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Polyethylenimine—Poly(vinyl Chloride) Crosslinked Polymers and Their Use in Adsorption of Mercuric and Cupric Salts

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ABSTRACT

The alkylation reaction of polyethylenimine (PEI) by poly(vinyl chloride) (PVC) was investigated. PEI-PVC crosslinked polymers with high PEI content were obtained in good yields. Study of the adsorption by complexation of mercuric chloride and cupric sulfate from aqueous solution by these polymers showed that they can be used effectively to remove mercuric and cupric salts from aqueous solutions.

INTRODUCTION

PEI is well known for its ability to complex with heavy metal salts. The reactions of PEI with organic halides such as ethylene dichloride [1] and ethylene dibromide [2] were utilized to crosslink the polymer and to render it water-insoluble. The crosslinked polymer formed stable complexes with copper(II) as well as cobalt(III), probably by chelate ring formation [1]. The complexed polymers were used as anion-exchange resins. Similarly [3], by reaction of PEI with more reactive unsaturated organic halides such as allyl chloride, chelating resins were obtained under milder reaction conditions. PEI was also used as an ion-exchange and complexing resin by crosslinking it within cotton fabric [4]. This fabric was prepared by crosslinking PEI prepolymer with 1,2-dichloroethane within the fabric. It was found that the PEI-containing fabric had a high capactiy for complexing certain heavy metal salts from aqueous solution. The advantage in removal of mercuric salts from aqueous solution by this fabric was reported recently [5].

It was of interest to investigate the possibility of chemically binding PEI to other polymers which will be stable in acidic media. PVC was chosen because of its stability at low pH and because its alkyl halide segmers are capable of reacting with the amine groups of the PEI. Alkylation of PEI with PVC should lead to insoluble crosslinked polymers. The preparation of such polymers was studied as well as their use in the removal of mercuric chloride and cupric sulfate from aqueous solution.

EXPERIMENTAL

Materials

Polyethylenimine 50% in water (Fluka), poly(vinyl chloride) (Frutarom), benzyltrimethylammonium hydroxide 40% in methanol (Triton B), (practical, Fluka) benzene (Frutarom), and DMF (Riedel de Hoën) were used.

Alkylation of PEI by PVC in the Presence of Triton B

A typical procedure is described. A 50% aqueous solution of PEI containing 43 g PEI was dried by azeotropic distillation with benzene. The benzene was removed in vacuo, the PEI was dissolved in DMF (200 ml) and was added to a solution of PVC (52.5 g) in DMF (300 ml). The solution was kept at room temperature for two weeks and then Triton-B, 40% in methanol (10 ml) was added. Precipitation of the crosslinked polymer took place immediately. The solution was allowed to stand for 4 hr and filtered. The crosslinked polymer was Soxhlet-extracted with DMF for 24 hr in order to remove any unreacted

PEI and PVC. The crosslinked polymer was triturated in ethanol, filtered, and dried in vacuo. The crosslinked polymer obtained (54.8 g) showed on analysis 18.1% N and 4.23% Cl.

Removal of Hydrogen Chloride Attached to the PEI-PVC Crosslinked Polymer

Crosslinked polymer (10 g) was allowed to stand in 20% sodium hydroxide solution (50 ml) for 24 hr, filtered, washed with 2% acetic acid solution and then with water, and dried.

Alkylation of PEI by PVC at High Temperature

PEI was dried as described before. A solution of PVC (2.63 g) and PEI (2.15 g) in DMF (25 ml) was allowed to stand for 24 hr at 100°. The crosslinked polymer precipitated out, was filtered and Soxhlet-extracted with DMF. Free chloride was removed by sodium hydroxide treatment as described before. PEI-PVC crosslinked polymer (2.23 g) was obtained; analysis showed 17.2% N and 3.50% Cl, corresponding to 52.8% PEI content.

Adsorption of Mercuric Chloride and Cupric Sulfate by PEI-PVC Crosslinked Polymer

Crosslinked polymer (0.1 g) was allowed to stand in mercuric chloride solution or cupric sulfate solution (10 ml) at room temperature for the required time. The polymer was filtered, and the decrease in the concentration of the cations was determined by an atomic adsorption spectrophotometer, Perkin-Elmer 303, by means of calibration curves.

RESULTS AND DISCUSSION

Alkylation of PEI by PVC

The alkylation of PEI by PVC was investigated. The reaction was carried in DMF solution, using equisegmer amounts of the two polymers. Alkylation of PEI with PVC should lead to a three-dimensional, insoluble, crosslinked polymer. When a DMF solution of the two polymers was kept at room temperature for more than 14 days, no precipitation of a crosslinked polymer took place. On the other hand, the UV and visible spectra of the reaction mixture showed the appearance of conjugated double bonds systems. The extent of conjugation increased with reaction time, as may be concluded from the appearance of new absorptions at higher wavelengths. Thus, after 3 days absorptions at 307, 324, and 375 nm appeared, while additional absorptions at 412 and 434 nm appeared after 10 days and at 455 and 470 nm after 50 days. Similar absorptions were reported to appear during degradation of PVC by alcoholic potassium hydroxide in THF or DMF at room temperature and also for thermally degraded PVC [6, 7].

The degradation of the PVC is by hydrochlorination, leading to formation of conjugated double bond systems responsible for the spectra obtained; PEI, being a basic polymer, facilitates this dehydrohalogenation. As a result of dehydrochlorination, chloride atoms adjacent to double bonds are converted into more reactive allylic chlorine. Thus dehydrochlorination should increase the reactivity of the PVC due to introduction of allylic chlorine along the polymer chain. Both in the dehydrochlorination of PVC and in the alkylation of PEI by PVC, chloride ions are formed as reaction by product.

The extent of participation of the PVC in both reactions can be determined from the amount of chloride ions liberated in the reaction mixture. It was found (Fig. 1) that after 10 days at room

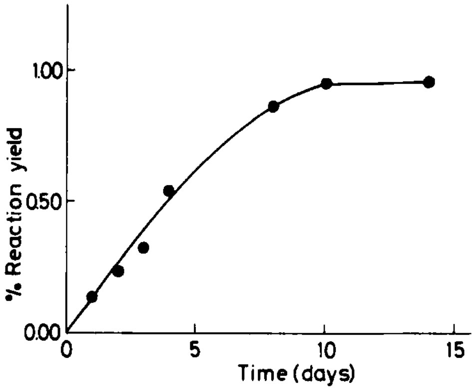

FIG. 1. Chloride formation in the reaction between PVC and PEI. PVC (52.5 g) and PEI (43.0 g) were allowed to stand in DMF (500 ml) at room temperature.

temperature, in DMF, less than 1% of chloride ion was liberated. Since no precipitation of a crosslinked polymer took place, it can be assumed that the alkylation reaction under these conditions, even by allylic chlorine is negligible. The main reaction occurring is dehydrochlorination. In order to promote alkylation of the PEI by the PVC a strong organic base, benzyltrimethylammonium hydroxide (Triton B) was added to the reaction mixture. It was found, however, that the time of reaction of PVC and PEI prior to the addition of the Triton B was very important. It can be seen (Table 1) that extent of alkylation leading to an insoluble crosslinked polymer increased with the time allowed for dehydrochlorination of the PVC prior to the Triton B addition. At long reaction times, when enough allylic chlorine groups were present, insoluble polymers containing 50% PEI could be obtained in good yields.

Insoluble crosslinked polymer composition was determined from nitrogen and carbon analysis of the reaction product. Chlorine analysis was not used for this purpose, since extent of dehydrochlorination varied from polymer to polymer. It was found (Table 2) that Triton B as well as lithium hydroxide leads to dehydrochlorination of PVC in DMF solution. It can be seen that extent of reaction, even by these strong bases, is low. After nine days only 3.47 and 3.20% of chlorine in the polymer was converted to chloride due to dehydrochlorination when Triton-B and lithium hydroxide were used. No

TABLE 1. Reaction between PVC and PEI[a]

Reaction time (hr)[b]	Crosslinked polymer Amt (g)	N (%)	Cl (%)	Reaction yield PEI (%)[c]	PVC (%)[d]	PEI in polymer (%)
1	0.13	9.8	13.5	1.8	5.8	30.1
8	0.57	13.3	8.4	10.8	20.4	40.8
100	2.12	16.0	6.4	48.5	69.9	49.1
240	2.74	16.3	4.8	63.8	93.3	50.0

[a] PVC (2.63 g) in DMF (15 ml) was added to PEI (2.15 g) in DMF (10 ml). The reaction mixture was kept at room temperature for different time intervals before Triton B (40% in methanol, 1 ml) was added.

[b] Reaction time before Triton B addition.

[c] Calculated from nitrogen analysis.

[d] Calculated from nitrogen and carbon analysis.

TABLE 2. Dehydrochlorination of PVC by Triton B and Lithium Hydroxide[a]

	Reaction yield[b]	
Reaction time (hr)	Triton B (%)	Lithium hydroxide (%)
1	2.29	1.40
4	2.69	2.03
24	2.83	2.40
72	3.08	2.85
96	3.36	3.13
220	3.47	3.20

[a] To a solution of PVC (4.69 g) in DMF (25 ml) Triton B, 40% in methanol, 1 ml) or lithium hydroxide (2% in methanol, 1 ml) was added. Reaction was carried at room temperature.

[b] Determined by titration of the chloride formed with silver nitrate solution.

precipitation of the PVC from its DMF solution due to dehydrochlorination took place. Alkylation of PEI by PVC in DMF in the absence of Triton B leading to the formation of insoluble crosslinked polymer in good yields was found to require elevated temperature. Thus, when a DMF solution of PVC and PEI was heated at 100° C for 24 hr, crosslinked polymer was obtained. Incorporation of the PEI and of PVC in the polymer was 54.8% and 70.1%, respectively.

Adsorption of Mercuric Chloride by PEI-PVC Crosslinked Polymer

The time dependence of adsorption of mercuric chloride by complexation from aqueous solution by PVC-PEI crosslinked polymer is shown in Fig. 2. Two polymers were compared: PVC-PEI crosslinked polymer of 50.0% PEI content and chloride free and PVC that was treated with Triton B in DMF alone. After 60 hr, when adsorption was completed, the complexation capacity of the chloride-free

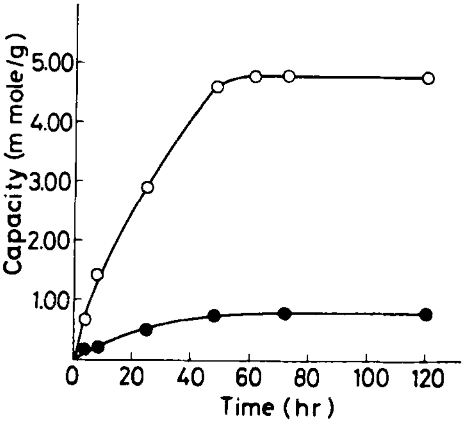

FIG. 2. Time dependence of adsorption of mercuric chloride by PEI-PVC crosslinked polymer (○) Crosslinked PEI-PVC of 48.2% PEI content; (●) Triton B-treated PVC. Polymer (0.1 g) was allowed to stand in 0.05 N solution of mercuric chloride at room temperature.

crosslinked polymer was 4.8 mmole/g. In these adsorption experiments a molar excess of mercuric chloride to amine groups in the crosslinked polymers was used. If complexation is by chelate ring formation, 86.4% of the amine groups in the polymer participated in complexation. The Triton B-treated PVC adsorbed mercuric chloride to a certain extent also. Nitrogen analysis of that PVC revealed that the polymer used contained 2.7% N, which could be introduced into the polymer by reaction between the dehydrochlorinated polymer and amine impurities in the Triton B solution. Adsorption by the Triton B-treated PVC can be attributed to the nitrogen present in the polymer. Adsorption by complexation of mercuric chloride by PEI-PVC crosslinked polymer, from aqueous solutions of different concentrations is described in Table 3. In these experiments a molar excess of amine groups in the crosslinked polymer was present. Since Triton B-treated PVC adsorbed mercuric chloride also, a control experiment with this polymer was run under the same conditions. In the concentrated mercuric chloride solutions used adsorption was mainly by the PEI in the crosslinked polymer. The contribution of the Triton B-treated PVC to complexation increased with decreasing solution concentration. At lower concentrations, an increase in

TABLE 3. Adsorption of Mercuric Chloride by PEI-PVC Crosslinked Polymer[a]

Mercuric chloride solution (10^{-3} M)	PEI-PVC adsorption capacity (mmole/g)[b]	PVC adsorption capacity (mmole/g)[b,c]	Adsorbed $HgCl_2$	
			PEI-PVC (%)	PVC (%)
7.5	4.85	0.85	65	11
5.0	4.80	0.85	96	17
3.5	3.35	0.65	96	19
2.0	1.90	0.45	95	23
0.5	0.50	0.15	100	30
0.1	0.01	0.05	100	50

[a] PEI-PVC crosslinked polymer of 48.2% PEI content (0.1 g) was allowed to stand in mercuric chloride solution (10 ml) for 72 hr at room temperature.

[b] Determined from the decrease in solution concentration.

[c] Triton B-treated PVC was used.

TABLE 4. Adsorption of Mercuric Chloride by PEI-PVC Crosslinked Polymer at Different Solution pH[a]

Solution pH	PEI-PVC adsorption capacity (mmole/g)[b]	PVC adsorption capacity (mmole/g)[b,c]	Adsorbed $HgCl_2$	
			PEI-PVC (%)	PVC (%)
3.0	3.85	0.60	77	12
4.0	4.00	0.65	80	13
5.0	3.90	0.55	78	11
6.0	3.85	0.60	77	12

[a] PEI-PVC crosslinked polymer of 48.2% PEI content (0.1 g) was allowed to stand in 0.05 M $HgCl_2$ solution (10 ml) for 72 hr at room temperature.

[b] Determined from the decrease in solution concentration.

[c] Triton B-treated PVC was used.

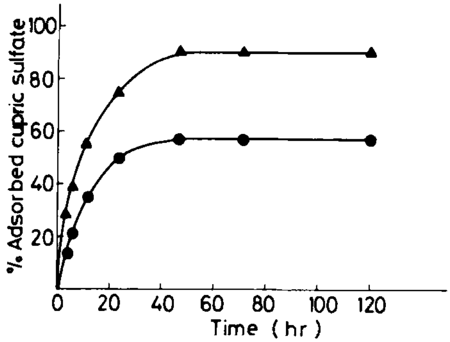

FIG. 3. Time dependence of adsorption of cupric sulfate by PEI-PVC crosslinked polymer: (▲) 5×10^{-4} M cupric sulfate solution; (●) 5×10^{-2} M cupric sulfate solution. Polymers (0.1 g) of 48.2% PEI content were allowed to stand in cupric sulfate solution at room temperature.

extent of complexation was observed. At the very lowest concentration determined, removal of the mercuric salts from aqueous solution was almost quantitative.

Since complexation of the mercuric chloride is by the free amine groups in the polymer it was of interest to determine the extent of complexation of the PEI-PVC crosslinked polymer at different pH values (Table 4). In the 3.0-6.0 pH range, the extent of complexation did not change significantly from the control experiments with Triton B-treated PVC. It can be seen that adsorption in crosslinked polymer is mainly by the PEI.

Adsorption of Cupric Sulfate by PEI-PVC Crosslinked Polymer

The time dependence of adsorption by complexation of cupric sulfate from aqueous solution by PEI-PVC crosslinked polymer is described in Fig. 3. Adsorption experiments were carried out at two different concentrations. It can be seen that adsorption was completed after 60 hr. Adsorption of cupric sulfate from aqueous solutions of different concentrations is reported in Table 5. Adsorption was investigated in the concentration range of 5×10^{-2} - 5×10^{-4} M. All experiments were carried out in the presence of a molar excess of amine groups in the crosslinked polymer. The extent of adsorption by complexation

TABLE 5. Adsorption of Cupric Sulfate by PEI-PVC Crosslinked Polymer[a]

Cupric sulfate solution (10^{-3} M)	PEI-PVC adsorption capacity (mmole/g)[b]	Adsorbed cupric sulfate (%)
0.05	0.45	90
0.10	0.43	85
2.00	0.68	84
3.50	2.54	72
5.00	2.89	58

[a] PEI-PVC crosslinked polymer of 48.2% PEI content (0.1 G) was allowed to stand in cupric sulfate solution (10 ml) for 60 hr at room temperature.

[b] Determined from decrease in solution concentration.

TABLE 6. Adsorption of Mercuric Chloride by PEI-PVC Crosslinked Polymer at Different Solution pH[a]

Cupric sulfate concn (M)	Solution pH	PEI-PVC adsorption capacity (mmole/g)[b]	Adsorbed cupric sulfate (%)
Series A			
5.0×10^{-3}	2.0	1.18	24
5.0×10^{-3}	3.0	1.29	26
5.0×10^{-3}	4.0	1.52	30
5.0×10^{-3}	5.0	1.83	37
Series B			
5.0×10^{-6}	1.0	1.69×10^{-2}	34
5.0×10^{-6}	2.0	3.06×10^{-2}	61
5.0×10^{-6}	3.0	4.17×10^{-2}	83
5.0×10^{-6}	4.0	4.25×10^{-2}	85
5.0×10^{-6}	5.0	4.31×10^{-2}	86

[a] PEI-PVC crosslinked polymer of 48.2% PEI content (0.1 g) was allowed to stand in cupric sulfate solution for 60 hr at room temperature.

[b] Determined from decrease in solution concentration.

increased with decreasing solution concentration. At the lowest concentration used, 90.3% of the cupric sulfate was removed by the crosslinked polymer from the solution. Complexation was mainly by the PEI in the crosslinked polymer. In control experiments with Triton B-treated PVC it was found that at the same cupric sulfate concentration range, the extent of adsorption was low and varied between 0.28 mmole/g for the highest solution concentration to 3.0 μmole/g for the lowest concentration. The pH dependence of adsorption of cupric sulfate by the PEI-PVC crosslinked polymer is shown in Table 6. The pH dependence of adsorption was determined in two different concentrations at pH range of 1.0-5.0. Experiments were carried out at a molar excess of amine groups in the crosslinked polymer. It can be seen that the crosslinked polymer is more effective in removing cupric sulfate from solution as solution concentration decreases. Adsorption decreased with decreasing solution pH; nevertheless, even at pH 1 the crosslinked polymer adsorbed cupric sulfate.

It can be seen that the PEI-PVC crosslinked polymer may be of interest in removal of metal salts such as mercuric and cupric salts from aqueous solution. This polymer can be used even under acidic conditions.

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