

Synthesis and Characterization of Amide Linkage-Incorporated Polyethyleneimine-Based Chelating Resins and Studies of the Crosslink Density and Surface Properties on Metal Ion Uptake

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SYNOPSIS

The chelating resins incorporating amide linkages were synthesized in open reaction vessels (OV) by polycondensing different proportions, *viz.*, 1 : 1, 1 : 1.3, and 1.3 : 1 of polyethyleneimine (PEI) and diethylenetriaminepentaacetic acid (DTPA), respectively, at 145–155°C, and at varying curing times (15 h and 22 h). For the proportion 1 : 1, the synthesis was performed in a closed reaction vessel (CV) as well. The resins were characterized by FTIR, elemental, and thermogravimetric analysis, apart from sorptometric surface studies. The extent of crosslinking was evaluated by swelling measurements and the chemical stability was assessed by acid and alkali treatment. The effect of the mode of heating and curing times on the extent of crosslinking and pore structure modifications were evaluated. The influence of these factors on the capacities, the kinetics, and the break through curve trends of these resins were studied using zinc and cadmium metal ions as references. The reproducibility of the resins were ascertained by assessing the extent of change in the break through curve trends of their different batches, synthesized under identical conditions.

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INTRODUCTION

An important new class of synthetic multifunctional substrates, with enhanced molecular/ionic recognition,¹ is the chelating ion exchange resins, which, due to their complexing abilities and enhanced selectivities, play important roles in the preconcentration² and separation³ of metal ions from a variety of matrices. Included among these polymers are the promising PEI-based resins,^{4,5} because PEI with low molecular weight per monomer unit provides a high content of functional groups per unit weight. The presence of primary and secondary amino groups allows suitable modifications through polycondensation and crosslinking by simple methods.

Crosslinked PEI resins, obtained from reactions

between PEI and a variety of crosslinking agents, have been reported.^{6,7} Since nitrogen- and oxygen-containing resins are more effective, due to their extended utilities, for a wide variety of metal ions, modifications of PEI resin matrix necessitated a further careful choice from the incorporating groups. The simple introduction of carboxyl functions can be achieved by treating PEI with 4-chloro 2,6-pyridine dicarboxylic acid⁸ and subsequent crosslinking with epichlorohydrin. In this respect, condensation of PEI with other potent groups, as explained in our studies, is another useful pathway to useful modification of PEI.

One of the earlier studies, based on polycondensation, involved an amine–isocyanate reaction, using toluene diisocyanate as the second reactant,⁹ which led to a product with a comparatively low capacity for the metal ions, since the urea linkages formed could not participate in the complexation process. To overcome this drawback, in the present study,

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condensation of PEI with a polyamino polycarboxylic acid [Diethylenetriaminepentaacetic acid (DTPA)] was attempted, keeping in view an earlier report¹⁰ elucidating the use of a dithiocarbamate derivative of polyamine-polycarboxylic acid condensate for uranium recovery. It was predicted that the amide linkages, resulting from the condensation of PEI and DTPA, would also make a contribution toward the total capacity of the resin, thus leading to enhanced metal ion uptakes. This is the genesis of innovative PEI-based chelating resins. The incorporation of amide groups for specific metal ion concentrations has been reported upon earlier,^{11,12} but the synthesis of these polymers, many of them with polystyrene-DVB backbones, is difficult because of additional disadvantages, such as lesser functionalities and steric factors.¹¹

The utilities of ion exchange resins also depend on the extent of crosslinking (rigidity) and suitable surface properties. The need for the controlling these factors are explained by Lieser.¹³ Hence, in order to select the resin with the best possible properties, three different proportions, *viz.*, 1 : 1, 1.3 : 1, and 1 : 1.3, of PEI and DTPA, respectively, were tried. The first combination was attempted under two different conditions, which were the utilization of open and closed reaction vessels (OV, CV) for the synthesis. The other proportions were synthesized in open reaction vessels only.

In this article, apart from the characterization studies, the effect of heating methods and curing time on the extent of crosslinking and the pore structure modifications have been assessed. Their influence on the capacities, kinetics, and breakthrough curve trends has also been evaluated and the reproducibility conditions have been established.

EXPERIMENTAL

Apparatus

Metal ions were estimated using an Elico CL 25 D DC automatic recording polarograph.

Wide-mouthed bottles of 125 mL capacity were used for batch equilibration.

Glass columns (1 ft \times 5 mm i.d.) were used for column operations.

Reagents and Materials

A 50% aqueous solution of PEI (*M*, 6 lakh – 10 lakh) and 99% DTPA were Fluka products. ZnSO₄

\times 7 H₂O (AR grade) and 3 CdSO₄ \times 8 H₂O (Fluka) were used for preparing standards.

Buffer solutions were prepared from sodium acetate and acetic acid of AR grade. KCl for maintaining the ionic strength and as a supporting electrolyte for metal ion estimations was of AR grade. Deionized water was utilized for preparing all the solutions.

Resin Synthesis

The syntheses of the resins were based on an earlier report¹⁰ and a suitably modified procedure, adapted here, is detailed below:

Chelating resins, of proportions 1 : 1, 1 : 1.3, and 1.3 : 1 (by weight), of PEI and DTPA were prepared by homogenizing DTPA as slurries with aqueous PEI solutions, taken in the appropriate ratios. The resulting, slightly viscous solutions were heated in reaction vessels, between 145–155°C, in a hot oven with occasional stirring and the heating was continued until the initial formation of pale yellow solid condensates. They were then cured for 15 h at the reaction temperature to get brownish yellow masses as final products. The resin, with equal proportion of the reactants, was synthesized under a closed condition also, by leaving just the beak gap open, and the occasional stirring was stopped after the attainment of complete homogenization, which occurs normally within the initial 30–45 min of the heating process. The resins obtained were washed with hot, double-distilled water, to remove unreacted materials, were dried, were grained, and were sieved to obtain resin particles of 60–100 mesh. In order to correlate the relationship between the physical structures and the utility of these resins, the curing time was increased to 22 h and the effect on the metal ion uptake was studied.

CHARACTERIZATION OF THE RESINS

IR, TGA Studies and Elemental Analysis

The functional groups present were identified by IR (FT) spectral studies. The spectra of the samples were recorded using a Perkin-Elmer instrument (1760) in the region of 60–4000 cm⁻¹ in KBr pellets.

The resins were subjected to thermogravimetric analysis in a Stanton Redcroft Thermal Analyser (STA—780 series) in the temperature range 100–400°C with a heating rate of 10°C/min in nitrogen atmosphere.

Elemental analysis was performed using a Heraeus CHN—O— Rapid Analyser for the estimation of carbon, nitrogen, and hydrogen percentage contents.

Swelling Behavior¹⁴

Samples of the resins were allowed to stand in deionized water for 48 h. The resins were then filtered by mild suction for 1 min and were pressed gently between filter papers to remove the surface moisture. Weighed amounts of the above swollen resins were then dried at 100°C for 48 h and were reweighed to determine water regaining values. Triplicate measurements were carried out for confirmation.

Chemical Stability

Resin stabilities in acids and bases were tested by equilibrating resin samples with 10 N HCl, 0.5 N NaOH, and 4 N aq NH₃ for 7 days. The loss in N₂ content was estimated and considered to be a measure of chemical stability.

Surface Properties

The nature of pores and their size distribution, along with specific surface area and pore volume, were characterized sorptomatically, using a Carl Erba Instrumentazino instrument. The porosities of the dry resins were calculated from the apparent density and pore volume values,¹⁵ using the formula

$$P_o = \left(\frac{\rho_m}{\rho_m U_o + 1} \right) U_o$$

where P_o is the porosity, ρ_m is the apparent density, and the U_o is the specific pore volume.

When the pore structure pattern is not well pronounced, as is especially evident in the case of 1 : 1.3 and 1.3 : 1 [15 h cure; Fig. 1 (e, g)], which show broad pore structures with considerable discontinuity, in order to give a true picture of pore size range we have represented it in terms of the relative percentage of a different class of pores (micro, meso, and macro) in the entire pore spectrum, calculated from the percentage contribution of pore volume at each pore size region. In this way it is possible to assess the relative magnitude of different pore size ranges. A similar method can be adapted for all of the resins.

EQUILIBRATION STUDIES

Batch Process

Measurement of Total Capacity

A 0.1 g sample of the resins were equilibrated with Zn²⁺ and Cd²⁺ ions in 50 mL solutions of various concentrations, buffered to pH 4.6 with sodium acetate-acetic acid for 24 h. The resins were filtered and the aqueous solutions were estimated polarographically for the metal ion concentrations in order to determine the metal ion uptakes by the resins at each concentration. From this, total capacities were obtained at points where the resins attain saturation limits for the respective metal ions.

The polarogram was run after deoxygenating the test solutions, with KCl as the supporting electrolyte. A well-defined reduction wave was obtained for both metal ions, with $E_{1/2}$ values of -0.61 V for cadmium and -1.1 V for zinc.¹⁶ The concentrations of the metal ions left in the aqueous phase were calculated from their diffusion current values, using a calibration curve, drawn for known concentration, against the diffusion current.

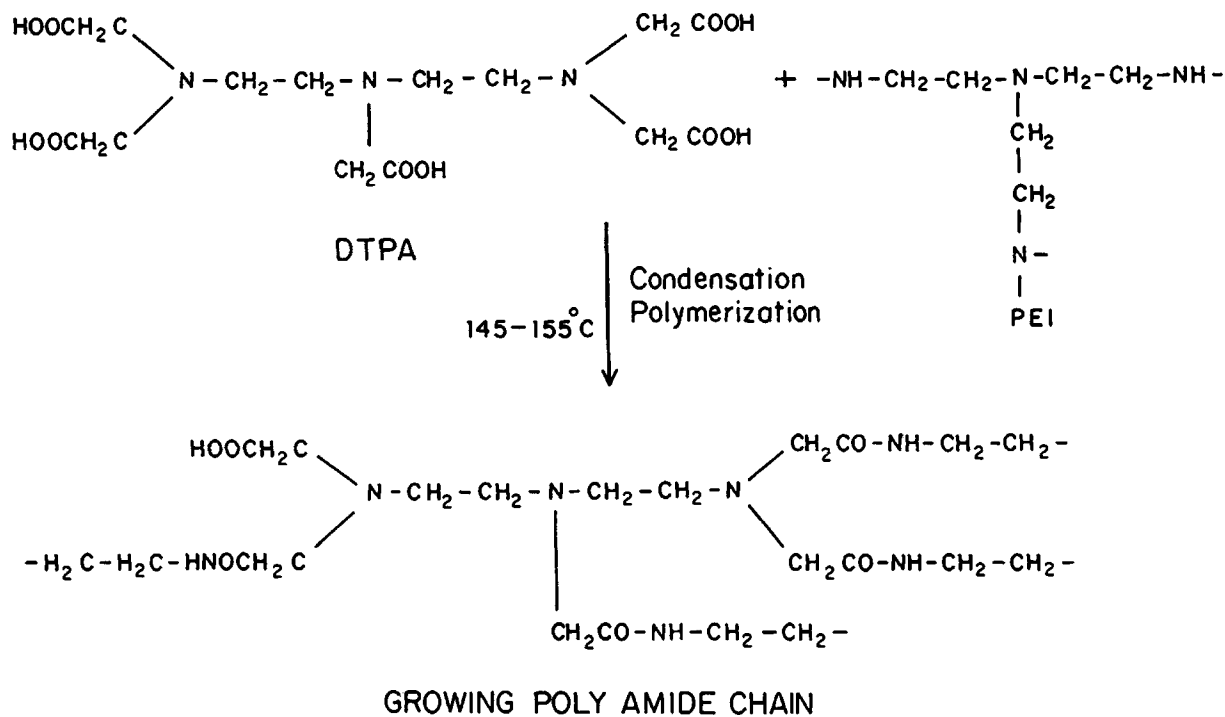
Kinetic Studies

The $t_{1/2}$ values were measured for each resin by equilibrating them with metal ion solutions of a concentration that was double their capacities, in a series of equilibration bottles, each meant for a particular time interval. The metal ion uptakes of the resins were determined at different intervals to arrive at the $t_{1/2}$ value, that is, the time needed for half saturation of the total resin capacity. The net volume of the metal ion solutions and the pH maintained were the same as before.

Column Operation

Breakthrough Studies

One gram of each of the swollen resins was loaded on a filter paper-supported glass wool, in columns of 0.5 mm i.d. and 30 cm in length. The resins were washed twice with the buffer medium at a rate of 1 mL/min. Solutions, containing 0.2 mg of metal ions/mL, were passed through the columns at a flow rate of 1 mL/min. The effluents were collected in 10 mL fractions and were tested for the presence of the metal ions. Breakthrough curves were plotted from the points where the detection of metal ions through the resin beds (breakthrough volume) were observed.



Scheme 1 Resin synthesis.

The effect of flow rates on column behavior was determined by changing the flow rates of the influents from 1 mL/min to 2 mL/min; the breakthrough curve studies were repeated.

RESULTS AND DISCUSSION

Scheme 1 shows the reaction involved in the preparation of the resins. The first batch of resins was cured for 15 h at the reaction temperature. The condensation of the primary amino group of PEI, and the carboxylic groups of DTPA, results in the formation of amide linkages. This type of polyamino-

polycarboxylic condensation leads to a three-dimensional network through intercrosslinking. The percentage yield (Table I) varied from 67–77, with the 1.3 : 1 proportion producing the minimum and the 1 : 1 OV proportion producing the maximum, leaving behind 1 : 1 CV and 1 : 1.3, with 72% and 71.5%, respectively.

Effect of Closed Heating

The closed heating method, adapted in this work, requires an extended reaction time for polymerization, but the yield is about 5% lower than the OV method. This may be due to continuously existing,

Table I Percentage Yield, Nitrogen Content, and End Group Analysis (—COOH)

Resin Proportion	Percentage Yield	Nitrogen Content (%)	Carboxylic Content (% Equivalents per 10 ⁶ Gram Resin)
1 : 1 OV	77.0	15.86	1650
1 : 1 CV	72.0	16.44	1560
1 : 1.3	71.5	15.40	2800
1.3 : 1	67.0	16.57	1530

(OV) Open reaction vessel condition.
(CV) Closed reaction vessel condition.

relatively high vapor pressure, which restricts the molecular motion and thereby, to some extent, prevents the free and random choice of reaction sites needed for high conversion. Further, stopping the occasional stirring after thorough homogenization also aids the nonrandomization, and these factors produce a high order of uniformity in the pore size [Fig. 1(c)], consequently increasing the chemical (Table II) and thermal stabilities (Fig. 2). Hence, this method is useful for the synthesis of polymer-based supports, especially of the polycondensate types, where a nonuniform pore structure is more probable for critical separations involving size exclusions in column chromatography.

IR AND ELEMENTAL ANALYSIS

The resins show characteristic IR peaks (Fig. 3) for the amide groups, the most prominent of these bands being the 3350–3450 cm^{-1} , which is a broad band that is due to the N—H stretching vibration of the secondary amide; the 1650 cm^{-1} amide I band is principally associated with the carboxyl stretching vibration and the 1300–1350 cm^{-1} amide II band for a mixed vibration by C—N stretch and N—H bend.

From the elemental analysis (Table I), it is inferred that the nitrogen content of the resins varies from 15.4% (1 : 1.3 proportion) to 16.57% (1.3 : 1 proportion). In the latter case, the higher proportion

of PEI involved in the reaction results in higher nitrogen content.

SWELLING BEHAVIOR AND STABILITY FACTORS

Resins of equal proportions, of both the CV and OV methods, produce highly crosslinked matrices and showed low water uptakes. The water uptakes are considerably higher for the resins of 1.3 : 1 and 1 : 1.3 proportions, which shows that the resins in increased amounts of either of the reactants produce a lesser degree of crosslinking. Since, however, in the case of 1.3 : 1, there is a considerable extent of macropores, the possible contribution to the water uptakes also has to be considered.¹⁷ Thus, the actual extent of crosslinking may possibly be higher with this proportion. Supporting evidence is obtained from the proportion's comparable thermal and chemical stabilities. The exceptionally good thermal and chemical stabilities of 1 : 1 CV is due to the more ordered structure, apart from high crosslinking.

All the resins withstood temperatures up to 230°C (Fig. 2) without any major weight loss. The thermogram reveals four distinct stages of weight loss. The slight loss at weight *a*, below 110°C, is due to the removal of moisture, including the coordinated water molecules¹⁸ and the weight loss *b*, between 110–205°C, is due to slow condensation, since the

Table II Chemical Stability

Medium	Resin Proportion	Actual Nitrogen Content (%)	Nitrogen Content after Equilibration ^a (%)	Loss in Nitrogen Content (%)
10 N HCl	1 : 1 OV	15.86	15.86	—
	1 : 1 CV	16.44	16.45	—
	1.3 : 1	16.57	16.57	—
	1 : 1.3	15.40	15.41	—
4 N aq. NH ₃	1 : 1 OV	15.86	15.85	0.063
	1 : 1 CV	16.44	16.43	0.061
	1.3 : 1	16.57	16.57	—
	1 : 1.3	15.40	15.35	0.324
0.5 N NaOH	1 : 1 OV	15.86	15.53	2.081
	1 : 1 CV	16.44	16.35	0.547
	1.3 : 1	16.57	16.23	2.052
	1 : 1.3	15.40	14.43	6.201

(OV) Open reaction vessel condition, (CV) closed reaction vessel condition.

^a Equilibration for a week.

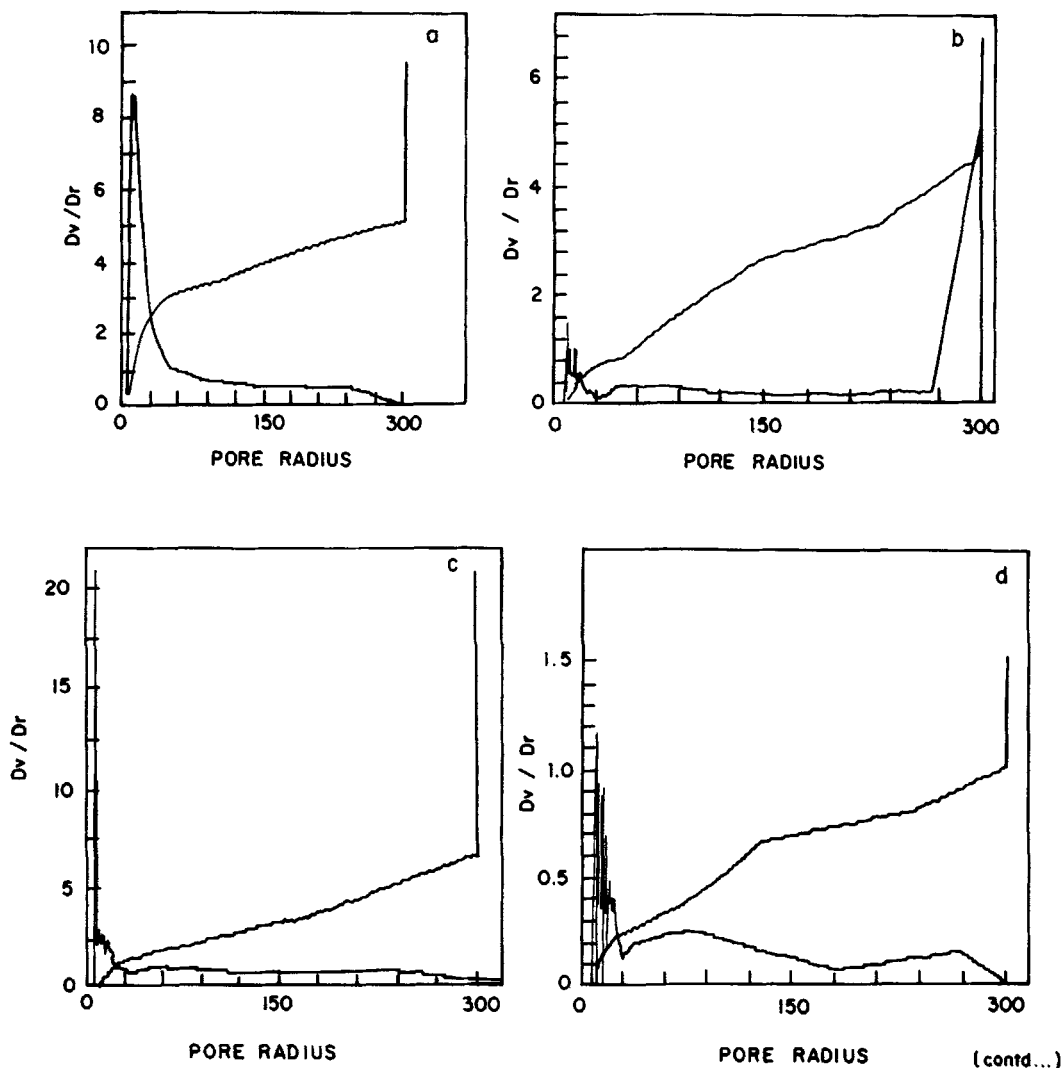


Figure 1 Pore size distribution and cumulative pore volume: (a) 1 : 1 OV 15 h cure, (b) 1 : 1 OV 22 h cure, (c) 1 : 1 CV 15 h cure, (d) 1 : 1 CV 22 h cure, (e) 1 : 1.3 15 h cure, (d) 1 : 1.3 22 h cure, (g) 1.3 : 1 15 h cure, and (h) 1.3 : 1 22 h cure.

end groups on the polymer can react upon further heating. This is similar to that of the postpolymerization of polyoxyamides¹⁹ during the thermal analysis. This process, however, is presumably less marked beyond 160°C. The weight loss *c*, which is due to decarboxylation²⁰ of the free carboxylic groups, is higher for 1 : 1.3 proportion and it begins at 205°C, becomes augmented from 235°C onwards, and possibly goes up to 310°C. For other resins, the weight loss due to decarboxylation is less and it follows the same pattern of decomposition as in the case of 1 : 1.3, but with lesser magnitude. The presence of a greater number of free carboxyl groups, in the case of the 1 : 1.3 proportion (Table I), estimated

by titrimetry in presence of benzyl alcohol,²¹ can account for the overall increased weight loss due to decarboxylation. The considerable weight loss beyond 310°C is due to the loss of various decomposition products, as reported in the case of nylon²² and aliphatic derivative polyamides from diisindoline.¹⁸

High stabilities (Table II) are exhibited by all the resins in strong acid (10 N HCl) and weak base (4 N aq NH₃), but the stabilities are slightly less in a strong base (0.5 N NaOH). The resin of proportion 1 : 1.3, due to its low crosslinking, shows enhanced dissolution in a strongly basic medium, leading to a slightly higher loss in nitrogen content.

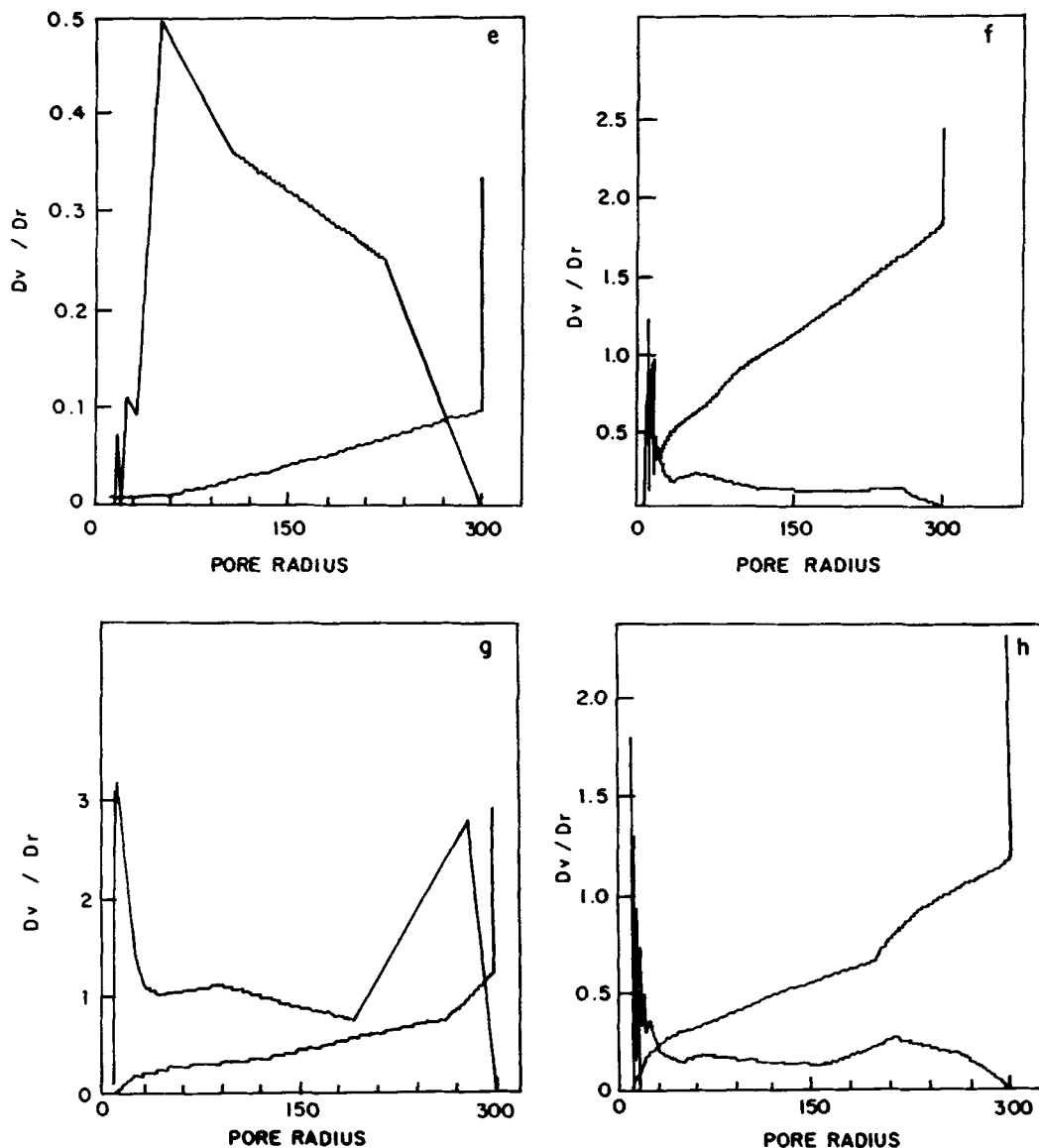


Figure 1 (Continued from the previous page)

Comparing the 1 : 1 OV and 1.3 : 1, the mere arithmetical difference of loss in nitrogen content is misleading when accounting for the stability factor, as the former shows a slightly higher percentage loss in nitrogen content than the latter. This is due to the fact that the percentage of amide content is supposed to be higher in the case of 1 : 1 OV, as it produces the highest yield and, hence, the actual percentage loss might have been much lower than 1.3 : 1, which produces the lowest percentage yield. The higher crosslinked nature of 1 : 1 OV, deduced from swelling measurements and its high surface area value, supports this fact.

SURFACE PROPERTIES

The resins exhibit varied pore structures. The 1 : 1 CV produces a highly uniform pore structure [Fig. 1(c)] of high order of microporosity, with a fraction of meso- and macropores, and the presence of over 50% of the micropores, which constitutes an average radius of $\sim 6\text{--}7 \text{ \AA}$, which might have resulted in a low monolayer volume adsorption of nitrogen gas and is the cause for its low surface area value. The resin 1 : 1 OV shows mainly a microrecticular network [Fig. 1(a)] with a fraction of meso- and macropores with high surface area (Table III).

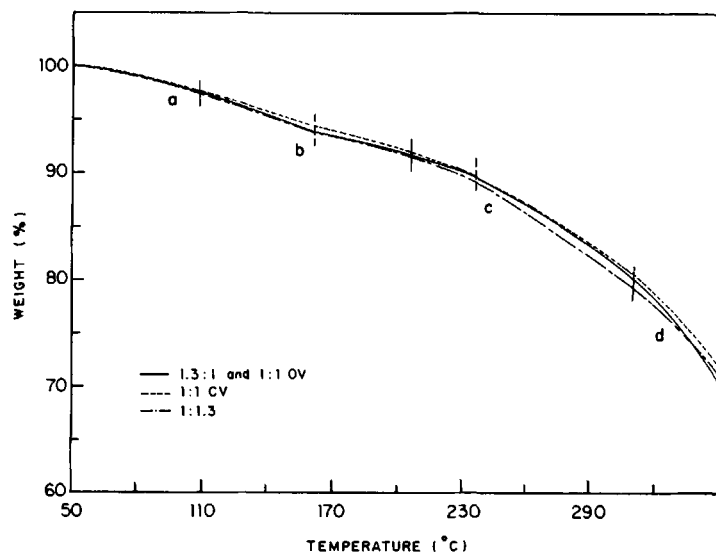


Figure 2 TGA thermogram analysis of the resins cured for 15 h (nitrogen atmosphere).

The increased proportion of PEI results in a microreticular structure, but with a considerable number of macropores [Fig. 1 (g)], which accounts for its high pore volume (Table III). The resin with a higher DTPA content produces a mesoreticular structure [Fig. 1 (e)], with a small fraction of macropores, and shows decreased surface area and pore volume. The decreased pore volume of the latter is due to poor pore formation. Only a few points are found in the entire pore spectrum (up to 300 Å in radius). Moreover, since the pore size distribution is presented as the percentage pore volume contri-

bution of each class of pore structure (micro-macro), its lower specific pore volume, with fewer pores, causes each class of pores in the spectrum to be unduly significant, thus presenting a higher percentage of macropores when compared with other resins.

EQUILIBRATION STUDIES

Batch Process

All the resins have similar capacities for zinc and cadmium ions (Fig. 4). The $t_{1/2}$ values [Fig. 5 (a)] are also the same in all cases, with a slightly faster rate for cadmium ions. However, the values are dependent on the extent of crosslinking, as is explained below.

Column Behavior

A decreased flow rate is found to affect the column behavior positively, because nearly double the breakthrough volume [Fig. 6 (a, b, c, d)] is observed when the flow rate is reduced from 2 mL/min to 1 mL/min in the case of zinc. For cadmium ions, however, which have a higher affinity and higher breakthrough volumes, the difference is not as high. The breakthrough curve studies are vital to demonstrate the high accessibility of the resins, because, although they vary in the extent of crosslinking and pore structure patterns, and exhibited different surface areas with different proportions of PEI and

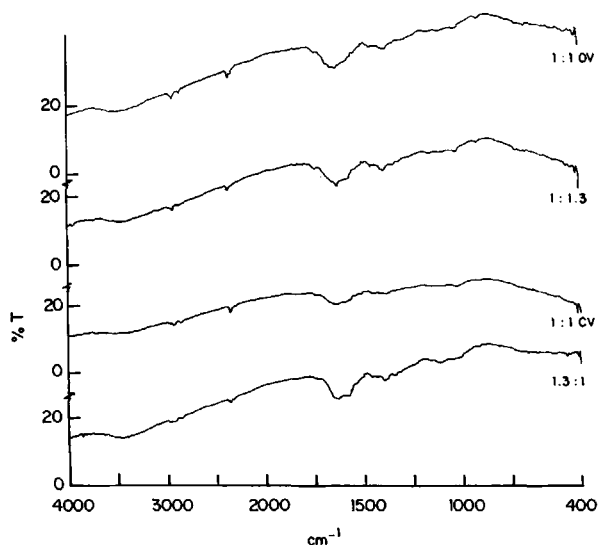


Figure 3 FTIR spectrum of the resins cured for 15 h.

Table III Pore Structure Characteristics of the Resins

Parameters	CT (h)	Resin			
		1 : 1 OV	1.1 CV	1 : 1.3	1.3 : 1
Specific surface area m ² /g	15	218.00	45.98	30.30	55.54
	22	7.67	13.46	11.34	13.81
Radius at maximum pore volume Å	15	11.00	7.70	66.00	11.00
	22	300.00	12.60	12.00	11.40
Relative % of different classes of pores	15	89.130 ^a	93.790 ^a	0.073 ^a	74.28 ^a
		10.630 ^b	6.207 ^b	76.554 ^b	16.00 ^b
		0.236 ^c	0.674 ^c	18.180 ^c	8.00 ^c
	22	48.952 ^a	72.68 ^a	79.05 ^a	79.96 ^a
		16.703 ^b	25.94 ^b	19.88 ^b	21.59 ^b
		34.340 ^c	1.38 ^c	1.06 ^c	1.44 ^c
Specific pore volume (Cm ³ /g)	15	0.557	0.52	0.233	0.684
	22	0.080	0.07	0.06804	0.108
Total porosity	15	0.202	0.1649	0.0687	0.2135
	22	0.043	0.0380	0.0266	0.0489
Apparent density (g/m ³)	15	0.450	0.385	0.325	0.397
	22	0.525	0.455	0.402	0.477
Water regain capacity (%)	15	51	58	85	82
	22	32	36	45	33

(CT) Curing time, (OV) open reaction vessel condition, (CV) closed reaction vessel condition.

^a Micro (< 20 Å).

^b Meso (20–250 Å).

^c Macro (> 250 Å).

DTPA, the breakthrough volumes were found to be almost the same in the case of 1 : 1 OV, 1 : 1.3, and 1 : 1 CV (Fig. 6 (a, b, d)). Among these, a slightly decreased breakthrough volume is observed in the case of 1 : 1 CV, which claims, for the minimum requirement of average pore radius for the metal ions studied, to gain considerable breakthrough capacity, since rigidity cannot be the factor because a slightly higher water uptake than for OV resin is observed. Moreover, as the hydration of high order micro spheres, which are bound together, restricts the expansion of the structure, a major portion of the pore structure retains a relatively constant pore diameter as fully hydrated resins are used in column studies. In the case of macropore 1.3 : 1 ratio resin, a low breakthrough volume is observed [a $\frac{1}{3}$ decrease; Fig. 6(c)], which is due to the presence of a considerable number of oversized pores. Also, the greater chance of having macropores above a 300 Å

radius, due to the limitation of the desorption studies, should be considered here, as with only this resin there is a considerable and sudden increase in pore volume toward macropores when the distribution passes through mesopores. The ease of complex formation, based on the structural pattern, is presumed to be more or less the same with all these resins, since all the proportions exhibited almost the same capacities and $t_{1/2}$ values [Figs. 4 and 5(a)].

Effect of Curing Time

An increase in the curing time from 15 h to 22 h shifts the pore structure toward the microreticular side for all the resins [Fig. 1(b, d, f, h)], except the 1 : 1 OV resin, which shows significant nongel porosity [Fig. 1(b)]. This shift is possibly due to the high-order, macroreticular nature before curing, as compared with the microreticular form produced in

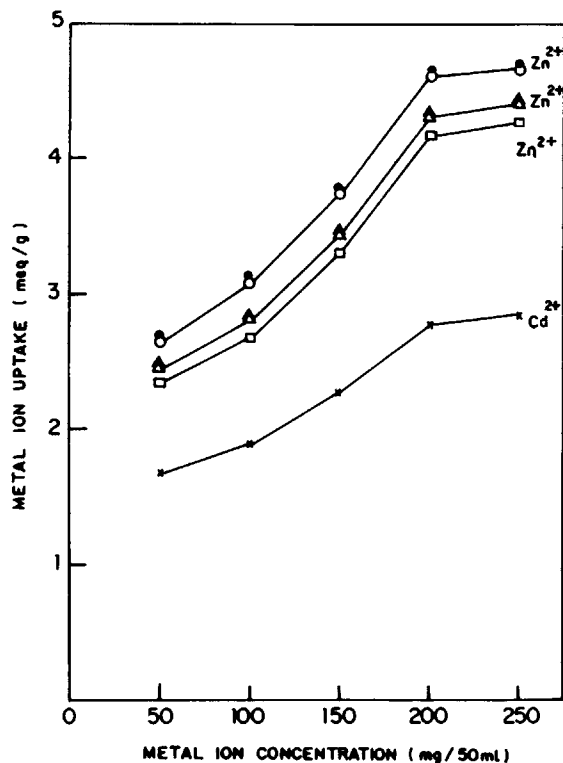


Figure 4 Capacity of the resins for zinc and cadmium metal ions: (O) resins of all proportions of 15 h cure, (●) 1 : 1.3 22 h cure, (Δ) 1 : 1 CV 22 h cure, (▲) 1.3 : 1 22 h cure, (□) 1 : 1 OV 22 h cure, and (×) resins of all proportions of 15 h cure.

the first batch resin cured for 15 h. This factor predictably creates uncertainty in the pore structure formation during the resin synthesis. However, a considerable decrease in surface area and pore volume (Table III) is common for all the resins. Apart from this, the enhanced curing time causes the resin matrix to be more rigid, which consequently decreases the water uptake. Because of these factors, the capacity decreases (Fig. 4) and, more important, the rate of chelation is appreciably slowed down [Fig. 5(b)]; this causes a considerable decrease in breakthrough volumes (Table IV) with 1 : 1 OV, 1 : 1 CV, and 1.3 : 1 resins, with respect to zinc ions employed for comparison purposes. Unlike other resins, the resin of 1 : 1.3 shows comparable capacity (Fig. 4), kinetics [Fig. 5(b)], and breakthrough volume (Table IV, batch II resins), since the rigidity factor or the water uptake level was not as much affected in this case. This result is because the resin might have reached a comfortable saturation limit for the extent of crosslinking, as repeated batches (III and IV), prepared at the enhanced curing time, showed reproducible breakthrough volumes (Table IV).

CONCLUSIONS

The observations clearly emphasize the need for a minimum requirement of surface area, pore volume, and average pore radius to obtain convincing capacity values and fast kinetics, but, considering the rigidity of the resin matrices, more careful control of the curing time is necessary.

Since the reproducibility of the pore structure pattern is not fully dependable in this type of polycondensation, the resin, with the proportion 1 : 1.3, is more reliable and yields better advantages than other proportions, as it shows comparable breakthrough volumes, regardless of curing time variation and surface modifications. This resin is also cost effective, even if a slight compromise has to be made due to the decreased percentage yield. Moreover, its lower stability in a strong base (0.5 N NaOH) can be avoided, since a weak base, such as aq NH_3 of 4 M concentration, is more suitable for

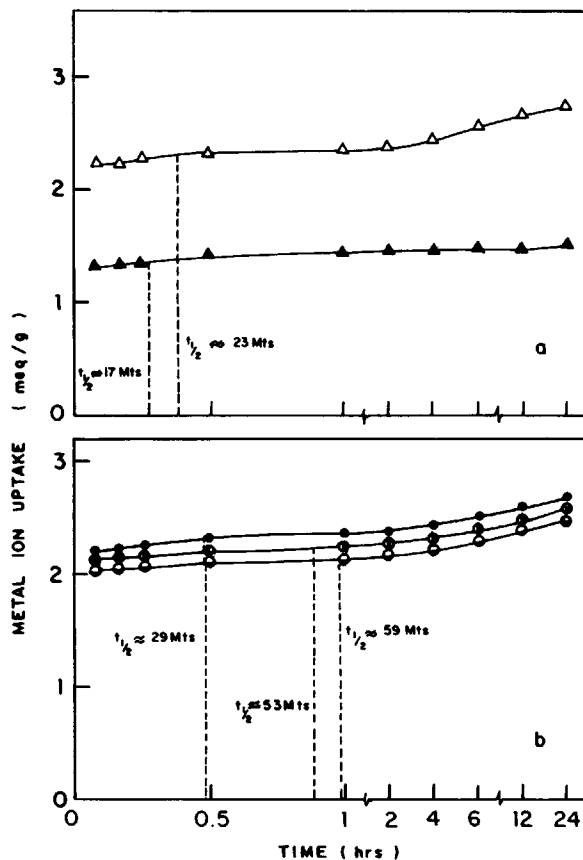


Figure 5 (a) Kinetics; (Δ) resins of all proportions of 15 h cure for Zn^{2+} metal ion, (▲) resins of all proportions of 15 h cure for Cd^{2+} ion. (b) Kinetics; 22 h cured resins for Zn^{2+} metal ion, (●) 1 : 1.3, (○) 1 : 1 CV, (×) 1.3 : 1, (⊙) 1 : 1 OV.

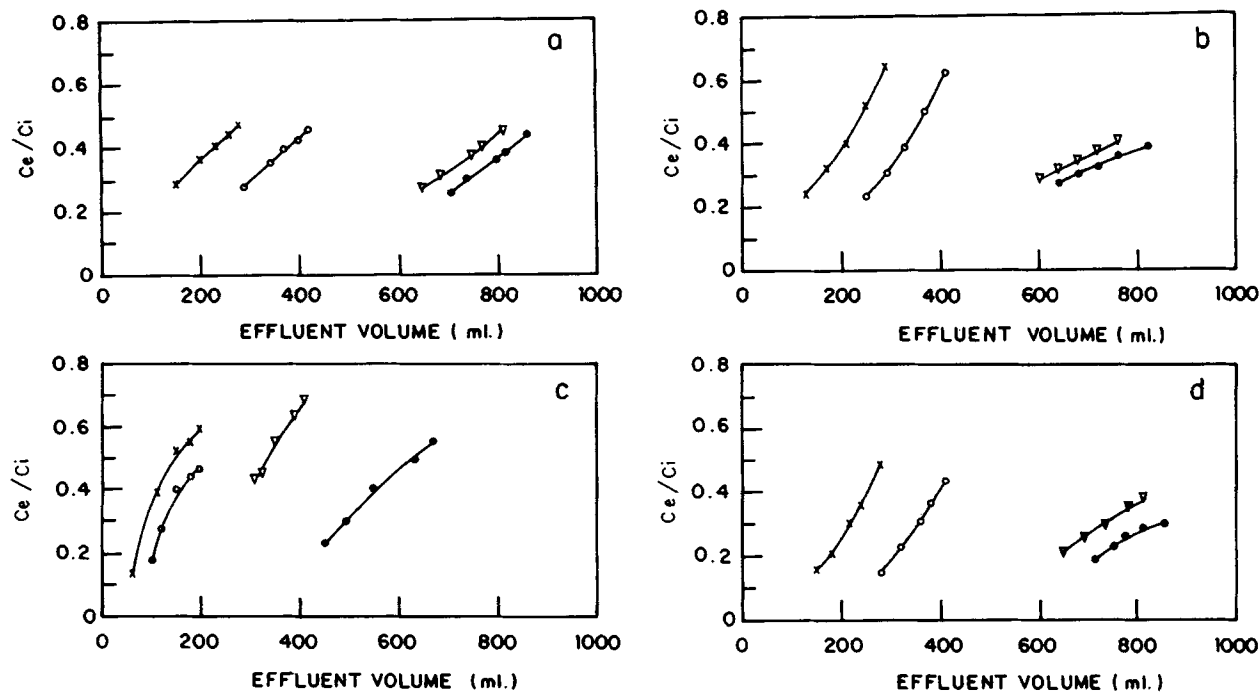


Figure 6 Breakthrough curves of 15 h cured resins (a) 1 : 1 OV, (b) 1 : 1 CV, (c) 1.3 : 1, (d) 1 : 1.3; (X) for Zn^{2+} at a flow rate of 2 mL/min, (O) for Zn^{2+} at a flow rate of 1 mL/min, (Δ) for Cd^{2+} at a flow rate of 2 mL/min, (\bullet) for Cd^{2+} at a flow rate of 1 mL/min. Concentration of the metal ion: C_e = effluent, C_i = influent.

neutralization after acid treatment of the resin for elution purposes.

While the high order microgellular network is noncompatible, due to diffusion limitations, the use

of a macroporous resin (1.3 : 1, 15 h curing time), though less effective for smaller ions, is more useful when larger ions, such as CrO_4^{2-} are involved (unpublished results).

Table IV Comparison of Breakthrough Volume Based on Curing Time and Reproducibility Factor^a

Batch	Resin Proportion	Breakthrough ^b Volume in mL
I ^c	1 : 1 OV, 1 : 1.3	270
	1 : 1 CV	250
	1.3 : 1	90
II ^d	1 : 1.3	230
	1 : 1 CV	110
	1 : 1 OV, 1.3 : 1	90
III ^d	1 : 1.3	240
	1 : 1 OV	90
IV ^d	1 : 1.3	240
	1 : 1 OV	90

(OV) Open reaction vessel condition, (CV) closed reaction vessel condition.

^a Compare the breakthrough volume of I, III, and IV batch resins with II batch.

^b For zinc metal ion at a flow rate of 1 mL/min.

^c 15 h curing time.

^d 22 h curing time.

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