

# Dialkyldithiophosphate Substituted on Poly(Vinylchloride): Synthesis and Performance

LEV BROMBERG\* and GIDEON LEVIN

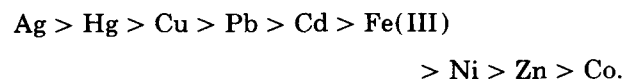
Department of Materials and Interfaces, The Weizmann Institute of Science, P.O. Box 26, Rehovot 76100, Israel

## SYNOPSIS

Preparation of sodium salt of di(2-ethylhexyl)dithiophosphoric acid (DTPANa) by reaction of the corresponding DTPA with sodium hydride has been described. Nucleophilic substitution of chlorine on poly(vinylchloride) (PVC) by a di(2-ethylhexyl)dithiophosphate group resulting in modified polymer (MP) was characterized by the second order rate constant equal to  $6.6 \times 10^{-5} M^{-1} s^{-1}$ . Formation of homogeneous stable gelled phases composed of MP and DTPA, as well as MP, PVC, and DTPA, was demonstrated. The gelled material is capable of selective separation of metal ions under the conditions of extraction chromatography. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

In recent years, a great amount of work has been done on the substitution of chlorine in poly(vinylchloride) (PVC) by nucleophiles such as thiolate, xantate, and dithiocarbamate.<sup>1-3</sup> The substitution of chlorine in PVC was reported to produce a material for membranes used in pervaporation.<sup>4</sup> A gelled membrane composed of PVC modified by dialkyldithiocarbamate with a specific extractant played as both an ion carrier and a solvent was recently described.<sup>5</sup> The membrane was shown to be capable of selective separation of mercury or silver from many other cations when di(2-ethylhexyl)dithiophosphoric acid (DTPA) was used as an ion carrier. DTPA is a very strong extractant for a number of metals with the extraction sequence as follows:<sup>6</sup>



The excellent extraction properties of DTPA are already used in solvent-extraction plants in which metals are being recovered from low grade residues

in the hydrometallurgical industry.<sup>7</sup> Hence, it was of interest to find a way to introduce DTPA into a polymeric system giving material to be packed in ion exchange columns. To do so, we modified PVC by dithiophosphate. The resulting modified polymer (MP) formed stable gelled phases with DTPA. The synthesis and performance of the above MP are outlined below.

## EXPERIMENTAL

### Synthesis of DTPANa

DTPA was synthesized by the reaction of 2-ethylhexyl alcohol (Merck) with phosphorus pentasulfide (BDH Chemicals) according to a procedure described recently.<sup>8</sup> DTPA (0.01 mol) was carefully mixed with sodium hydride (0.01 mol) suspension (Merck) in water-free conditions until no more hydrogen was evolved from the reactionary mixture. The NaH was added slowly into DTPA with stirring to avoid excessive frothing. Bis[di(2-ethylhexyloxy)thiophosphoryl]disulfide (BTPD) was synthesized and purified as was described elsewhere.<sup>8</sup> The resulting DTPANa, DTPA, and BTPD were analyzed by <sup>1</sup>H and <sup>31</sup>P NMR.

### Preparation of MP

The general procedure derived for the displacement of chlorine on PVC by dithiocarbamate group<sup>1,2,5</sup>

\* Present Address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

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was adopted with slight variation. The modification by dialkyldithiophosphate group was carried out in the following way.

PVC, 0.06 mol (43 grade, Frutarom, Israel), was mixed with dried *N,N*-dimethylformamide, 40 mL (DMF) (Merck), until a clear solution was obtained. To this solution DTPANa (0.03 mol) in DMF (20 mL) was added. The mixture was stirred under a stream of nitrogen at 45°C. Samples were withdrawn intermittently from the reaction mixture and precipitated in methanol. The polymer was washed with water to remove the unreacted DTPANa, washed again with methanol, and dried under vacuum at room temperature.

The sulfur and chlorine content of each sample was measured by elemental sulfur and chlorine analysis. NMR spectra were recorded at 400 MHz on a Bruker AMX400 spectrometer. A Nicolet 510 FTIR spectrometer was used to record infrared spectra of the modified polymer cast as thin films.

#### Preparation of Beads and Ion Exchange Procedure

The mixture of MP (S, 4.1%; Cl, 42.1%), PVC, and DTPA in the weight ratio 1.0 : 0.9 : 1.1 was stirred in dioxane at 40°C until the transparent solution was obtained. The weight percent of dioxane in the solution was equal to 86–87%. Then the viscous polymeric solution was extruded into drops from a syringe into stirred solution of 4 v/v % surfactant (polyethyleneglycol,  $M_w = 4000$ ) in deionized water. An abrupt coagulation led to the round-shaped beads formation. Then the coagulation solution was filtered off and beads were dried under vacuum. The content of the dried beads is as follows: S, 7.0%; Cl 32.9%.

Blank material (no MP was included) was also prepared by mixing 0.22 g PVC and 0.22 g DTPA in 5 g dioxane at 40°C. The beads (content: S, 8.6%; Cl, 33.65%) were prepared as described above.

A series of ion-exchange columns were prepared. Each column consisted of a poly(ethylene) pipe (internal diameter 4.5 mm) closed at the end by the three-way stopcock connected to the syringe. A resin bed height was set at 33–35 mm. The dried beads of a known weight were given a preliminary treatment with 0.1M  $H_2SO_4$  and rinsed with distilled water. An aqueous solution of the corresponding metal acetate or nitrate (each metal content ranged from 60 to 120 ppm) was passed through the resin bed. The percolation of the solution was then discontinued and the bead was rinsed with three bed volumes of distilled water. Then the solutions were eluted down the columns at a flow rate of 7–15 mL/min. Metal

ion concentrations in the effluent were monitored with a Perkin Elmer Model 5100 PC atomic absorption spectrophotometer.

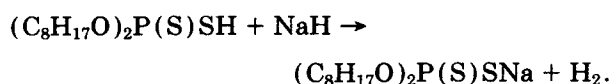
## RESULTS AND DISCUSSION

### Characterization of Nucleophilic Agent

Substitution of chlorine on PVC by functional group is very much dependent on the nucleophilicity of the latter.<sup>9</sup> Furthermore, the nucleophilic substitution is extremely sensitive to the conditions in which it is carried out, since the elimination of hydrogen chloride may easily occur.<sup>3</sup>

Such undesirable dehydrochlorination can be accelerated by the presence of a base that might also lead to a crosslinked polymer. This fact predetermined our choice for the way in which nucleophilic agent should be prepared.

Alkali metal salts of the dithiophosphoric acids can be obtained by neutralization of the acids with hydroxides or carbonates.<sup>10,11</sup> However, we chose to use the neutralization of DTPA by NaH according to the scheme:



Since neither hydroxides nor additional solvents are used, this method minimizes the formation of undesired impurities in the product that can be used without any purification. Careful "titration" of the DTPA by NaH avoids the excess of base in the mixture and thus prevents undesired reactions.

The  $^1H$  NMR in  $CDCl_3$  (400 MHz) spectrum of DTPANa prepared according to the above scheme shows the expected integration ratio between the different protons. The methyl group is a triplet centered around 0.9 ppm. The proton absorption of different methylene groups is in the range of 1.3 ppm. The CH group located  $\beta$  to oxygen gives a peak at 1.59 ppm, and methylene group attached to oxygen shows a multiplet centered around 3.85 ppm. The ratio between the above peaks found from the spectrum is as follows: 6.0 : 8.4 : 0.8 : 1.8, and the corresponding calculated one is 6.0 : 8.0 : 1.0 : 2.0.

Table I shows the  $^{31}P$  NMR peaks found in DTPANa, together with the approximate percentage and the structure assignments made comparing NMR spectra of DTPANa with the spectra of pure DTPA and BTPD.

**Table I**  $^{31}\text{P}$  NMR Peaks of DTPANa

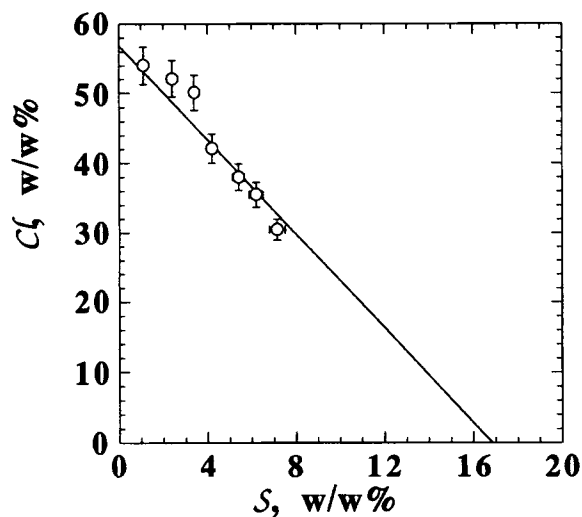
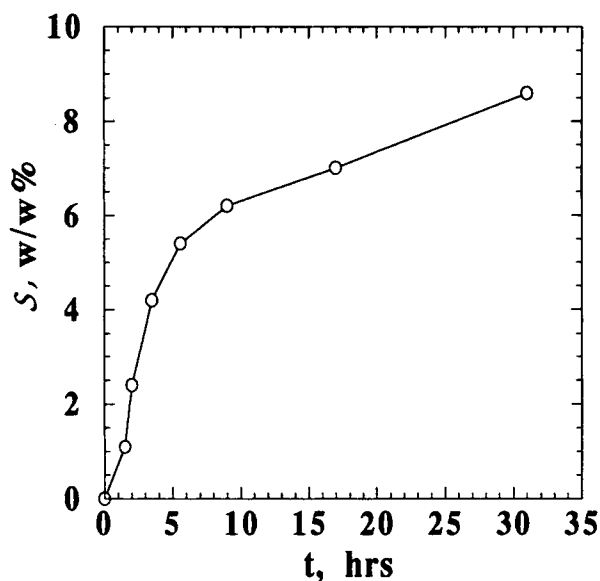
| Chemical Shift, Relative to 85% $\text{H}_3\text{PO}_3$ (ppm) | Percent | Assignment   |
|---|---------|--------------|
| 108.6   | 53.8    | DTPANa       |
| 84.8  | 7.9     | BTPD         |
| 82.7  | 11.6    | DTPA         |
| 56.9  | 23.4    | DTPANa, DTPA |
| other   | 3.3     | Unassigned   |

**Characterization of MP**

The modified polymer was characterized by means of the time-dependent progress of its sulfur and chlorine content. The relation between the percent weight of sulfur  $S$  and chlorine  $Cl$  is given in Figure 1. The theoretical relation is shown as a solid line. The experimental points correspond to the theoretical line quite well. Thus, we conclude that each DTPA group displaces one chlorine atom from the polymer. Other reactions such as dehydrochlorination are minor or nonexistent.

The progress of the reaction can be followed by measuring the percent of sulfur as a function of the reaction time. This kind of relation can be seen in Figure 2. The kinetics of the substitution fits at an early stage of the reaction (33% conversion) to a second order reaction that can be described by the following equation:

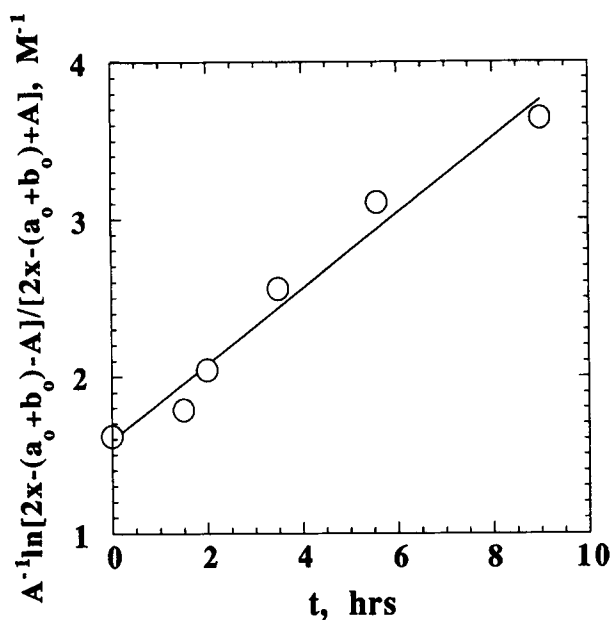
$$dx/dt = k_2(a_0 - x)(b_0 - x) \quad (1)$$

**Figure 1** Relation between the weight percent of chlorine ( $Cl$ , w/w %) and sulfur ( $S$ , w/w %) on the modified polymer.**Figure 2** Content of sulfur on the modified polymer as a function of the reaction time.

where

$$k_2 t = A^{-1} \ln \left\{ \frac{[2x - (a_0 + b_0) - A]}{[2x - (a_0 + b_0) + A]} \right\} \quad (2)$$

Here  $a_0$  is the initial concentration of PVC (0.857 M);  $b_0$  is the initial concentration of DODTC sodium salt (0.429 M),  $x = a_0 S / 16.84$  is the concentration of the substituted PVC;  $k_2$  is the second order rate constant; and  $A = [(a_0 + b_0)^2 - 4a_0 b_0]^{1/2}$ , M.

**Figure 3** Kinetics of the modification of PVC expressed in terms of Eq. (2).

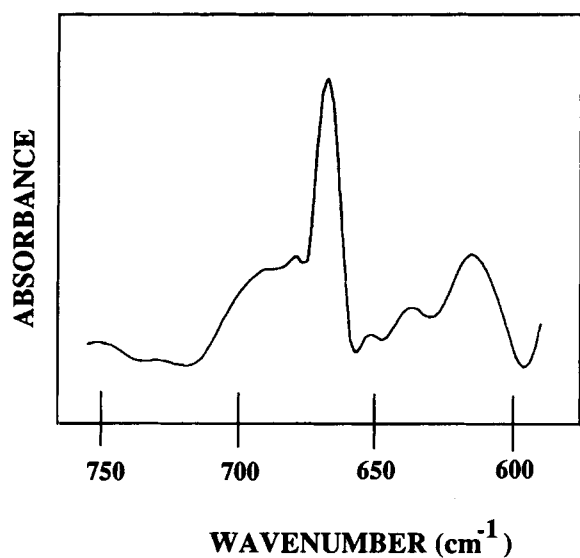


Figure 4 FTIR spectrum of the film composed of MP.

The plot of eq. (2) is given in Figure 3. The second order rate constant was calculated to be  $6.6 \times 10^{-5} M^{-1} s^{-1}$ . Note that the above value is similar to those found by Levin<sup>12</sup> for the substitution of chlorine by various dithiocarbamates on PVC ranged from  $3.7$  to  $11.0 \times 10^{-5} M^{-1} s^{-1}$ .

Figure 4 represents the infrared spectrum of MP (content S 4.1%; P 2.0%; Cl 42.1%). The appearance of the strong peak at  $669 \text{ cm}^{-1}$  corresponding to the P = S antisymmetric stretching<sup>8</sup> can be clearly seen. This peak is absent in the spectrum of unmodified PVC.

NMR spectra were conducted on samples of MP dissolved in THF, separated on fractions by centrifuge, precipitated by D<sub>2</sub>O and methanol, dried, and then dissolved in (CD<sub>3</sub>)<sub>2</sub>CO/CS<sub>2</sub> (1 : 1) mixture. Figure 5 shows a typical 400 MHz <sup>1</sup>H NMR spectrum of a fraction containing: S 1.5%; Cl 52.2%. Comparison with the previously published spectra of

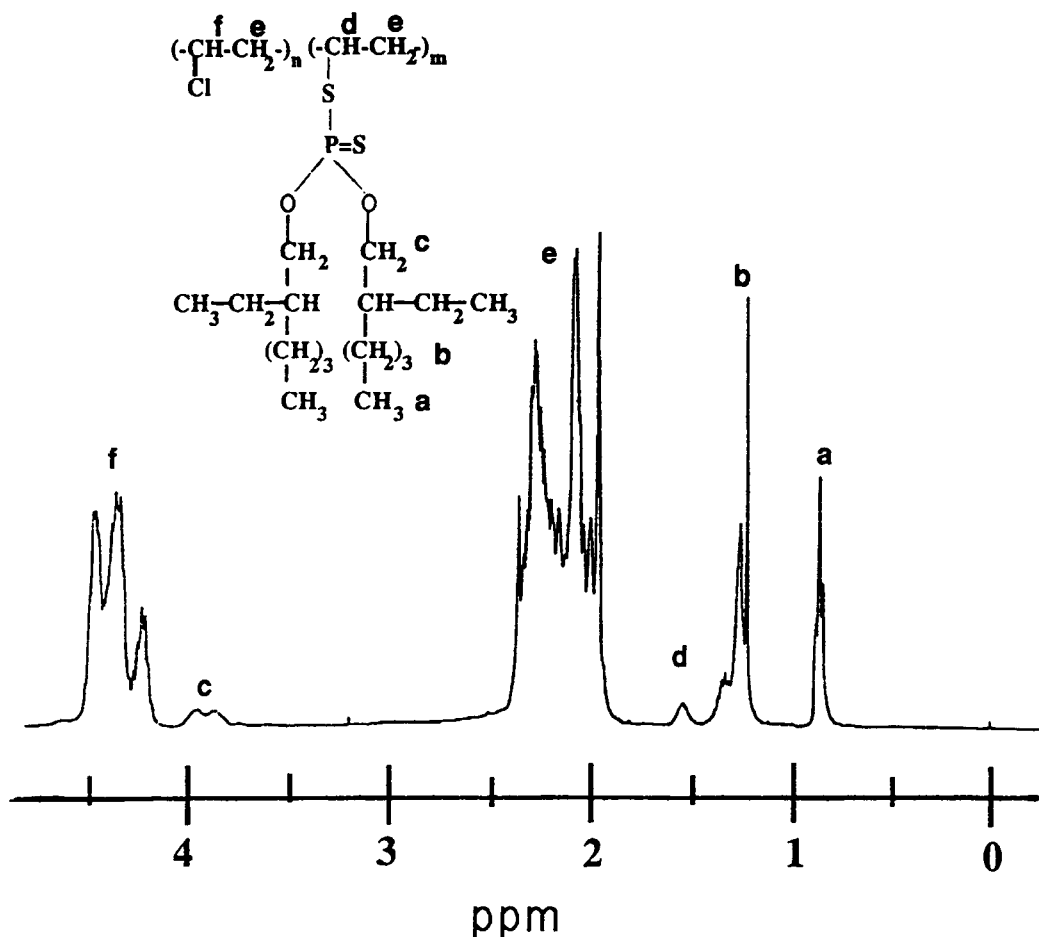


Figure 5 Typical <sup>1</sup>H NMR spectrum of the modified polymer and assignments made for the corresponding protons.

modified PVC<sup>5</sup> allowed the assignments shown in Figure 5 to be made. The pentet centered around 2.0 ppm corresponds to acetone. The obtained ratio of the protons assigned as in Figure 5 a : b : c : d is 3.0 : 5.0 : 0.8 : 0.2, which is in agreement with the calculated ratio 3.0 : 4.0 : 1.0 : 0.2.

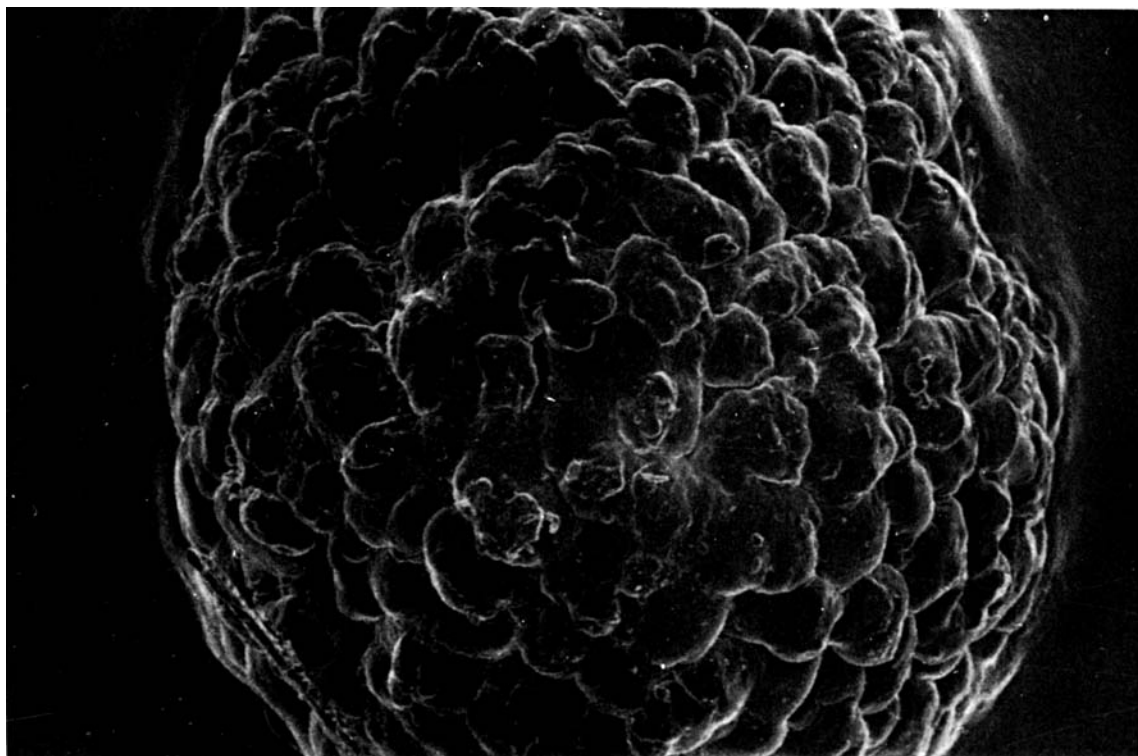
Elemental analysis of the given sample shows that about 1.6% of chlorine-containing groups are substituted by dithiophosphate. Using this value one can calculate the ratio of the protons f : e : d : a to be approximately 1.00 : 2.00 : 0.02 : 0.19. The above ratio found from the NMR spectrum (Fig. 5) is equal to about 1.02 : 2.29 : 0.01 : 0.17. Thus, NMR and elemental analysis fit the expected structure of MP.

### Performance of MP in Metal Ion Separations

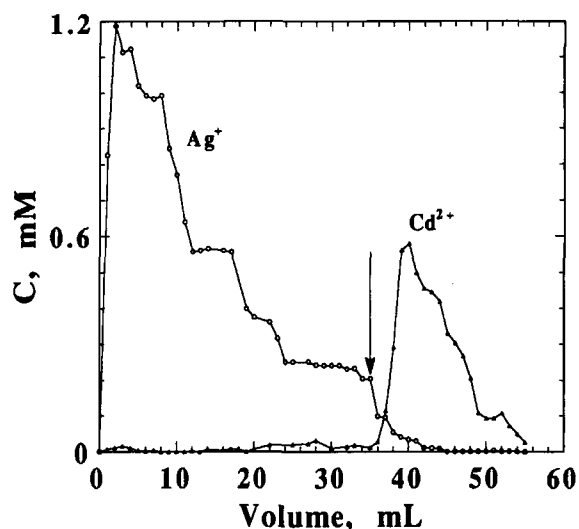
Mixtures of modified polymer and DTPA dissolved in THF or dioxane and then dried, formed homogeneous transparent gelled phases at any ratio between MP and DTPA. However, the external surface of the resultant gels being very hydrophobic in nature (distribution coefficient of DTPA between hexane and water<sup>6</sup> is lower than  $4 \times 10^{-6}$ ) when the gels are placed in water gives strong agglomeration of the gels. To eliminate the bead agglomeration keeping their high capacity, we introduced PVC in

the initial solutions of MP and DTPA, lowering MP concentration. The concentration of the extractant, DTPA, remained constant. The resulting beads possessed round shape with the developed surface (Fig. 6). The diameter of the beads ranged from 0.1 to 1.1 mm depending on the internal diameter of the needle during the extrusion (see Experimental).

In the experiments with the blank material composed of unmodified PVC and DTPA, the beads were dispersed into separated fibrilles and almost entirely lost their ion-exchange capacity after the first extraction-stripping cycle. However, the cation exchange columns containing modified polymer gelled with DTPA and PVC demonstrated the ability to work during 20 or more extraction-stripping cycles without losing their ion selectivity. Ion-exchange capacity of the beads decreased by 20–30% during the first 5–10 cycles and then reached the equilibrium. The content of the beads after 25 cycles was as follows: S, 3–5%; Cl, 42.3–47.5%. The performance of the MP gelled with PVC and DTPA in ion separation is shown in Figures 7–10. The mixtures of the corresponding cations have been extracted into columns and certain cations that form strong neutral or anionic complexes were stripped off preferentially by passing through the bead eluent solu-

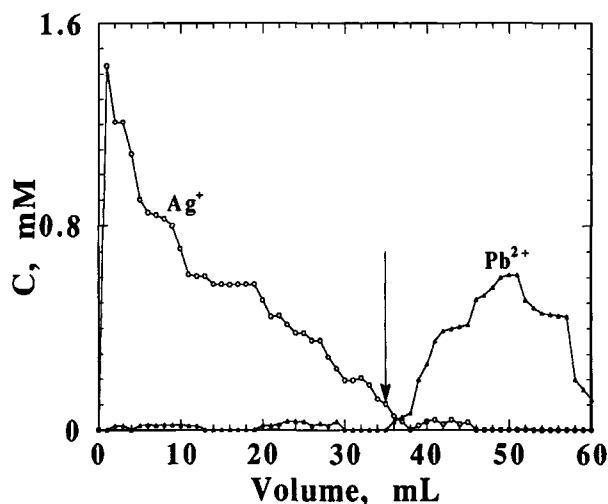


**Figure 6** SEM microphotograph of external surface of a bead composed of MP, PVC, and DTPA. Magnification,  $\times 120$ .

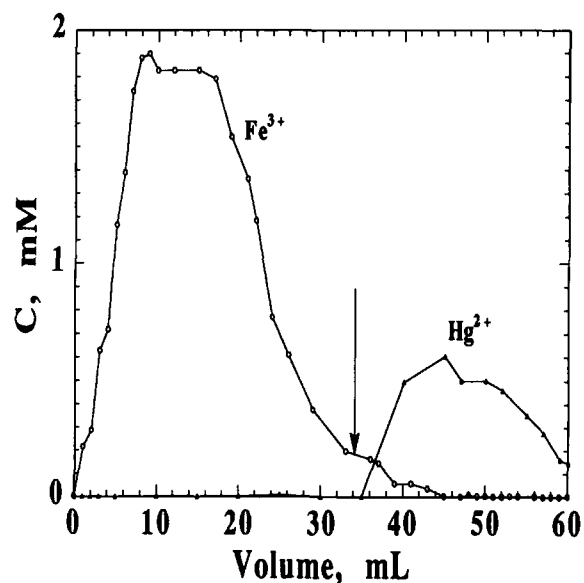


**Figure 7** Stripping of silver and cadmium from the ion exchange column containing beads composed of MP gelled with PVC and DTPA. Beads were presaturated by  $\text{AgNO}_3$  and  $\text{Cd}(\text{CH}_3\text{COO})_2$ . Stripping conditions:  $1\text{M H}_2\text{SO}_4$  saturated by TU (initial);  $9\text{M HCl}$  (after arrow).

tions containing the proper complexing anion. One cation after another could be stripped off by changing an eluent. Thus,  $\text{Hg}^{2+}$ ,  $\text{Ag}^+$ , and  $\text{Cu}^{2+}$  were separated from many other metal ions by stripping with acidic solutions saturated by thiourea. Stripping sequences and conditions were found to be in accordance with the extractability of metals by DTPA and the stability of the corresponding complexes used in the stripping phases (Table II). Note that

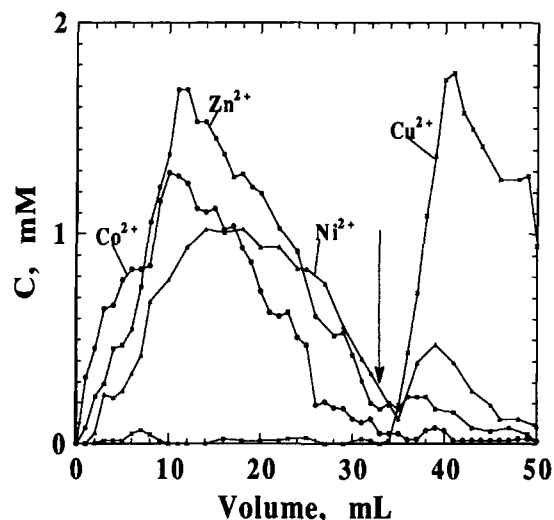


**Figure 8** Stripping of silver and lead from the ion-exchange column containing beads composed of MP gelled with PVC and DTPA. Beads were presaturated by  $\text{AgNO}_3$  and  $\text{Pb}(\text{CH}_3\text{COO})_2$ . Stripping conditions:  $1\text{M H}_2\text{SO}_4$  saturated by TU (initial);  $40\text{ g/L EDTANa}$  (after arrow).



**Figure 9** Stripping of iron and silver from the ion exchange column containing beads composed of MP gelled with PVC and DTPA. Beads were presaturated by  $\text{Fe}(\text{NO}_3)_3$  and  $\text{AgNO}_3$ . Stripping conditions:  $1\text{M}$  oxalic acid (initial);  $1.5\text{M H}_2\text{SO}_4$  saturated by TU (after arrow).

despite the fact that extraction constants of  $\text{Ag}^+$  or  $\text{Hg}^{2+}$  by DTPA are much higher than the stability constant of  $\text{Ag}(\text{TU})_n^+$  or  $\text{Hg}(\text{TU})_n^{2+}$  complexes, silver and mercury were stripped off by  $1\text{--}1.5\text{M}$  sulfuric acid saturated by thiourea (see Figs. 7–9). This phenomenon can be explained by the greater increase of the stripping power of thiourea in the presence of the acid.<sup>13,14</sup>



**Figure 10** Stripping of cobalt, zinc, nickel, and copper acetates from the ion exchange column containing beads composed of MP gelled with PVC and DTPA. Stripping conditions:  $1\text{M}$  sulfuric acid (initial);  $1.5\text{M H}_2\text{SO}_4$  saturated by TU (after arrow).

**Table II Extraction Constants of Metal Ions by DTPA and Stability Constants of Some Stripping Complexes**

| Metal Ion        | Extraction Constant With DTPA Solutions in Octane, <sup>6,17</sup> $\log K_{ex}$ | Complex                              | Total Stability Constant, <sup>15,16</sup> $\Sigma \log \beta$ |
|------------------|--|--------------------------------------|--|
| Ag <sup>+</sup>  | 41.3   | Ag(TU) <sub>n</sub> <sup>+</sup>     | 13.1   |
| Hg <sup>2+</sup> | 40.18  | AgCl <sub>n</sub> <sup>n-1</sup>     | 18.8   |
|                  |  | Hg(TU) <sub>n</sub> <sup>2+</sup>    | > 72   |
| Cu <sup>2+</sup> | 12.30  | Hg(OX) <sub>n</sub> <sup>-2n+2</sup> | < 4  |
|                  |  | Cu(TU) <sub>n</sub> <sup>2+</sup>    | > 15   |
| Fe <sup>3+</sup> | 8.62   | CuSO <sub>4</sub>                    | 2.35   |
|                  |  | Fe(OX) <sub>n</sub> <sup>-2n+3</sup> | 36.4   |
| Pb <sup>2+</sup> | 8.09   | PbEDTA <sup>2-</sup>                 | 18.2   |
|                  |  | Pb(TU) <sub>n</sub> <sup>2+</sup>    | 1.77   |
| Cd <sup>2+</sup> | 7.04   | CdCl <sub>n</sub> <sup>2-n</sup>     | 10.6   |
|                  |  | Cd(TU) <sub>n</sub> <sup>2+</sup>    | 7.1  |
| Ni <sup>2+</sup> | 3.14   | NiSO <sub>4</sub>                    | 2.40   |
| Zn <sup>2+</sup> | 2.25   | ZnSO <sub>4</sub>                    | 2.31   |
| Co <sup>2+</sup> | 0.02   | CoSO <sub>4</sub>                    | 2.47   |

OX, oxalate. EDTA, ethylenediamine tetraacetic acid.

Hence, the MP gelled with DTPA and PVC demonstrates the ability to effectively separate metal ions in the conditions of extraction chromatography.

## CONCLUSIONS

The procedure of preparation of DTPANa by reaction of the parent DTPA with NaH has been reported. The nucleophilic substitution of chlorine by DTPANa on PVC was characterized by the second order rate constant equal to  $6.6 \times 10^{-5} M^{-1} s^{-1}$ . The structure of the obtained MP was characterized by NMR and elemental analysis. The method of preparation of the beads composed of MP gelled with DTPA and PVC to be packed in ion exchange columns was described. Effective separation of metal ions by extraction-stripping procedure was demonstrated.

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