	3.02	6.00	30	6.57	59.2	8.64	6.04	6.35	6.6	7.3	8.4

[a] CH$_2$Cl group content, 1.89 mmol/g of PSt-CH$_2$Cl. [b] Obtained by elemental analysis. [c] Calculated by N (%) in the product polymer. [d] Calculated by the conversion. [e] Determined by NMR in CD$_3$OD.

polymers of PSt–CH$_2$Cl cross-linked with 3% divinylbenzene, DMF was employed as the polymerization solvent (Table III).

Under the polymerization conditions of Table III, MeOZO was completely consumed in all runs except one. The MeOZO content, i.e., *N*-acetylethylenimine unit content, in the graft copolymer was determined by (A) elemental analysis (from N content) and (B) monomer conversion. In addition to these two methods, NMR spectroscopy was used with the methanol soluble polymers (Table II). These methods gave corroborating values of the MeOZO content.

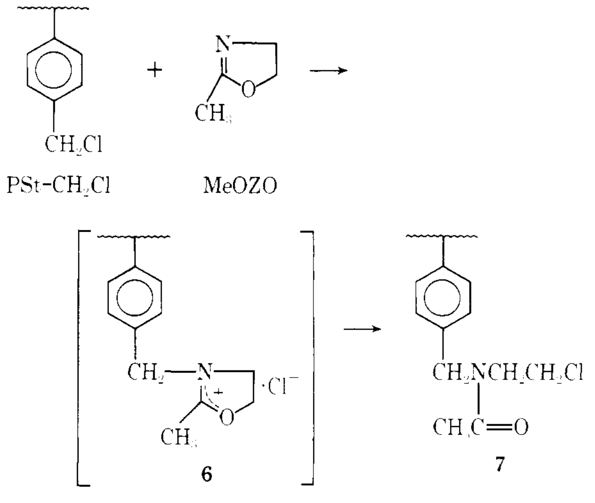
Copolymerization of MeOZO with cross-linked PSt–CH$_2$Cl gave not only the graft copolymer but also homopolymer of MeOZO. The former was, of course, insoluble in DMF and the latter was soluble in DMF. Therefore, it was easy to separate these two kinds of polymers. The amount of MeOZO introduced into PSt–CH$_2$Cl reached to almost 20 times as much as CH$_2$Cl group (Table III). The value corresponds to a MeOZO/styrene unit ratio of more than 16 since the content of CH$_2$Cl group = 5.71 mmol/g indicates that 85.1% of the phenyl group was chloromethylated.

In the polymerization using noncross-linked PSt–CH$_2$Cl, however, the copolymer and the homopolymer of MeOZO have not been separated from each other (Tables I and II). The solubility property of the copolymer resembled the homopolymer. From the results with the cross-linked PSt–CH$_2$Cl, it is very likely that the homopolymer was formed during the copolymerization.

The ir spectrum of the graft copolymer (sample no. C-5) shows a strong absorption band of $\nu_{C=O}$ at 1620 cm^{-1} (Figure 1b). The characteristic band due to the CH$_2$Cl group at 1260 cm^{-1} almost disappeared. Although the extent of conversion of the CH$_2$Cl group was not known in the graft polymerization, the chain length of the grafted MeOZO per CH$_2$Cl group was calculated on the assumption that all of the CH$_2$Cl group initiated the MeOZO polymerization (last column of Tables II and III).

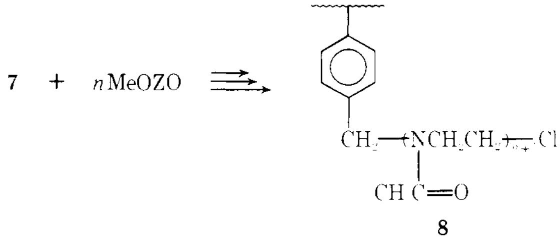
The polymerization of MeOZO by PSt–CH$_2$Cl is considered to proceed according to the reaction scheme (eq 1 and 2) which has been proposed for the MeOZO polymerization initiated by benzyl chloride.[7]

Initiation



(1)

Propagation



(2)

In both the initiation and propagation, a transient oxazolinium salt such as **6** must be involved. The intermediate species **6**, however, rearranges quickly to the covalent

Table III
Graft Polymerization of MeOZO onto Cross-Linked PSt-CH_2Cl

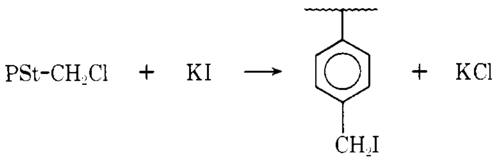
No.	PSt-CH_2-Cl,[a] g	MeOZO, g	DMF, ml	Temp, °C	Time, hr	Yield, g: Graft copolymer	Yield, g: Homopolymer of MeOZO	Conversion, %: Graft copolymer	Conversion, %: Homopolymer of MeOZO	N (%)[b] in graft copolymer	MeOZO unit in graft copolymer, mmol/g: A[c]	MeOZO unit in graft copolymer, mmol/g: B[d]	Grafted MeOZO, mol[c]/CH_2Cl, mol
C-1	1.01	6.00	20	110	38	2.75	4.26	29.0	71.0	10.67	7.62	7.43	3.79
C-2	3.08	20.22	50	80	80	9.42	13.88	31.4	68.6	11.16	7.97	7.91	4.34
C-3	0.10	1.00	Bulk	80	24	0.83	Trace	73.2	Trace			10.28	14.39
C-4	2.11	26.46	Bulk	100	18	20.87	7.70	70.9	29.1	14.87	10.62	10.56	19.53
C-5	1.81	26.00	Bulk	80	30	17.66	10.16	60.9	39.1	14.84	10.60	10.54	18.95

[a] PSt-CH_2Cl cross-linked with 3% divinylbenzene, CH_2Cl group content, 5.71 mmol/g of PSt-CH_2Cl. [b] Obtained by elemental analysis. [c] Calculated by N (%) in the graft copolymer. [d] Calculated by the conversion.

species **7** because of the larger nucleophilic reactivity of Cl^- anion than that of MeOZO. Therefore the propagating species of the MeOZO polymerization are covalent-bonded alkyl chloride species such as **7** and **8**.

The formation of homopolymer of MeOZO during the graft polymerization is probably due to the chain transfer to monomer. Such a chain transfer has been discussed[8] although its mechanism has not been well established.

The rate of the graft polymerization increased with the addition of KI as shown in Figure 2. It is known that the polymerization of MeOZO by methyl iodide (MeI) in CD_3CN proceeds via the oxazolinium iodide propagating species.[6] Therefore, the addition of KI changed the nature of the propagating end from alkyl chloride species **8** to oxazolinium iodide species **10** and **11**, e.g.,



(3)

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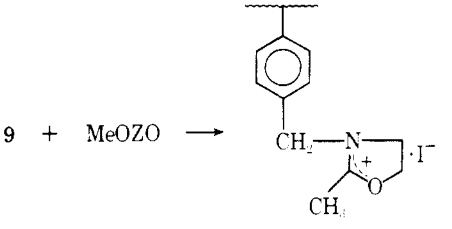
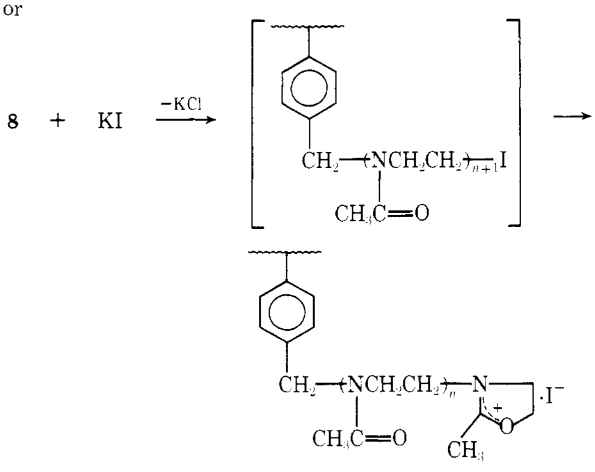


(4)

10

or



(5)

11

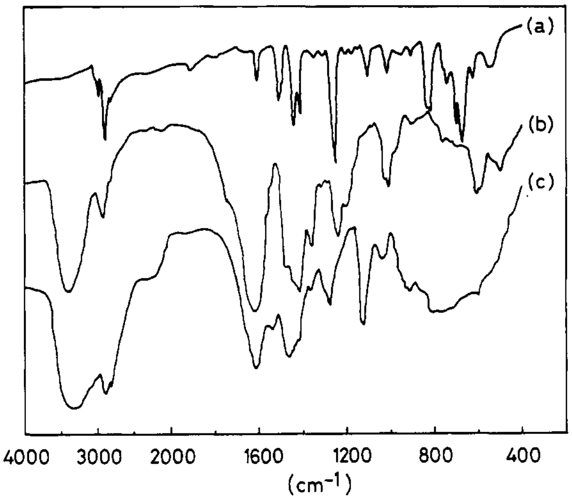


Figure 1. Ir spectra of polymers: (a) PSt-CH_2Cl cross-linked with 3% divinylbenzene; (b) poly(styrene-*g*-MeOZO) (sample C-5); (c) hydrolyzed graft copolymer (sample C-5H).

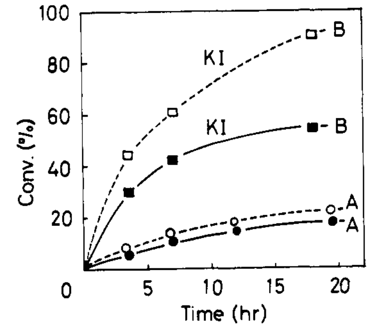


Figure 2. Effect of KI addition on the graft polymerization at 50°: (A) PSt-CH_2Cl (0.084 g) and MeOZO (0.60 ml) in 1.6 ml of DMF; (B) KI (0.11 g) was added to the system A; (○, □) total conversion of MeOZO; (●, ■) grafted part.

It is considered that an exchange reaction of chloride with iodide took place between PSt-CH_2Cl and KI (eq 3) and/or between propagating end (**8**) and KI (eq 5). It is estimated that conversion of the alkyl chloride propagating end to an oxazolinium iodide brings about rate enhancement of about 40 times in the MeOZO polymerization at 40° in CD_3CN.[6,7]

Alkaline Hydrolysis of Poly(styrene-*g*-MeOZO) to Poly(styrene-*g*-ethylenimine). Poly(styrene-*g*-MeOZO) was subjected to alkaline hydrolysis, in which most of the *N*-acetylethylenimine unit was converted into the ethylenimine (EI) unit. The cross-linked poly(styrene-*g*-MeOZO)

Table IV
Alkaline Hydrolysis of Poly(styrene-*g*-MeOZO)

No.[a]	Graft copolymer, g	NaOH, g	H_2O, ml	Temp, °C	Time, hr	Yield, g	N (%)[b] in hydrolyzed copolymer	MeOZO and EI units in hydrolyzed graft copolymer, mmol/g: MeOZO	EI	Degree of hydrolysis, %
C-1H	2.23	1.48	10	100	15	1.70	13.39	3.50	6.06	63.4
C-2H	9.29	6.76	25	80	40	6.22	15.46	1.87	9.17	83.1
C-4H	20.81	20.74	60	100	50		18.65	7.27	6.05	45.4
C-5H	11.58	7.82 7.78	30 30	100 100	22 35 [c]	6.63	24.35	2.14	15.25	87.7

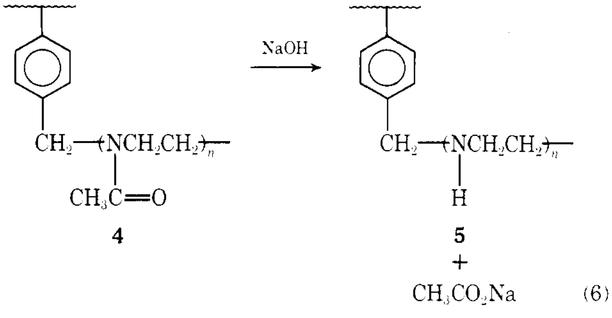
[a] Run no. is related to that of Table III, e.g., C-1H shows the experiment using the copolymer sample obtained by C-1. [b] Determined by elemental analysis. [c] Hydrolysis was repeated twice.

Table V
Grafting of PolyEI onto Cross-Linked PSt-CH_2Cl

PSt–CH_2Cl,[a] g	PolyEI,[b] g	Solvent	Temp, °C	Time, hr	Yield, g	Grafting efficiency, %	EI unit in the graft copolymer, mmol/g
1.02	1.13	Toluene (9 ml)	100	6	1.10	7.1	1.52
1.02	1.85	DMF (20 ml)	100	17	1.17	8.1	3.04

[a] PSt-CH_2Cl cross-linked with 3% divinylbenzene, CH_2Cl group content, 5.71 mmol/g of PSt-CH_2Cl. [b] Linear polyEI prepared by alkaline hydrolysis of polyMeOZO, the degree of hydrolysis = 95%; [η] = 0.23 in $CHCl_3$.

was hydrolyzed in an aqueous alkaline solution. The results are shown in Table IV. The extent of hydrolysis and EI unit content were determined from the difference between the N content of the starting and hydrolyzed copolymer. In experiment C-2H the degree of hydrolysis was also determined by NMR from the amount of CH_3CO_2Na, which was produced by hydrolysis (eq 6). The result, 83%, is in good agreement with the calculated value 83.1% from the N content. The alkaline hydrolysis of **4** did not proceed quantitatively; i.e., a small portion of *N*-acetylethylenimine unit still remained in the hydrolyzed copolymer **5**. A higher degree of hydrolysis was achieved by repeating the hydrolysis (no. C-5H).

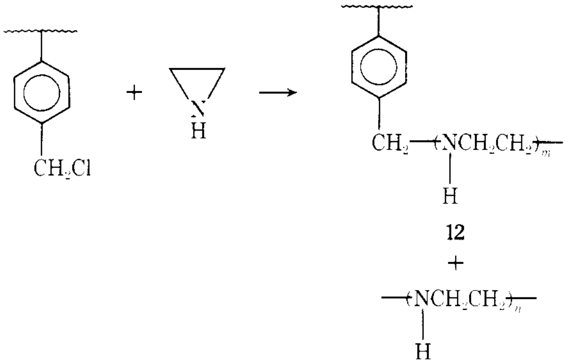


(6)

The ir spectrum of the hydrolyzed graft copolymer (sample C-5H) shows a weak absorption of amide group and a strong, new absorption at 1130 cm^{-1}[2] of ν_{N-C} due to the polyEI (Figure 1c).

Grafting of PolyEI onto PSt-CH_2Cl. An attempt was made to prepare poly(styrene-*g*-EI) by direct grafting of polyEI with cross-linked PSt-CH_2Cl. PolyEI employed was a linear, crystalline polymer obtained by the repeated alkaline hydrolysis of polyMeOZO (Table V). The grafting efficiency and the EI unit content were calculated from the yield. The grafting efficiency, i.e., (grafted polyEI/initial polyEI) × 100, was much lower than that of the graft polymerization of MeOZO onto PSt–CH_2Cl as shown in Table III. This low grafting efficiency indicates the difficulty of the reaction of the solid PSt–CH_2Cl with polyEI solution in DMF and with melted polyEI in heterogeneous phase in toluene.

Graft Copolymerization of EI onto PSt–CH_2Cl. In order to make a comparison with the present method, the graft polymerization of monomer EI (aziridine) onto cross-linked PSt–CH_2Cl was examined to introduce EI unit directly into polystyrene (Table VI). Although EI monomer was consumed quantitatively under the reaction conditions the grafted fraction was at most 5.0% of the charged EI. This finding demonstrates that the chain transfer to monomer predominated during the polymerization to produce homopolymer of EI. The ratio of EI unit to CH_2Cl group in the copolymer (*m* value in **12**) was very low, e.i., *m* ≤ 1.54, whereas that of Table IV was much higher, e.g., *n* in **5** of C-5H = 16.62. Therefore, the direct graft polymerization of EI monomer onto PSt–CH_2Cl is not a suitable method to prepare poly(styrene-*g*-EI) having long EI branches.



Adsorption of Metal Ions by the Graft Copolymers

Table VI
Graft Copolymerization of EI onto Cross-Linked PSt-CH_2Cl[a]

Solvent	N (%)[b] in the graft copolymer	Grafting efficiency, %[c]	EI unit, mmol/g	EI unit, mol/CH_2Cl, mol
DMF (3 ml)	8.64	4.8	6.17	1.47
p-Dioxane (3 ml)	8.82	5.0	6.37	1.54
Bulk	8.79	4.9	6.28	1.51

[a] Polymerization conditions: cross-linked PSt-CH_2Cl, 0.20 g; EI, 1.50 g; $[EI]_0/[CH_2Cl]_0$ = 30.6; temperature, 50°; time, 40 hr. [b] Obtained by elemental analysis. [c] Calculated by N (%) in the graft copolymer. Total conversion of EI was more than 98% in every case.

by a Batch Method. It should be worth while to examine the adsorption of metal ions by graft copolymers containing high EI unit concentration. Metal ions examined were Cu^{2+}, Hg^{2+}, and Cd^{2+}. The effect of pH on the adsorption of Cu^{2+} by graft copolymer C-2H was studied to determine the optimum pH for Cu^{2+} adsorption. As shown in Figure 3, the optimum pH range is between 4 and 6. The Cu^{2+} adsorption was very low at pH 8. This is due to the formation of $Cu(OH)_2$.

The adsorption rate of Cu^{2+} at pH 4 was investigated. It is seen that the adsorption reached saturation within 72 hr (Figure 4).

The effect of pH on the adsorption of Hg^{2+}, Cu^{2+}, and Cd^{2+} by graft copolymer C-5H is shown in Figure 5. The Hg^{2+} adsorption showed a relatively low pH dependence. The adsorption selectivity was $Hg^{2+} > Cu^{2+} > Cd^{2+}$ in the pH range examined. This tendency is in agreement with the order of the stability constant of the amine complex of these metal ions.[9] Metal ions were adsorbed in greater amount at pH 6 than at pH 4 in three series of experiments. This is contrary to the results shown in Figure 3, where the adsorption equilibrium had not been reached. It is probably responsible for the reason that the adsorption rate was faster at pH 4. The results obtained with a commercial polyamine type anion-exchange resin are also shown in Figure 5. Graft copolymer C-5H exhibited a greater adsorption capacity for Cu^{2+} than that of the commercial resin.[10-12]

Poly(styrene-*g*-MeOZO) exhibited a poor adsorption capacity for these metal ions. For example, under the same conditions in Figure 5 graft copolymer C-5 had the adsorption capacity of 0.11 mmol/g − R for Cu^{2+} at pH 4 and of ≃0 mmol/g − R for Cd^{2+} at pH 4. The hydrolysis of poly(styrene-*g*-MeOZO) is, therefore, very important to obtain a chelating resin.

Adsorption and Elution of Cu^{2+} by Column Method. The adsorption and elution experiments of Cu^{2+} with graft copolymer C-4H were carried out using the column method. Although a small leak of Cu^{2+} was observed even in the initial effluent solution (below 0.4 ppm), the leak was less than 2 ppm until ca. 100 l./l. − R of 166 ppm Cu^{2+} ($Cu(NO_3)_2$) solution passed (Figure 6). The adsorbed Cu^{2+} was readily eluted from the copolymer C-4H by passing a 1 *N* HCl solution. Complete recovery of Cu^{2+} was observed (Figure 7). The very pale yellow copolymer turned to blue by complexation with Cu^{2+} and it was decolorized completely upon treatment with an HCl solution.

These results suggest that cross-linked poly(styrene-*g*-EI) (**5**) prepared by the graft polymerization of MeOZO onto PSt–CH_2Cl can be applied to the recovery of metal ions. The higher the polyEI content in the graft copolymer, the larger the adsorption capacity for metal ions.

Experimental Section

Materials. Commercial reagents of MeOZO (from Aldrich Co.), EI monomer, and all solvents were dried and distilled under nitrogen.

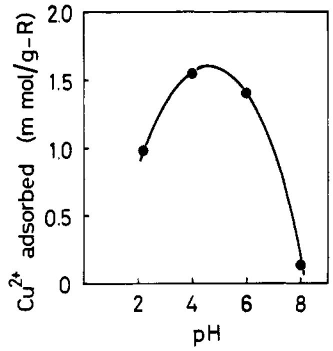


Figure 3. Effect of pH on the adsorption of Cu^{2+} by graft copolymer; copolymer C-2H (0.25 g) in 50 ml of Cu^{2+} (0.01 mol/l) solution at 30° for 24 hr.

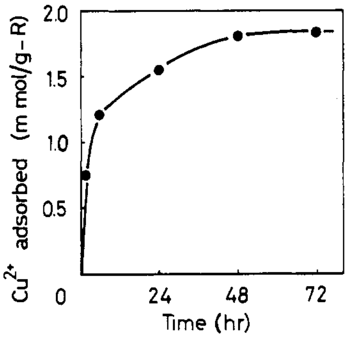


Figure 4. Adsorption rate of Cu^{2+} at pH 4 (30°); copolymer C-2H (0.25 g) in 50 ml of Cu^{2+} (0.01 mol/l.) solution.

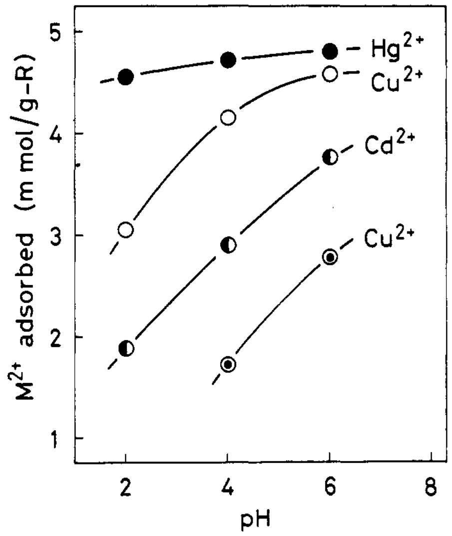


Figure 5. Effect of pH on the adsorption of Cu^{2+}, Hg^{2+}, and Cd^{2+} (30° for 72 hr): (● ○ ◐) copolymer C-5H (0.25 g) in 50 ml of metal ion (0.025 mol/l.) solution; (⊙) commercial resin (0.25 g) in 50 ml of Cu^{2+} (0.025 mol/l.) solution.

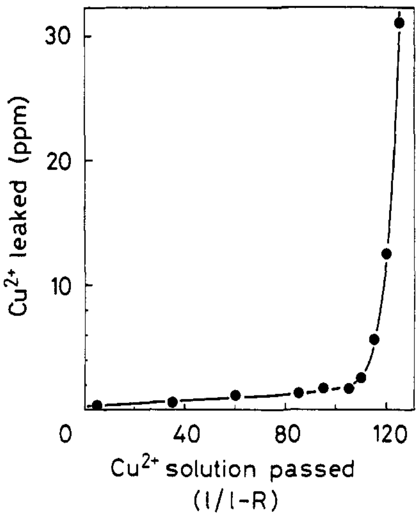


Figure 6. Adsorption of Cu^{2+} by the column method. A Cu^{2+} solution (166 ppm, pH 4.9) was passed through a column packed with 20 ml of copolymer C-4H at a flow rate of SV 9 (3 ml/min) at room temperature.

Preparation of noncross-linked chloromethylated polystyrene ($PSt-CH_2Cl$) was carried out as follows.[13-15] To 10.4 g of commercial polystyrene ($\bar{M}_n = 1.7 \times 10^4$) dissolved in 52 ml of ethylene dichloride and 12 ml of chlorodimethyl ether was added at 10° 40 ml of chlorodimethyl ether solution containing 2.0 g of anhydrous $ZnCl_2$. The mixture was stirred for 1 hr at 10°. Then, 20 ml of a water/*p*-dioxane (10:90) mixture was added to stop the reaction and the mixture was poured into a large amount of methanol. The precipitated polymer was isolated by filtration and washed with hot water and methanol. The polymer was purified by reprecipitation using a *p*-dioxane/methanol system and dried in vacuo at 70° to give 11.0 g of polymer. Anal. Found: C, 86.03; H, 7.11; Cl, 6.68. The CH_2Cl group content was determined by NMR and elemental analysis data. From the integration ratio of peaks at δ 4.40 (CH_2Cl, 2 H) and at 6.5 and 7.0 (aromatic protons) of an NMR spectrum (in CCl_4) it was found that 22% of the phenyl group was chloromethylated (degree of chloromethylation = 22%). On the other hand, the elemental analysis of Cl gave a degree of chloromethylation of 21.5%, which is in very good agreement with the value determined by NMR. The degree of chloromethylation of 21.5% corresponds to 1.89 mmol/g of $PSt-CH_2Cl$.

Macroporous bead $PSt-CH_2Cl$ cross-linked with 3% divinylbenzene was supplied by Mitsubishi Chemical Industries Co., which was washed in refluxing *p*-dioxane using a Soxhlet apparatus to remove acidic impurities and noncross-linked polystyrene and dried in vacuo. Anal. Found: Cl, 20.24. A degree of chloromethylation was calculated by Cl content to be 85.1% of the styrene unit, which corresponds to 5.71 mmol/g of $PSt-CH_2Cl$.

Graft Copolymerization. A general procedure was as follows. Graft polymerization was carried out in a glass tube under nitrogen. MeOZO was added at room temperature to noncross-linked $PSt-CH_2Cl$ dissolved in a solvent. Then, the tube was sealed and heated at a desired temperature. After polymerization methanol was added to the system and the mixture was poured into a large amount of diethyl ether. The graft copolymer was filtered and purified by reprecipitation using a methanol/diethyl ether system or a chloroform/diethyl ether system, followed by drying in vacuo until the weight of the copolymer became constant.

In the case of a cross-linked type polymer, $PSt-CH_2Cl$ was swollen in a mixture of monomer and solvent or in monomer for 1 day at room temperature. Then, the mixture was slowly shaken at a reaction temperature for a desired period. The reaction product was washed with methanol, Soxhlet extracted using methanol as a solvent in order to remove homopolymer of MeOZO, and dried in vacuo at 70° to constant weight. The washings were concentrated and poured into a large amount of diethyl ether. The precipitated homopolymer of MeOZO was dried and weighed. More detailed reaction conditions may be found in Tables I-III.

The effect of an addition of KI into a graft polymerization system was studied as follows. Cross-linked $PSt-CH_2Cl$ (CH_2Cl content = 5.71 mmol/g) (0.084 g) was swollen in 1.6 ml of DMF. Then, 0.11 g of KI and 0.60 ml of MeOZO were added to the mixture under nitrogen. The mixture was heated at 50° with stirring. After the fixed period of time, the amount of unreacted monomer and homopolymer in the supernatant solution was determined by NMR.

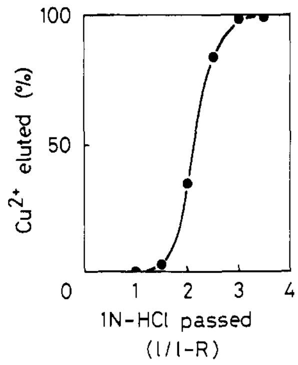


Figure 7. Elution of the adsorbed Cu^{2+} (total 6.56 mmol) with 1 *N* HCl (flow rate = SV 2.5).

Hydrolysis of Poly(styrene-*g*-MeOZO). Poly(styrene-*g*-MeOZO) was hydrolyzed in an aqueous NaOH solution. A typical experiment (C-2H) was as follows. A mixture of 9.29 g of cross-linked poly(styrene-*g*-MeOZO), 6.76 g of NaOH, and 25 ml of water was heated at 80° for 40 hr in a sealed tube with stirring. After the reaction the hydrolyzed copolymer was isolated by filtration and washed with water until the washings became neutral, followed by washing with methanol and diethyl ether, and then dried in vacuo at 70° to a constant weight of 6.22 g. The filtrate and aqueous washings were combined and concentrated on a steam bath. To the remaining solution known amounts of methanol and benzene were added. The quantity of the produced CH_3CO_2Na was determined by NMR spectroscopy as 61 mmol, which corresponds to 83% of a degree of hydrolysis. An elemental analysis of the hydrolyzed copolymer gave an N content of 15.46%, being equal to the degree of hydrolysis of 83.1%. Other experimental conditions and results may be found in Table IV.

Grafting of polyEI onto polystyrene. Cross-linked $PSt-CH_2Cl$ was swollen in a solvent (toluene or DMF) and polyEI ($[\eta]$ = 0.23 in $CHCl_3$, degree of hydrolysis = 95%) was added. The mixture was stirred at 100° for a fixed period of time. The reaction product was filtrated and washed successively with 1 *N* HCl, 1 *N* NaOH, hot water, methanol, and diethyl ether, followed by vacuum drying at 70°. Experimental conditions and results are given in Table V.

Graft Copolymerization of EI onto Cross-Linked $PSt-CH_2Cl$. A typical experiment was as follows. $PSt-CH_2Cl$ (0.20 g) was swollen in 3 ml of DMF in a glass ampoule under nitrogen for a day at room temperature. EI (1.50 g) was added to the ampoule at −78° and the ampoule was sealed. The mixture was then warmed up slowly to room temperature and heated at 50° for 40 hr with occasional shaking. The copolymer was separated by filtration, washed with 1 *N* HCl, 1 *N* NaOH, hot water, methanol, and diethyl ether, and dried in vacuo at 70° to give 0.24 g.

Adsorption of Metal Ions by Graft Copolymer (Batch Method). A general procedure was as follows. A graft copolymer (0.25 g) and a metal ion solution (50 ml) were placed in a 100 ml Erlenmeyer flask. The mixture was allowed to stand at 30° with occasional shaking. After a fixed period of time the metal ion concentration of the supernatant solution was determined by chelatometry. The quantity of the metal ion adsorbed (mmol/g − R) was calculated from the difference of the ion concentration before and after the adsorption.

In order to keep pH constant during the adsorption experiment, a metal ion solution was prepared by dissolving the metal salt of $Cu(NO_2)_2$, $HgCl_2$, or $CdCl_2$ in Clark Lubs' buffer solution in a desired concentration.

Adsorption and Elution of Cu^{2+} by a Column Method. Graft copolymer of C-4H (20 ml in the wet state, 5.2 g in the dry state) was packed into a column of 11 mm of internal diameter. An aqueous solution of Cu^{2+} (concentration of 166 ppm, pH 4.9) was allowed to flow through the column at a flow rate of SV 9 (3 ml/min). The effluent solution was sampled every 50 ml and the Cu^{2+} concentration was determined as follows. A mixture of the sample solution (4 ml), tartaric acid (0.2 g), hydroxylamine hydrochloride (0.2 g), and NaOH (0.1 g) was placed in a 10 ml volumetric flask, to which 5 ml of a 0.2% neocuproine-DMF solution was added, and then the solution was diluted to the mark with water. The absorbance at 454 nm[16] was used to determine the concentration of Cu^{2+}

After the adsorption experiment, the column was washed with 200 ml of water. An eluting agent (1 *N* HCl aqueous solution) was passed through the column at a flow rate of SV 2.5. The content of Cu^{2+} in every 10 ml of eluate was determined by chelatometry.

Acknowledgment. This work was supported by a Grant in Aid for Scientific Research, the Ministry of Education, Japan. The authors are grateful to the Mitsubish Chemical Industries Co. Ltd. for a gift of cross-linked $PSt-CH_2Cl$ samples.

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Anionic Polymerization of the Barium Salt of One-Ended Living Polystyrene. I. Conductance and Kinetic Studies

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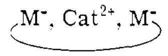
ABSTRACT: The barium salt of *one-ended* living polystyrene was prepared by converting on a barium mirror dibenzylmercury into dibenzylbarium; the latter was reacted with α-methylstyrene and the resulting oligomer with styrene. This procedure yields the required salt. The conductance of the barium polystyryl was determined in THF in the temperature range −70 to +20°. The results indicate that two equilibria are simultaneously maintained: $Ba^{2+},(\text{poly-S}^-)_2 \rightleftarrows Ba^{2+},(\text{poly-S}^-) + \text{poly-S}^-$ (K_1) and $2Ba^{2+},(\text{poly-S}^-)_2 \rightleftarrows Ba^{2+},(\text{poly- S}^-) + Ba^{2+},(\text{poly-S}^-)_3$ (K_2), and for all the investigated temperatures the values of K_1 and K_2 were calculated from the experimental data. The propagation involving the free poly-S^- anions accounts for the observed kinetics of polymerization, the contribution of the other species to the reaction being negligible. This mechanism predicts, in accordance with our observations, that the pseudo-first-order rate constant of propagation is virtually independent of the total concentration of the salt and provides, therefore, an alternative explanation of the results reported earlier by Francois et al.

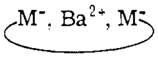
It is well established[2] that several distinct reactive species are involved in the propagation of alkali salts of living polymers. For example, in ethereal solvents ion pairs, $—M^-,Cat^+$, as well as the free $—M^-$ anions, contribute to the propagation,[3-5] and the contribution of intra- or intermolecular triple ions has been observed[6-9] at least in some of the investigated systems. The behavior of the alkaline-earth salts of living polymers is less documented. Their description requires a sharp delineation between the salts formed from polymers endowed with two growing end groups and those possessing one living end group only. The former may exist either in a cyclic form



$$M^-, Cat^{2+}, M^-$$

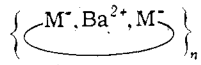
or as polymer-linked aggregates, $—M^-,Cat^{2+},M^-—M^-,Cat^{2+},M^-—$, etc., whereas the latter are composed from two living polymers linked to one bivalent cation, i.e., $\{X—M^-,Cat^{2+},^-M—X\}$.

Kinetic studies of polymerization of the barium salt of living polystyrene have been reported recently by Francois and his coworkers.[10] They claim that their system involves polymers terminated by carbanions on both of their ends and that the salt is cyclic in nature. The rate of propagation in THF, studied over a wide range of temperatures, was found to be independent of living end concentration when the latter was varied by two powers of ten, i.e., from about 10^{-5} to 10^{-3} *M*. This observation was accounted for by a mechanism postulating the existence of a minute fraction of single cyclic species, viz.



$$M^-, Ba^{2+}, M^-$$

which remain in equilibrium with large aggregates



$$\left\{ M^-, Ba^{2+}, M^- \right\}_n$$

However, our study of the polymerization of the barium salt of living polystyrene endowed with one growing end casts some doubt on their suggestion and leads to an alternative explanation for their findings. Moreover, our results allow us to compare the reactivities of the neutral salt, $Ba^{2+}(M^-—X)_2$, and of the pair $(X—M^-),Ba^{2+}$ with that of the free $X—M^-$ anions.

Preparation of the Barium Salt of One-Ended Living Polystyrene. The preparation involves three steps. (1) Conversion of mercury dibenzyl into barium dibenzyl, $Ba^{2+}(PhCH_2^-)_2$, by prolonged contacting of a THF solution of $Hg(PhCH_2)_2$ with a barium mirror freshly prepared in vacuum according to the procedure of Sigwalt et al.[11] The yield is quantitative. After filtering the resulting solution from the excess of metallic barium its spectrum was examined (λ_{max} = 343 nm and the decimal $\epsilon = 1.31 \times 10^4$ per mol of $PhCH_2^-$ anions).

(2) The addition of a 3.5-fold excess of α-methylstyrene (α-MeS) to the solution of $Ba^{2+}(PhCH_2^-)_2$ yields the barium salt of living α-MeS oligomer, $Ba^{2+}(PhCH_2\cdots\alpha\text{-MeS}^-)_2$. Although the reacting mixture was kept for 20 hr at 40°, about 5% of the benzyl carbanions and 10% of the added α-MeS were left unreacted. The presence of the unreacted $PhCH_2^-$ anions was revealed by the formation of toluene