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### Syntheses of some Terpolymer Resins and Studies on Their Structure and use as Cation Exchangers

Senay Taşçıoğlu<sup>a</sup>

<sup>a</sup> Department of Chemistry, Gazi University Faculty of Art and Science, Teknikokullar, Ankara, Turkey

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# **SYNTHESES OF SOME TERPOLYMER RESINS AND STUDIES ON THEIR STRUCTURE AND USE AS CATION EXCHANGERS**

SENAY TAŞÇIOĞLU

Department of Chemistry  
Gazi University Faculty of Art and Science  
Teknikokullar, 06500 Ankara, Turkey

## **ABSTRACT**

Terpolymer resins have been synthesized by the condensation of various phenols, aldehydes, and amino acids. The dependence of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  exchange capacities on the natures of the monomers, pH, and regeneration has been studied and is discussed. Studies have been made to elucidate the structures.

## **INTRODUCTION**

The syntheses of phenol–formaldehyde resins are based on the Lederer–Manasse reaction (1894) [1, 2]. The hydroxymethyl derivatives of phenol formed by this reaction are linked to each other by methyl linkages with the elimination of water between the methylol group of one molecule and the ortho- or para-hydrogen of another molecule. The extent of hydroxymethylation and polymerization, and so the properties of the resulting resin, is based on the reaction conditions, especially on the phenol:aldehyde molar ratio. Decreases in this ratio lead to polymers with more rigid structures. With excess formaldehyde and in the presence of an acid or base as a catalyst, a three-dimensional polymer is formed [2, 3].

It is possible to insert another kind of molecule in this structure; e.g., a primary or secondary amine by the Mannich reaction (1917) [3–8]. Thus, triple polymers can be synthesized. Amino acids can be used as amino compounds. There

is some evidence from the mechanism of this reaction that hydroxymethyl derivatives of amino acids formed by their reaction with formaldehyde condense with phenol compounds via methylene bridges to form terpolymers [3, 4, 6, 9-16].

Phenol-formaldehyde resins can function as cation exchangers via the phenol groups in their structure, but their exchange capacities are not good enough for them to be used commercially [2-4]. Insertion of amino acid molecules in their structure leads to increases in exchange capacities because the carboxyl groups of amino acids also function as cation exchangers and contribute to the exchange process.

There are some studies on the reactions between some phenols and aldehydes [17-21]; amino acids, amines, and aldehydes [9, 15, 22-25]; and amino acids and phenols [10, 26, 27]. Fewer studies have been reported on their triple reactions, and only a few of the resulting terpolymer resins have been analyzed with respect to their cation-exchange capacities [8, 10-13, 19, 28-36].

In this study, terpolymer resins are synthesized, mostly for the first time, by using various amino acids, phenols, and aldehydes in order to see the effect of the natures of the monomers on the cation exchange and other properties of the resulting resins. It is also aimed at synthesizing cation-exchanger resins with better exchange capacities than the phenol-formaldehyde-glycine terpolymer (PFG) suggested previously [28] so that can be used commercially.

## EXPERIMENTAL

### Materials and Apparatus

All the chemicals used were of analytical purity.

Synthesized polymers were ground in a porcelain mortar. A Retsch brand sieve was utilized to separate the particles of selected sizes.

Glass columns of 1 cm diameter and 20 cm length were used in the determination of ion-exchange capacities. Glass wool was placed at the bottom of the columns.

A Linceis Thermowage L-81 type combined DTA-TG Thermal Balance, and Perkin-Elmer IS-599 and Carlo Erba 1106 model instruments were used in connection with thermal degradation, IR, and C, H, N analyses, respectively.

$^1\text{H-NMR}$  spectra were taken by a Bruker Instrument (100 MHz) following approximately 500 scans for the DMSO- $d_6$  soluble parts of the polymers. The internal standard was TMS.

Specific surface area determinations and electron microscopic studies were made by a Model 2200 High Speed Surface Area Analyzer and by a Jeol JSM 840-A electron microscope, respectively.

### Procedures

*Method 1.* A mixture of 47 parts (by weight) phenol, 80 parts formaldehyde (37% solution), and 20 parts amino acid was allowed to stand overnight. Then the mixture was heated at 100°C for 15-30 minutes under reflux. It was then kept at 120-130°C for 1 day [28].

*Method 2.* Phenol, aldehyde, and amino acid were mixed in the same proportions as in Method 1, and heated at 100°C under reflux for 3 hours. The mixture was then kept at 120–130°C for 1 day [11].

The resins were heated to 60°C to remove unreacted aldehyde prior to C, H, N analyses.

*Estimation of Ion-Exchange Ability.* The synthesized polymer was ground, and a given amount of the portion of selected size was put in a column.

The  $Mg^{2+}$  and/or  $Ca^{2+}$  exchange abilities of the resins were studied in order to determine their usability in hard-water treatments. Since we intended to compare the exchange abilities of the resins, they were not allowed to stand in  $Ca^{2+}$  and  $Mg^{2+}$  solutions to estimate their exact exchange capacities. Instead, the solutions were poured on the resins in the columns and the eluates were collected. The amounts of  $Ca^{2+}$  and  $Mg^{2+}$  ions captured by the resins in the columns were estimated by EDTA titration.

Since the synthesized resins were weakly acidic, the ion-exchange processes were performed at neutral and basic pHs (pH 7 and 10).

Regenerations were performed with 4 N HCl. The resins in the columns were allowed to stand in this solution for 5 minutes.

Before every usage, the polymers were rinsed until the eluates became neutral.

## RESULTS AND DISCUSSION

### Determination of Optimum Working Conditions

In order to see the effects of particle size and the method of synthesis on ion-exchange ability, some experiments were carried out with PFG resin. The results are shown in Table 1.

Experiments 1 and 2 were performed by taking into account that the particle sizes of the commercial resins were generally between  $-10+50$  mesh, ideally between  $-40+80$  mesh.

From their results and with the consideration that smaller particles could cause some problems in large-scale studies, it was decided to carry out this research using resins with particles of  $-60+80$  mesh size.

TABLE 1. Effect of Particle Size and Method of Synthesis on Ion Uptake

Experiment no.	Method	Particle size, mesh	Metal ion taken up at pH 7 [(meq/g) $\times 10^2$ ]	
			$Ca^{2+}$	$Mg^{2+}$
1	1	$-35+60$	1.15	2.78
2	1	$-60+80$	1.31	3.10
3	1	$-60+80$	1.32	3.12
4	2	$-60+80$	1.03	2.30

Both Methods 1 and 2 from the literature were used in polymer syntheses. They were compared, and some alterations in their conditions were made to improve them.

The results of Experiments 3 and 4 showed that Method 1 was better relative to Method 2, which required a shorter time, for the synthesis of cation-exchange resins.

We tried to shorten the duration of these methods by increasing their heating times under reflux. An increase in the heating time of Method 1 from 30 to 45 minutes did not provide any improvement in ion-exchange ability of PFG. An additional heating time of 1 hour increased the amounts of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  captured to  $3.5 \times 10^{-4}$  and  $2.5 \times 10^{-4}$  meq/g, respectively, by Method 2.

The effect of the mole ratios of the monomers used in the synthesis of PFG, as a model compound, on ion-exchange capacity was also investigated. In the first set of experiments performed for this purpose, the mole ratios of phenol and formaldehyde were fixed as 1 and 2, respectively, and the mole ratio of glycine was changed. The results obtained are given in Table 2.

It can be seen from Table 2 that an increase in the amino acid mole ratio induces increases in the exchanged ion amounts. This may be due to the increased number of amino acid molecules, i.e., carboxyl groups, involved in the structures of the resins.

Regeneration seems to have a positive effect on the exchange capacities of the resins in Experiments 7 and 8. This can be attributed to the removal of some impurities that bind to the resins more strongly than  $\text{Ca}^{2+}$  ions. On the other hand, the resins synthesized in Experiments 9, 10, and 11 cannot be used as ion exchangers because their regenerations result in decomposition. An explanation we have considered is that resins with low phenol and formaldehyde contents are formed by the insertion of relatively large numbers of amino acids in the structures, and such loose structures may be affected by any acidic hydrolyses of the bound amino acids.

In some additional experiments it was observed that the resin from Experiment 2 was not subjected to any decomposition, even after the fifth regeneration. Thus, it was concluded that a mole ratio of 0.5 for the amino acid monomer is suitable for a synthesis of this kind of ion-exchange resin.

TABLE 2. Effect of Amino Acid Mole Ratio on Ion Uptake

Experiment no.	Glycine mole ratio	Metal ion taken up at pH 7 [(meq/g) $\times 10^2$ ]		
		$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$ <sup>a</sup>
7	0.25	1.01	2.30	1.60
8	0.50	1.35	3.07	1.93
9	0.75	1.40	3.12	<sup>b</sup>
10	1.00	1.61	3.17	<sup>b</sup>
11	1.25	1.63	3.20	<sup>b</sup>

<sup>a</sup>After the first regeneration.

<sup>b</sup>Decomposed.

In the second set of experiments, phenol and formaldehyde ratios were changed and resins with phenol:formaldehyde:glycine mole ratios of 1:1:0.5 and 2:1:0.5 were synthesized. These resins could not be hardened, even at prolonged times of curing, probably because of the formation of novolac-type resins due to the lack of excess formaldehyde in the media.

Thus, optimum monomer ratios were found to be the same as those of Method 1. The rest of the experiments in this study were performed with these mole ratios, but the particle size used was reduced to particles of  $-60 + 80$  mesh.

### Resins with Different Amino Acid Residues

The ion-exchange abilities of some terpolymer resins synthesized by the condensation of phenol, formaldehyde, and different amino acids were compared, and results are given in Table 3. Since an increase in  $Mg^{2+}$  exchange capacities following successive regenerations was observed, the exchanged amounts following the third regeneration are given for  $Mg^{2+}$  in Table 3.

Reference 15 reports that the condensation product of asparagine with  $H_2CO$  is formed in low yields, and that arginine reacts with  $H_2CO$  mainly via its guanidyl group. Products from these amino acids are subject to hydrolysis at moderately acidic pHs. This can be the reason for the decomposition of the terpolymers with asparagine and arginine on regeneration.

Of the synthesized resins, the most effective one seems to be the resin synthesized with aspartic acid. This can be attributed to the higher carboxyl content of this resin due to the extra carboxyl group in the aspartic acid residue.

Though some increase in the exchange capacities with pH was observed in most experiments the study was not extended in the following experiments to pH 10 since it was aimed at synthesizing some polymers to treat hard waters. This increase

TABLE 3. Effect of the Nature of the Amino Acid on Ion Uptake

Amino acid	Amount of metal ion taken up [(meq/g) $\times 10^2$ ]				
	Ca <sup>2+</sup> (pH 7)		Mg <sup>2+</sup> (pH 7)	Ca <sup>2+</sup> (pH 10)	
	After the first regeneration	After the second regeneration			
Glycine	1.33	1.96	1.79	3.19	1.36
Alanine	1.16	1.98	1.67	2.97	1.13
Tryptophane	1.10	1.78	1.73	2.76	1.24
Phenylalanine	1.00	1.95	1.80	2.63	0.98
Tyrosine	0.79	1.55	1.47	2.48	1.88
Arginine	0.70	<sup>a</sup>			0.96
Aspartic acid	1.56	2.10	2.40	3.95	1.67
Asparagine	1.37	<sup>a</sup>			1.41

<sup>a</sup>Decomposed.

can be attributed to the completed protolysis of phenolic groups at pHs between 8 and 10.

### Syntheses with Different Phenolic Compounds

The results of the experiments performed by using different phenolic compounds together with formaldehyde and glycine are given in Table 4.

Of the resins synthesized with different phenols, only *o*-cresol, gallic acid, and resorcinol (*A*) derivatives seem to be possible to use as ion exchangers. The negative effect induced by the substitution of phenol by *o*-cresol and pyrogallol can result from the decreased number of unsubstituted C atoms that can take part in the polycondensation. The number of C atoms that can be involved in the polycondensation is also less in salicylic acid and gallic acid molecules, but the carboxyl groups in these molecules can contribute to the ion-exchange capacities of the resins. Thus, the negative effect is compensated for or outweighed. This is also the reason why the exchange capacities of salicylic acid and *o*-cresol are different even though both the  $-\text{CH}_3$  and  $-\text{COOH}$  groups have the same electron repelling (+I) effect at pH 7.

4-Nitrophenol led to the formation of a resitoltype resin which softens on heating as an indication of the inadequate formation of crosslinkages. The negative effect caused by the existence of the  $-\text{NO}_2$  group in the phenolic molecule was more remarkable with 2,4-dinitrophenol because only a resole-type resin could be obtained with this compound. This has been attributed to the negative effect of  $-\text{NO}_2$  groups on the electrophilic *o*- and *p*-substitutions in the formation of resins, for they exert an electron-withdrawing (−I) effect.

From the results of the experiments performed up to this stage of the study, it was concluded that substitution of phenol and glycine by gallic acid and aspartic acid, respectively, would provide the most positive effect on the cation-exchange capacity of the resulting resins. Hence, a resin was synthesized from gallic acid, formaldehyde, and aspartic acid, but this resin was a resole-type resin that dissolved

TABLE 4. Effect of the Nature of the Phenolic Compound on Ion Uptake

Phenolic compound	Ca <sup>2+</sup> ion taken up [(meq/g) × 10 <sup>2</sup> ]	
		After the first regeneration
2,4-Dinitrophenol	—	—
4-Nitrophenol	—	—
<i>o</i> -Cresol	0.72	0.76
Pyrogallol	0.96	—
Salicylic acid	1.34	—
Gallic acid	1.60	1.41
Resorcinol	1.56	1.61

moderately in water. This suggests that increases in the molecular weights, i.e., in the bulks of both monomers at the same time, induce a negative effect on cross-linking.

### Resins Synthesized from Different Aldehydes

The resin obtained by substituting formaldehyde by benzaldehyde, i.e., synthesized from phenol, benzaldehyde, and glycine, had  $\text{Ca}^{2+}$  uptakes of  $0.98 \times 10^{-2}$  and  $1.04 \times 10^{-2}$  meq/g before and after regeneration. It was considered that the decrease in the exchange ability could arise from the decreased number of amino acid molecules in the structure because of the steric hindrance effect of the benzene ring.

Another resin was synthesized from phenol, acetaldehyde, and glycine with an increased  $\text{Ca}^{2+}$  uptake of  $1.66 \times 10^{-2}$  meq/g. Acetaldehyde is expected to have a negative effect on the formation of hydroxyalkyl derivatives of phenol because of the +I effect of the methyl group, which results in weakened and decreased linkages between the phenol rings. This has been confirmed by the formation of a resin slightly soluble in water and resistant to regeneration. On the other hand, the existence of a methyl group should not have a negative effect on the condensation of an amino acid which carries a strongly basic  $-\text{NH}_2$  group. The +I effect of methyl groups facilitates the binding of an active H atom by a hydroxyalkyl substituent, and so an increased number of amino acid molecules can be incorporated in the structure so that the ion-exchange capacity of the resin is increased.

A resin with similar properties was synthesized from gallic acid, acetaldehyde, and glycine. It had a  $\text{Ca}^{2+}$  uptake of  $1.28 \times 10^{-2}$  meq/g. This decreased uptake has been attributed to the cooperativity of the negative factors on the bind formation, from both  $\text{CH}_3\text{CHO}$  and gallic acid.

The problem that a regeneration-resistant resin cannot be obtained with acetaldehyde was attacked by substituting some portions of acetaldehyde with formaldehyde. The results, shown in Table 5, suggest that more than half of the acetaldehyde should be substituted for by formaldehyde in order to synthesize a regeneration-resistant resin. There was no need to try the mol numbers between 0.10 and 0.05 for  $\text{CH}_3\text{CHO}$  because the difference between the ion-exchange capacities of these resins was not large, and in this interval the resistance of the resin to regeneration was expected to lessen. With these considerations, it was decided that substitution of 0.05 mol of  $\text{CH}_2\text{O}$  by  $\text{CH}_3\text{CHO}$  could be favorable, and some

TABLE 5. Effect of the  $\text{CH}_3\text{CHO}:\text{CH}_2\text{O}$  Mole Ratio on Ion-Exchange Properties

Phenol: $\text{CH}_3\text{CHO}:\text{CH}_2\text{O}:$ glycine mole ratios	$\text{Ca}^{2+}$ ion taken up [(meq/g) $\times 10^2$ ]	Resistance to regeneration
0.10:0.20:0.00:0.05	1.66	—
0.10:0.10:0.10:0.05	1.42	—
0.10:0.05:0.15:0.05	1.36	+
0.10:0.00:0.20:0.05	1.33	+



TABLE 6. Results of C, H, N Analyses

Resin	C, %	H, %	N, %
A	57.88	5.05	4.18
B	55.52	5.14	4.15
C	53.72	4.90	4.20

additional experiments were performed by fixing these ratios and substituting glycine with glutamic acid and aspartic acid, i.e., with amino acids of an acidic character. The  $\text{Ca}^{2+}$  uptakes of these resins were  $1.70 \times 10^{-2}$  and  $1.78 \times 10^{-2}$  meq/g, respectively. The resin with glutamic acid was not resistant to regeneration while the one with aspartic acid residue was resistant. This confirms the prior conclusions that an increase in the chain length of the amino acid may induce a negative effect on crosslinking.

Another set of experiments was made after substituting 0.05 mol of  $\text{CH}_2\text{O}$  by  $\text{CH}_3\text{CHO}$  and by using some different phenolic compounds and amino acids.

The first two resins were synthesized from gallic acid, as the phenolic compound, and aspartic and glutamic acids. In both cases resole-type resins were obtained, the glutamic acid derivative being more water soluble. These results are consistent with the results of other experiments performed with the same compounds and can be explained in the same ways. The other two resins were synthesized by using resorcinol as the phenolic compound. The  $\text{Ca}^{2+}$  uptake of the aspartic acid derivative (C) was  $1.32 \times 10^{-2}$  and  $1.09 \times 10^{-2}$  meq/g before and after regeneration, respectively, while the corresponding values for the glutamic acid derivative (B) were  $1.43 \times 10^{-2}$  and  $1.04 \times 10^{-2}$  meq/g.

These results suggest that for resins synthesized with gallic acid or resorcinol, the inclusion of  $\text{CH}_3\text{CHO}$  in the reaction media causes a negative effect on exchange capacities. Substitution of gallic acid, a bulkier compound with less active H atoms to play a role in polymerization, by resorcinol induces an increase in the degree of polymerization.

### Structural Analyses

Structural analyses have been made of the resins A, B, and C. The results of C, H, N analyses are given in Table 6. The high percentage of O with respect to the amino acid contents of the resins is indicative of the existence of ether linkages

TABLE 7. Thermogravimetric Analysis Data

Resin	Weight loss at temperature ( $^{\circ}\text{C}$ ), %							Decomposition temperatures, $^{\circ}\text{C}$		
	100	200	300	400	500	600	700			
A	5.98	11.30	21.15	28.83	37.05	46.50	53.40	42- 94	190-231	468-620
B	5.98	10.50	21.35	33.53	42.40	50.40	55.00	34- 92	188-239	350-400
C	4.55	6.85	18.75	30.48	39.10	47.60	53.30	52-100	208-252	353-402

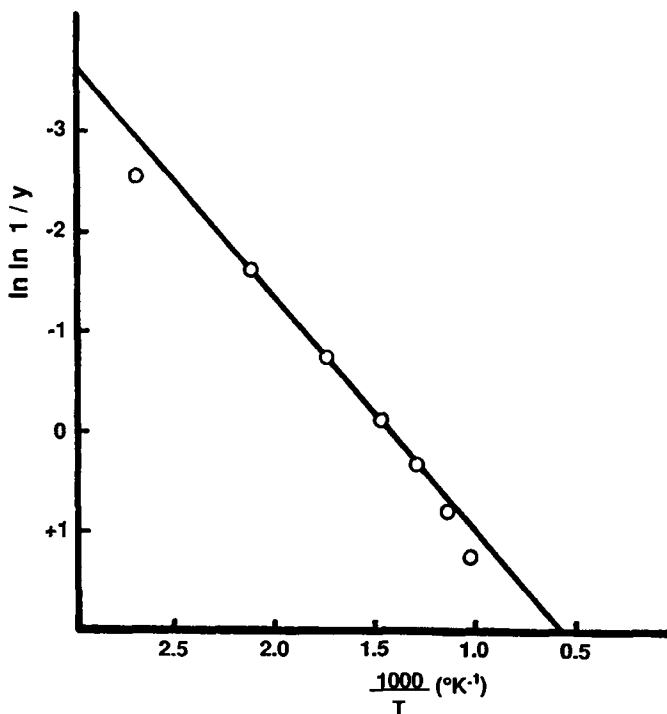


FIG. 1. Graph plotted to estimate the activation energy and the order of the degradation reaction of resin *B*.

and/or methylol groups on the aromatic rings that do not take part in intermolecular bridge formation.

Comparison of their IR spectra reveals that the resins do not significantly differ from each other. A broad absorption band containing several inflections appears in the 2200–3700  $\text{cm}^{-1}$  region. This band is assigned to the stretching vibration of  $-\text{OH}$  of the polymeric-associated phenolic group, aromatic  $\text{C}-\text{H}$ , and  $-\text{NH}$ . The hydroxyl stretching band appears in the 2480–2700  $\text{cm}^{-1}$  region. A broad band at nearly 3310–3500  $\text{cm}^{-1}$  may be due to  $-\text{NH}$ . The bands at about 3330  $\text{cm}^{-1}$  (amino groups) and 1300  $\text{cm}^{-1}$  (carboxyl anion) together with bands from the benzene ring (in the 1430–1620  $\text{cm}^{-1}$  region, aromatic  $\text{C}=\text{C}$  vibration bands) prove the presence of amino acids in the structure.

Carboxylate anion stretching bands appear in the 1280–1330 and 1550–1600  $\text{cm}^{-1}$  regions. In the 1230–1250  $\text{cm}^{-1}$  region a band appears due to the stretching of the ring-oxygen bond. There are also peaks characteristic of the aromatic ring  $\text{C}=\text{O}$  stretching modes in the 1550–1600  $\text{cm}^{-1}$  region together with out-of-plane deformation modes in the approximate interval of 700–830  $\text{cm}^{-1}$ . The latter bands can be assigned to the presence of *o-o* linkages along with *o-p* linkages. The bands displayed between 1650–1750  $\text{cm}^{-1}$  may be due to the  $\text{C}=\text{O}$  stretching vibration of carboxyl groups in amino acid residues because of the fact that no carbonyl group of aldehydes is expected to exist in the polymeric structure. The absorption

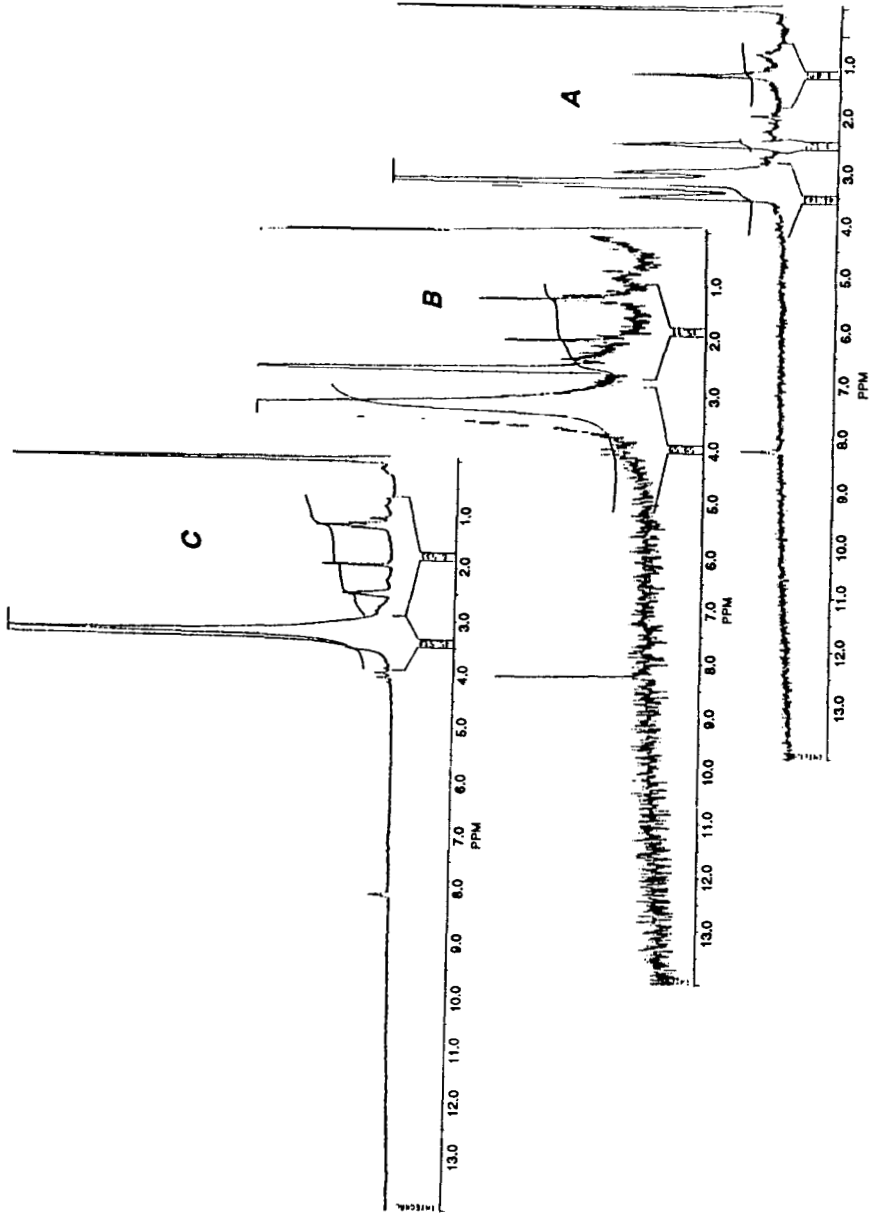


FIG. 2.  $^1\text{H-NMR}$  graphs of the resins A, B, and C.

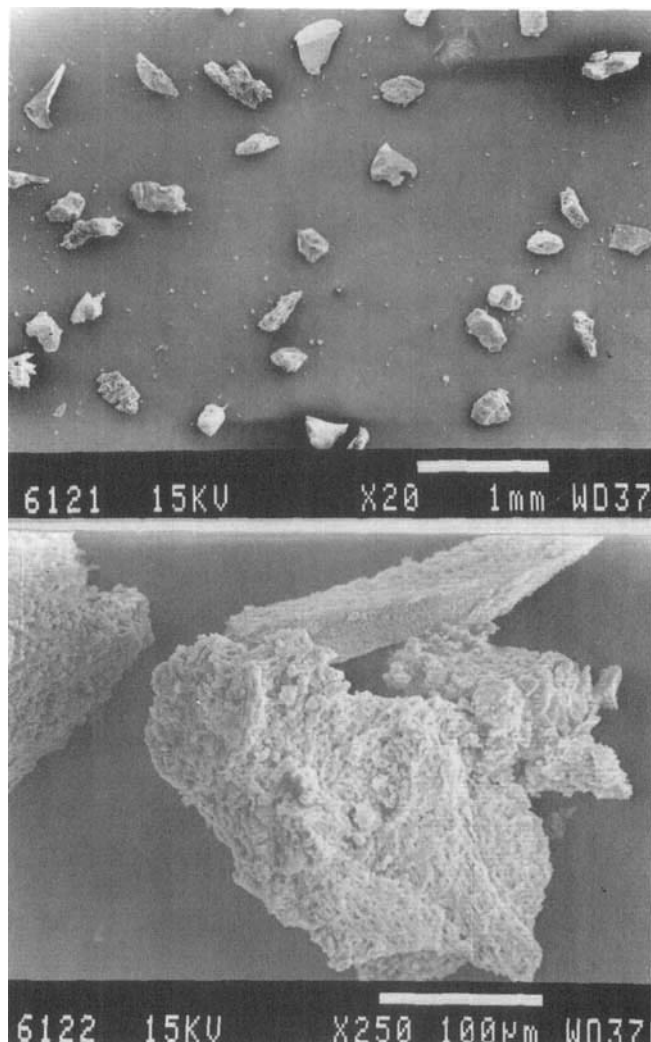


FIG. 3. Electron microscope image of the granulated resin *A*.

band of the  $-\text{CH}_2-$  linkage cannot be clearly observed, but the band in the  $800-900\text{ cm}^{-1}$  region may involve it. The weak bands at  $1110$ ,  $1150$ , and  $1410\text{ cm}^{-1}$  may be assigned to the aliphatic  $\text{C}-\text{N}$  vibrations.

In the spectra of the compounds *B* and *C*, the formation of methylene ether groups is indicated by peaks at about  $1045$ ,  $1120$ ,  $1355$ , and  $1720\text{ cm}^{-1}$ . Along with the band at  $890\text{ cm}^{-1}$  for the  $\text{C}-\text{H}$  bending modes of polysubstituted benzenes, these peaks provide evidence for the resol crosslinking process. Both the phenolic  $1240\text{ cm}^{-1}$  peak and its aliphatic counterpart at  $1010\text{ cm}^{-1}$  due to  $-\text{CH}_2\text{OH}$  are observed.

The results from TGA analyses are given in Table 7, and they show that the three resin samples do not differ much in their thermal stability and that weight loss

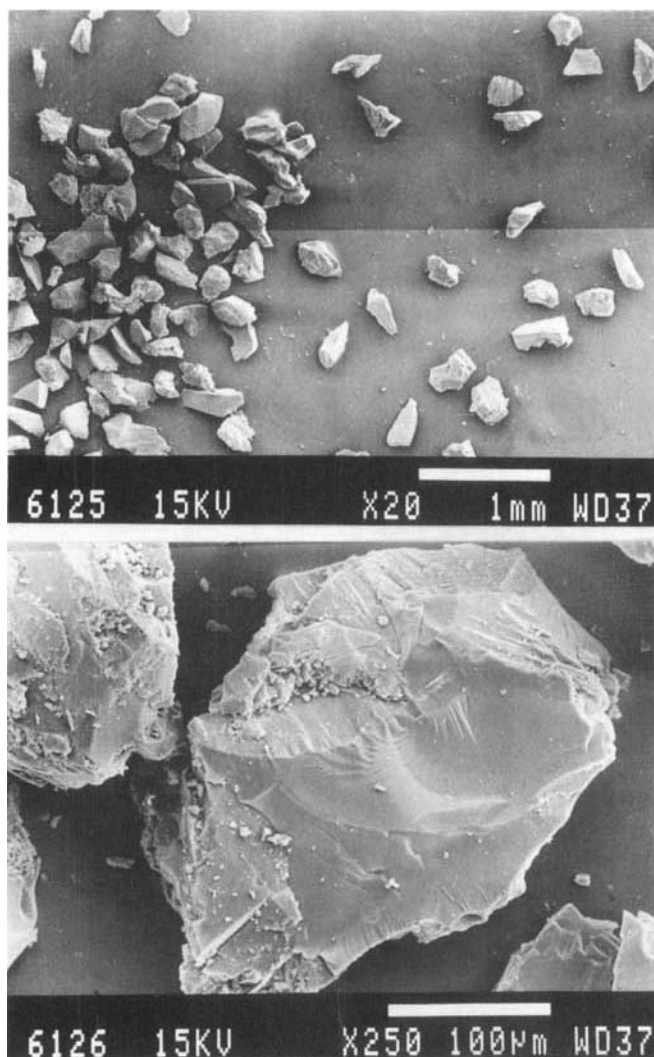


FIG. 4. Electron microscope image of the granulated resin *B*.

occurs in three stages. The initial mass loss may be due to the loss of moisture entrapped in the resin. This has been confirmed by a  $\ln \ln 1/y - 1/T$  graph, i.e., by treating the TGA data according to the method of Broido [37], one of the methods used to investigate the kinetics of thermal degradation [38, 39], where  $y$  is the fraction of initial molecules not yet decomposed. The activation energies of the pyrolysis reactions were estimated from the slope of this plot. The calculated activation energies for resins *A*, *B*, and *C* were 3.88, 4.61, and 4.84 kcal/mol, respectively.

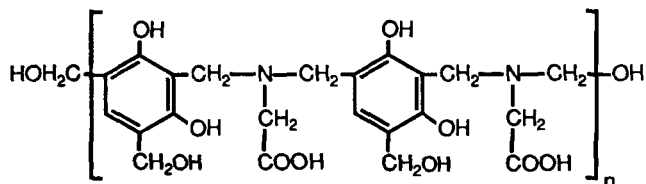
Similar curves have been obtained for all three resins. As an example, the plot for resin *B* is shown in Fig. 1. The deviation from linearity in the upper part of the plot points to an error in the initial weight of the sample. This error mostly arises



FIG. 5. Electron microscope image of the granulated resin *C*.

from the existence of some solvent residue in the sample. There is a second deviation in the lower part of the plot. Deviations in this direction indicate a reaction order smaller than 1 [37]. Of the plots, the plot for resin *A* show the largest deviation indicating a lower reaction order.

<sup>1</sup>H-NMR spectra of compounds *A*, *B*, and *C* also support differences between the structures of polymers *B* or *C* and *A* (Fig. 2). The NMR spectra were complex, especially in the 0–4 ppm range. Because of the low solubility of these polymers, NMR data could be obtained after 500 scans with the soluble parts of the polymers in DMSO-*d*<sub>6</sub>. Other polymer peaks are eclipsed by strong peaks or are in the unresolved parts of the spectra. The important point used to differentiate the structures



SCHEME 1. Structure of the resins synthesized from resorcinol, formaldehyde, and glycine (*A*).

of polymers prepared with or without acetaldehyde is obtained in these spectra. A quartet observed in the spectra of both compounds *B* and *C*, indicating the introduction of the  $\text{CH}_3\text{—CH—}$  moiety, is not observed in the spectrum of *A*. The chemical shifts of  $\text{—CH}$  absorptions of *B* and *C* are almost the same ( $\sim 4.00$  ppm) which makes the possibility for the peak belonging to the  $\text{—CH}_2\text{—}$  of glutamic acid moiety of *B* impossible since only one quartet is possible for the structure of *C*. The identified peaks in the spectra are given in the following.

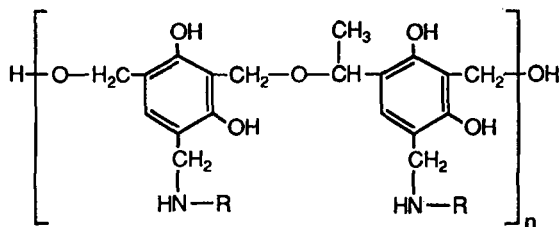
Polymer A ( $^1\text{H NMR}$ , 100 MHz,  $\text{DMSO-}d_6$ ;  $\delta$  ppm): 1.24 (s,  $\text{N—CH}_2\text{—}$ ); 2.00 (s,  $\text{aryl—CH}_2\text{—O—}$ ); 2.95, 3.23, 3.50 ( $\text{—CH}_2\text{—}$  linkages); 8.23 (s, arom. H)

Polymer B ( $^1\text{H NMR}$ , 100 MHz,  $\text{DMSO-}d_6$ ;  $\delta$  ppm): 1.23 (t,  $\text{N—CH—}$ ); 2.00 (s,  $\text{aryl—CH}_2\text{—O—}$ ); 3.26 ( $\text{—CH}_2\text{—}$  linkages); 4.00 (q,  $\text{CH}_3\text{—CH}$ ); 8.19 (s, arom. H)

Polymer C ( $^1\text{H NMR}$ , 100 MHz,  $\text{DMSO-}d_6$ ;  $\delta$  ppm): 1.26 (t,  $\text{N—CH—}$ ); 1.94 (s,  $\text{aryl—CH}_2\text{—O—}$ ); 3.21 ( $\text{—CH}_2\text{—}$  linkages); 4.00 (q,  $\text{CH}_3\text{—CH}$ ); 8.12 (s, arom. H)

Specific surface areas for resins *A*, *B*, and *C* have been determined to be 5.0, 12.5, and 24.5  $\text{m}^2/\text{g}$ , respectively.

Electron microscope studies have also been made on granulated particles of these resins. They all have the characteristic appearance of weak acid exchangers, and resins *B* and *C* have more glassy structures than resin *A* (Figs. 3, 4, and 5).



R = Amino Acid Residue

SCHEME 2. Structure of the resins synthesized from resorcinol, formaldehyde, acetaldehyde; and glutamic acid or aspartic acid (*B* and *C*).

## CONCLUSION

Of the resins synthesized in this study, the resin synthesized from phenol,  $\text{CH}_3\text{CHO}$ ,  $\text{CH}_2\text{O}$ , and aspartic acid with the mole ratio 0.10:0.05:0.15:0.05 has the best ion-exchange properties. It is followed by the resins synthesized from gallic acid, formaldehyde, glycine; resorcinol, formaldehyde, glycine; and phenol, formaldehyde, aspartic acid with the mole ratio of 1:2:0.5. Except for the gallic acid derivative, these resins have the additional advantage that their exchange capacities are increased by regeneration. The increase is more remarkable for the latter resin.

From the results of structural analyses, the most probable structures for the condensation units of resins *A* (Scheme 1) and *B* and *C* (Scheme 2) could be deduced.

For compounds *B* and *C*, the C, H, N results are within error limits when one acetaldehyde molecule is bound per resorcinol molecule. Crosslinking can proceed via amino acid nitrogens. It is also possible that some of the amino acid residues in compound *A* are bound to 4-substituted methylol groups and contribute to crosslinking. Crosslinking is also possible via 4-substituted methylol groups.

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