Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Patel, J. L. and Patel, S. R.(1984) 'Friedel-Crafts Polymers. 6. Friedel-Crafts Polycondensation of p-Xylylerte Dibromide with Salicylic Acid and β-Resorcyiic Acid', Journal of Macromolecular Science, Part A, 21: 11, 1427 — 1442
To link to this Article: DOI: 10.1080/00222338408055674
URL: http://dx.doi.org/10.1080/00222338408055674

J. MACROMOL. SCI.–CHEM., A21(11 & 12), pp. 1427-1442 (1984)

Friedel-Crafts Polymers. 6. Friedel-Crafts Polycondensation of p-Xylylene Dibromide with Salicylic Acid and β-Resorcylic Acid

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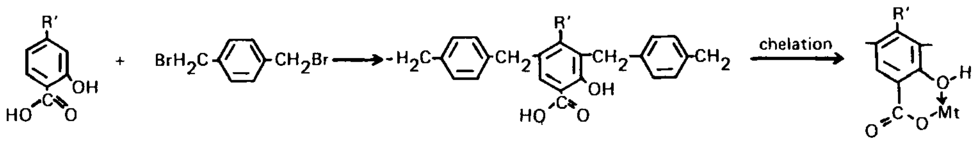
ABSTRACT

Polymers were prepared by condensing p-xylylene dibromide separately with salicylic acid and β-resorcylic acid in the presence of anhydrous ferric chloride in dioxane. The polymer samples were characterized by elemental analysis, by IR spectral study, by $\bar{M}_n$ determined by vapor pressure osmometry, by nonaqueous conductometric titration in pyridine, by TGA in air, and by viscosity measurements of polymer solutions in DMF. Polymeric metal chelates of Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, and Fe^{3+} with polymer samples were prepared and characterized by elemental analysis, by IR spectral study, and by TGA in air. The chelation ion-exchange properties of the polymer samples were studied by employing the batch equilibration method.

0022-233X/84/2111-1427$3.50/0

INTRODUCTION

In earlier communications, S. R. Patel and co-workers have reported polymers based on Friedel-Crafts self-polycondensation of 4,4'-dichloromethyl diphenyl ether (DDE) [1] and such polycondensations of DDE with benzene, toluene, xylenes, chlorotoluenes, and o-hydroxy carbonyl compounds [2-4]. Friedel-Crafts polycondensations of p-xylene dichloride (PXDC) with active aromatic compounds including phenol have also been reported [5-10]. The PXDC-phenol polymers are known as xylok resins and are reported to have better performance than phenolics, particularly at higher temperature. The present communication deals with the synthesis of polymers based on the Friedel-Crafts polycondensation of p-xylylene dibromide (PXDB) individually with salicylic acid (SA) and with β-resorcylic acid (BRA) in the presence of anhydrous ferric chloride in dioxane. The polymer samples PXDB-SA and PXDB-BRA were characterized by IR spectral studies and by estimations of their number-average molecular weight ($\bar{M}_n$). The latter were measured by VPO and by nonaqueous conductometric titration against standard sodium methoxide in pyridine. The viscosities of the polymer samples were measured in DMF. The TGAs of the polymer samples were determined in air under identical conditions. The polymeric metal chelates were prepared by mixing DMF solutions of the required metal nitrate and the polymer sample in stoichiometric amounts. The composition, the spectral characteristic, and the thermal properties of polymeric chelates were studied. The main aspect of the work reported here is the study of the ion-exchange capacities of both these polymeric ligands for selected metal ions and comparison of this properly with those of polymeric ligands prepared from each of the above-mentioned 2-hydroxycarbonyl compounds with bridges such as $-CH_2-$ and $-CH_2-CH_2-$ separating the ligand units in the polymer chains. The latter type of polymeric ligands were prepared by condensation of the required hydroxycarbonyl monomer with formaldehyde [11-13], methylene dichloride [14], or ethylene dichloride under appropriate conditions [15]. There is a report about the dependence of the ion-exchange capacity of a polymeric ligand prepared from the same ligand functioning as a monomer and the size of the bridge $-CH_2-Ph-O-Ph-CH_2-$ separating the ligand units in the polymer chains [4]. In the polymeric ligand described in the present communication, both the nature of the bridge and its size have been altered. The ion-exchange capacities of these polymeric ligands were measured by the application of the batch equilibration method developed by DeGeiso et al. [11] and employed by other workers [16].



where $R' = H$ or OH
Mt $= Cu^{2+}/2$, $Co^{2+}/2$, $Zn^{2+}/2$, $Ni^{2+}/2$, and $Fe^{3+}/3$

EXPERIMENTAL

Materials

The monomers p-xylylene dibromide [17] and β-resorcylic acid were prepared by the reported methods [18]. The anhydrous ferric chloride, dioxane, salicylic acid, metal nitrates, DMF, and sodium acetate were laboratory-grade reagents. The salts used for the equilibration study were AR-grade chemicals.

FRIEDEL-CRAFTS POLYCONDENSATION

Polycondensation of SA with PXDB in the Presence of Anhydrous Ferric Chloride Using Dioxane Formation of PXDB-SA

A well-powdered anhydrous ferric chloride (1.79 g 0.01 mol) was added in small lots with stirring to a mixture of PXDB (2.64 g, 0.01 mol) and salicylic acid (1.38 g, 0.01 mol) in dioxane (17 mL). The reaction mass was heated at 60° C for 2 h and then at 90° C for 2 h. The cooled mixture was poured into a 1:1 water:HCl mixture (100 mL) with stirring, and a slightly sticky product separated out. It was filtered and treated with boiling 5% HCl solution (50 mL) and then twice with boiling water. The light yellow colored solid thus obtained was dried and powdered. It was refluxed with petroleum ether (60-80° C) for half an hour. The polymer sample was designated as PXDB-SA. The yield was 1.5 g. It was soluble only in DMF.

Polycondensation of β-Resorcylic Acid (BRA) with PXDB in the Presence of Anhydrous Ferric Chloride Using Dioxane Formation of PXDB-BRA

The reaction was carried out in the manner described above using PXDB (2.64 g, 0.01 mol), BRA (1.94 g, 0.01 mol), $FeCl_3$ (1.7 g, 0.01 mol), and dioxane (17 mL). The polymer was obtained as a light brown solid, yield 1.3 g. It was soluble only in DMF.

Preparation of Polymeric Chelates. Preparation of the Polymeric Cu^{2+} Metal Chelate of the PXDB-SA Polymer

To a solution of $Cu(NO_3)_2.6H_2O$ (0.7375 g, 0.0025 mol) in DMF (30 mL), a solution of PXDB-SA polymer (1.20 g, 0.005 mol) in (50 mL)

DMF was added dropwise with constant stirring. The polymeric chelate was precipitated by adding a saturated solution of sodium acetate (10 mL). A light green colored polymeric chelate separated out. The mixture was digested for half an hour. It was filtered, washed with boiling DMF, boiling water, and finally with ethanol; and then air-dried. The polymeric chelate weighed 1.0 g.

Following this procedure, polymeric chelates PXDB-SA-Fe^{3+}, PXDB-SA-Ni^{2+}, PXDB-SA-Zn^{2+}, PXDB-SA-Co^{2+}, PXDB-BRA-Fe^{3+}, PXDB-BRA-Cu^{2+}, PXDB-BRA-Zn^{2+}, PXDB-BRA-Ni^{2+}, and PXDB-BRA-Co^{2+} were prepared. Results of the analysis of these polymeric chelates are presented in Table 1.

Apparatus and Methods of Characterization

Elemental analyses of the polymer samples and their polymeric metal chelates were carried out on a Coleman C, H Analyzer. The bromine content of the polymer samples was estimated by the Parr-bomb method in triplicate. The analyses of metal ions in the polymeric chelates were carried out by decomposition of a known amount of chelate by concentrated mineral acid followed by dilution with distilled water, filtration, and estimation of metal ions in solution by standard methods [19].

IR spectra of the polymer samples and polymeric metal chelates were taken in KBr on a UR-10 spectrophotometer.

The number-average molecular weights ($\bar{M}_n$) of the polymer samples were measured with a Hewlett-Packard vapor pressure osmometer using DMF as the solvent at 70°C; benzil was used as the calibrant.

Conductometric titration of both the polymer samples was carried out in pyridine against standard sodium methoxide in pyridine, using a Metrohm Herisan Konductoskop E 365, following the details described by Patel et al. [13].

The viscosities of the solutions of PXDB-SA and PSDB-BRA samples in DMF were measured at $35 \pm 0.1°C$ with an Ubbelohde-type viscometer. The measurements were carried out in the concentration range from 0.769 to 2.0%.

The intrinsic viscosity $[\eta]$ was measured from a linear plot of η_{sp}/c vs concentration.

Thermogravimetry of both the polymer samples and polymeric metal chelates was carried out on a Linseis (Germany) thermogravimetric analyzer in air at a heating rate of 10°C/min. The results are presented in Table 1.

The batch equilibration method was adopted for the ion-exchange properties [11, 20]. The evaluation of the influence of different electrolytes on the metal uptake by the polymer, the rate of metal uptake under specified conditions, and the distribution of various metal ions at different pH values were carried out following the procedures described earlier [4, 14].

TABLE 1. Characterization of Polymer Samples

Polymer samples	Elemental analysis C (%)	H (%)	Br (%)	$\bar{M}_n$ ± 30 by conductometric titration (VPO)	Intrinsic viscosity [η] (dL/g)
PXDB-SA	71.9	5.5	7.8	1010 (1040)	0.058
PXDB-BRA	65.8	5.1	6.1	1280 (1320)	0.065
PXDB-SA-Cu^{2+}	65.8	3.9	-	-	-
PXDB-SA-Fe^{3+}	69.5	4.0	-	-	-
PXDB-SA-Co^{2+}	65.2	3.1	-	-	-
PXDB-SA-Ni^{2+}	66.4	3.8	-	-	-
PXDB-BRA-Fe^{3+}	62.2	3.8	-	-	-
PXDB-BRA-Cu^{2+}	61.7	4.0	-	-	-
PXDB-BRA-Co^{2+}	62.9	3.5	-	-	-
PXDB-BRA-Ni^{2+}	62.0	3.2	-	-	-

RESULTS AND DISCUSSION

The polymer samples PXDB-SA and PXDB-BRA are light yellow and light brown powders soluble only in DMF. Examination of the molecular weights of the polymer samples presented in Table 1 reveals that the molecular weight values of each polymer sample estimated by the nonaqueous conductometric titration method and by the VPO method are comparable within the limits of experimental error.

Number-average molecular weights are found to be around 1000 and 1300 of PXDB-SA and PXDB-BRA, respectively. The observed values of Br % of these polymer samples agree well with the values of Br % calculated on the basis of $\bar{M}_n$ assuming a linear structure with OH$_2$Br as an endgroup. The important features of the IR spectrum (Fig. 1) of these polymer samples are a broad weak band extending from 2600 to 3500 cm^{-1} and the inflections in this broad band around 2850 and 2950 cm^{-1}. These inflections are attributed to symmetric and asymmetric stretching of CH of $-CH_2-$ bridges.

The carbonyl bands at 1650 in the IR spectra of PXDB-SA and PXDB-and Their Polymeric Metal Chelates

TGA in air at heating rate of 10°C/min			
Temperature at which rapid degradation started (±20°C)	Temperature beyond which the rate of weight loss is very low (±20°C)	Temperature at which 50% weight loss occurs (°C)	% Weight loss at 700°C
280	560	370	85
300	500	350	78
260	520	320	95
200	540	340	95
200	510	340	~100
200	520	310	~100
180	360	305	90
190	375	305	95
170	350	310	95
190	380	320	95

BRA are assigned to the –COOH group in the polymer. The bands around 910 and 830 cm^{-1} are assigned to the systems of isolated and two adjacent hydrogen atoms, respectively. The band at 670 cm^{-1} is attributed to C–Br stretching of the CH_2Br endgroup.

The intrinsic viscosities $[\eta]$ of PXDB-SA and PXDB-BRA polymer samples in DMF at 35 ± 0.1°C were found to be 0.058 and 0.065 dL/g, respectively.

Examination of the TGA data of PXDB-SA and PXDB-BRA reveals that both the polymers degrade in air in a single step. The order of degradation of both polymer samples is around one. The energy of activation of the degradation reaction is around 40 ± 10 kcal/mol. Of the two polymers, PXDB-SA seems to be more stable.

Characterization of Polymeric Chelates

The polymeric chelates are found to be insoluble in common organic solvents as expected. They are decomposed by mineral acids, giving original polymeric ligands, and seem to be uneffected when they are heated up to 360°C. The results of the metal composition

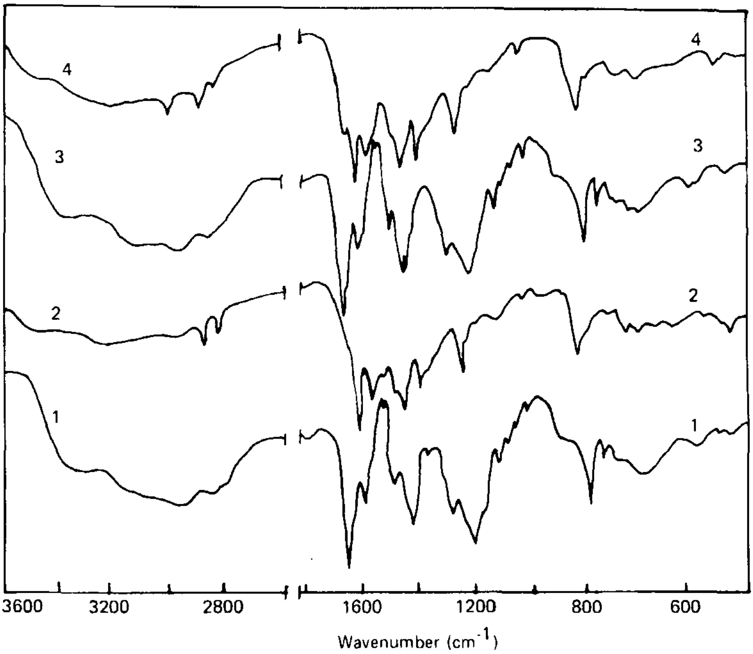


FIG. 1. IR spectra of polymers: (1) PXDB-SA, (2) PXDB-SA-Fe^{3+} chelate, (3) PXDB-BRA, (4) PXDB-BRA-Fe^{3+}.

suggest that the metal:ligand (M:L) ratio is 1:2 for divalent metal ions and 1:3 for trivalent metal ions. These results are supported by elemental analyses of the polymeric chelates. The IR spectra of all the polymeric chelates resemble each other in general shape and relative intensity of bands. A comparison of the IR spectrum of the polymeric ligand PXDB-SA and spectra of polymeric chelates PXDB-SA-Fe^{3+} reveals broad absorptions from 3500-2600 cm^{-1} in the spectrum of the polymeric ligand, due to the chelated OH group, has nearly disappeared in the spectrum of polymeric chelate as expected. This is in agreement with the observation of DeGeiso et al. [21]. A sharp band at 1650 in the IR spectrum of PXDB-SA and PXDB-BRA polymeric ligand assigned to C=O has vanished in the spectra of all the polymeric chelates; in its place a strong band around 1600 cm^{-1} appears. This may arise from the C=O of the COO^- group of chelated systems. Because of the very low intensity of the bands in the region of interest, it was not possible to observe the band due to the metal-carbon bond with any certainty. This region was rendered complex due to the presence of C–H out-of-plane bending vibrations. The above properties can be explained on the basis of the expected structure of the polymeric chelate shown earlier.

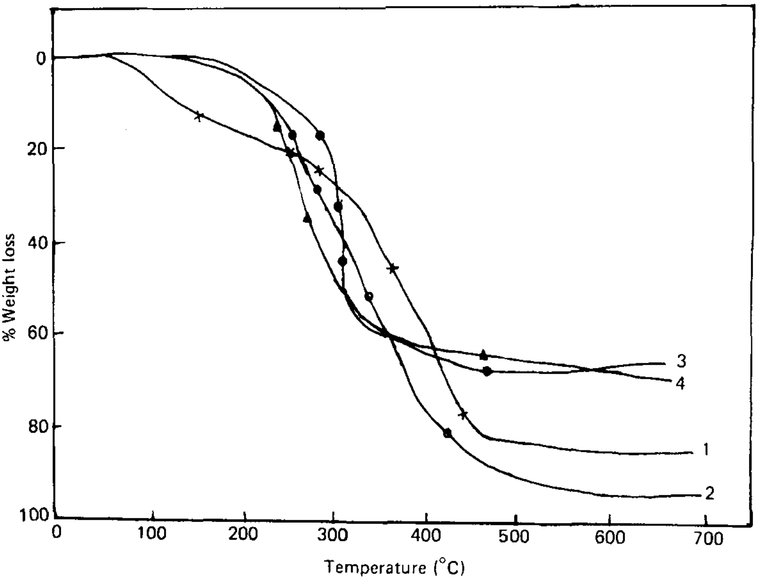


FIG. 2. TGA thermograms of polymers: (1) PXDB-SA, (2) PXDB-SA-Cu^{2+} chelate, (3) PXDB-BRA, (4) PXDB-BRA-Cu^{2+} chelate.

The typical TG thermograms of the PXDB-SA-Cu^{2+} and PXDB-BRA-Cu^{2+} chelates are shown in Fig. 2 for comparison. Examination of the TG thermograms of all polymeric chelates and their parent polymer samples PXDB-SA and PXDB-BRA reveals that the polymeric chelates also degrade in a single step but the rate of decomposition of the chelates is higher than that of the parent polymer. It seems that metal ions accelerate decomposition of the polymeric chelate [22].

Results of Ion-Exchange Capacity; Influence of Electrolytes on the Metal Uptake

Examination of the data presented in Tables 2 and 3 reveals that the amount of metal ions taken up by a given amount of PXDB-SA or PXDB-BRA polymer sample depends upon the nature and concentration of the electrolyte present in the solution. The amounts of Fe^{3+}, Cu^{2+}, and Ni^{2+} ions taken up by each of these polymer samples increases with an increase in the concentration of such ions as chloride, chlorate, and nitrate but decreases with an increase in the concentration of the sulfate ions. The amounts of metal ions Co^{2+} and Zn^{2+} taken up by the given polymer sample decreases with an increase in the concentration of chlorate, chloride, nitrate, and sulfate ions. DeGeiso et al. [11] have reported that the absorption of Fe^{3+} by sali-

TABLE 2. Evaluation of the Influence of Different Electrolytes on the Uptake of Several Metal Ions [(Mt(NO_3) = 0.1 mol/L)][a]

Metal ion	pH	Electrolyte (mol/L)	Adsorption of meq × 10^1 of the metal ion on PXDB-SA polymer[b]			
			NaCl	$NaNo_3$	$NaClO_4$	Na_2SO_4
Fe^{3+}	2.5	0.01	0.82	0.43	0.62	1.25
		0.05	0.01	1.11	0.88	1.24
		0.1	1.09	1.24	1.08	1.19
		0.5	1.23	1.28	1.16	1.16
		1.0	1.28	1.34	1.34	1.11
Cu^{2+}	4.5	0.01	0.03	0.06	0.13	0.74
		0.05	-	0.12	0.20	0.57
		0.1	0.14	0.20	0.25	0.21
		0.5	0.19	0.26	0.30	0.19
		1.0	0.35	0.37	0.34	0.18
Co^{2+}	4.5	0.01	0.22	0.74	0.79	0.59
		0.05	0.18	0.68	0.72	0.38
		0.1	0.16	0.48	0.71	0.21
		0.5	0.14	0.35	0.22	0.20
		1.0	0.13	0.12	0.18	0.11
Zn^{2+}	4.5	0.01	0.65	0.80	0.52	0.48
		0.05	0.59	0.72	0.49	0.45
		0.1	0.42	0.46	0.36	0.30
		0.5	0.26	0.32	0.29	0.20
		1.0	0.13	0.10	0.18	0.15
Ni^{2+}	4.5	0.01	0.01	0.02	0.03	0.13
		0.05	0.04	0.09	0.05	0.09
		0.1	0.05	0.12	0.06	0.08
		0.5	0.21	0.15	0.10	0.03
		1.0	0.24	0.17	0.19	0.02

[a] Volume of electrolyte solution, 40 mL; time, 24 h; volume of metal ion solution, 2 mL; temperature, 30°C.

[b] Weight of polymer 25 mg.

TABLE 3. Evaluation of the Influence of Different Electrolytes on the Uptake of Several Metal Ions [($Mt(NO_3)_2$ = 0.1 mol/L)][a]

Metal ion	pH	Electrolyte (mol/L)	Adsorption of meq × 10^1 of the metal ion on PXDB-BRA polymer[b]			
			NaCl	$NaNO_3$	$NaClO_4$	Na_2SO_4
Fe^{3+}	2.5	0.01	0.76	0.40	0.58	1.15
		0.05	0.98	1.00	0.80	1.13
		0.1	1.00	1.15	1.00	1.11
		0.5	0.15	1.20	1.10	1.00
		1.0	1.2	1.25	1.22	0.80
Cu^{2+}	4.5	0.01	0.02	0.01	0.12	0.70
		0.05	0.05	0.1	0.18	0.52
		0.1	0.11	0.18	0.23	0.18
		0.5	0.17	0.24	0.28	0.16
		1.0	0.50	0.34	0.30	0.13
Co^{2+}	4.5	0.01	0.18	0.68	0.75	0.54
		0.05	0.15	0.62	0.65	0.32
		0.1	0.12	0.43	0.61	0.18
		0.5	0.11	0.34	0.20	0.16
		1.0	0.08	0.10	0.16	0.09
Zn^{2+}	4.5	0.01	0.60	0.73	0.47	0.44
		0.05	0.56	0.65	0.42	0.40
		0.1	0.38	0.41	0.30	0.28
		0.5	0.21	0.27	0.24	0.15
		1.0	0.10	0.07	0.15	0.10
Ni^{2+}	4.5	0.01	0.01	0.02	0.01	0.12
		0.05	0.01	0.06	0.04	0.10
		0.1	0.03	0.10	0.06	0.07
		0.5	0.18	0.13	0.08	0.02
		1.0	0.20	0.16	0.15	0.01

[a] Volume of electrolyte solution, 40 mL; time, 24 h; volume of metal ion solution, 2 mL; temperature, 30°C.

[b] Weight of polymer, 25 mg.

cylic acid formaldehyde (SF) polymer increases with an increase in the concentration of chloride, chlorate, and nitrate ions and decreases with an increase in the concentration of sulfate and acetate ions.

Rate Of Metal Uptake

The rates of metal absorption by the polymer samples were measured for Fe^{3+}, Cu^{2+}, Co^{2+}, Zn^{2+}, and Ni^{2+} ions in the presence of 1 M $NaNO_3$ to determine the time required to reach the equilibrium stage. All experiments were carried out at pH 4.5. In these experiments both the polymer samples behave similarly. Examination of the results presented in Table 4 shows that Fe^{3+} ions require slightly more than 4 h for the establishment of equilibrium; Cu^{2+} and Zn^{2+} require 5 h for the establishment of equilibrium. In the experiments with solution containing Fe^{3+} ions, more than 55% of equilibrium was established in the first hour. Study has revealed that the rate of metal ion uptake follows the order $Fe^{3+} >$ (Co^{2+}, Zn^{2+}) and (Cu^{2+}, Ni^{2+}). It is interesting to note that a similar behavior was observed by DeGeiso et al. for both SF polymers [11].

Distribution Ratios of Metal Ions at Different pH Values

The results described in Table 5 reveal that the amount of metal ions taken up by the polymer samples PXDB-SA and PXDB-BRA at equilibrium increases with an increase in the pH at which the study was carried out. Selectivity of polymer samples for Fe^{3+} ions is higher than that for the other metal ions. In the case of Fe^{3+} ion, the distribution ratio is higher than for the other metal ions. Cu^{2+} and Ni^{2+} ions have a high distribution ratio value at pH 6.0 while two other metal (Co^{2+}, Zn^{2+}) ions have a lower distribution ratio in the 4 to 6 pH range. This has been attributed to the lower stability constants of the metal complexes [23, 24].

Comparative Study to Bring Out the Effect of the Nature and Size of the Bridge

There are reports about the results of studies of the ion-exchange capacities of polymeric ligands comprising salicylic acid, with consecutive ligands units being bridged by $-CH_2-$, $-CH_2-CH_2-$, and $-CH_2Ph-O-Ph-CH_2-$ units [4, 12, 15, 25, 26]. In the present polymeric ligands the bridging unit is $-CH_2-Ph-CH_2-$. Let these polymers be designated as L-F, L-ethyl, L-DDE, and L-PXDB, respectively, where L stands for SA. It is interesting to compare the be-

TABLE 4. Comparison of the Rates of Metal (Mt) Ion Uptake[a]

Time (h)	Percentage of the relative amount of metal ion uptake[b]									
	PXDB-SA					PXDB-BRA				
	Fe^{3+}	Cu^{2+}	Co^{2+}	Zn^{2+}	Ni^{2+}	Fe^{3+}	Cu^{2+}	Co^{2+}	Zn^{2+}	Ni^{2+}
1/2	54	13	08	10	17	45	10	08	10	20
1	57	19	25	30	35	50	15	24	20	30
2	70	32	50	50	47	68	28	50	49	40
3	79	46	67	70	59	75	45	70	75	50
4	87	51	92	90	70	85	50	90	90	70
5	100	67	100	100	88	100	70	98	96	80
6	-	100	-	-	100	-	100	-	-	90

[a] $[Mt(NO_3)_2]$ = 0.1 mol/L, volume, 2 mL; $(NaNO_3)$ = 1 mol/L, volume, 40 mL; pH for Cu^{2+}, Co^{2+}, Zn^{2+}, and Ni^{2+} = 4.5 and for Fe^{3+} = 2.5.

[b] Related to the amount of metal ions in the state of equilibrium (100%).

TABLE 5. Distribution Ratio, D of Different Metal Ions as a Function of the pH

	Distribution ratio[a] of the metal ions[b]									
	PXDB-SA					PXDB-BRA				
pH	Fe^{3+}	Cu^{2+}	Co^{2+}	Zn^{2+}	Ni^{2+}	Fe^{3+}	Cu^{2+}	Co^{2+}	Zn^{2+}	Ni^{2+}
1.0	160	-	-	-	-	140	-	-	-	-
1.5	183	-	-	-	-	160	-	-	-	-
2.0	240	-	10	18	78	200	65	8	12	70
2.5	670	-	-	-	-	600	-	-	-	-
3.0	-	110	48	44	153	-	100	45	40	135
4.0	-	140	68	54	182	-	120	65	50	165
5.0	-	183	110	102	245	-	170	100	92	220
6.0	-	295	140	163	289	-	275	125	145	260

[a] $D = \frac{\text{meq of metal ions taken up by 1 g of polymer}}{\text{meq of metal ions present in 2 mL of solution}}$

[b] Error ± 5%. $[Mt(NO_3)_2]$ = 0.1 mol/L, volume, 2 mL; $NaNo_3$ = 1 mol/L, volume, 40 mL; 30°C; 24 h (equilibrium state).

haviors of such polymers for different metal ions in the type of study under consideration.

For the salicylic acid-based polymeric ligands of the type mentioned above, the same type of selectivity is observed for the Fe^{3+} ion, nearly the same trend is observed in the K_D values for different metal ions, and the same trend is observed in the variation of K_D with pH. Among the polymeric ligands SA-F, SA-ethyl, SA-PXDB, and SA-DDE, the K_D values for the Fe^{3+} ion for experiments carried out under the same experimental conditions decreases in the stated order of polymeric ligands. Thus the K_D values decrease with an increase in the size of the bridge. The reason for this seems to be the decrease in the molar proportion of the ligand unit in the same weight of polymer with an increase in the size of the bridge.

REFERENCES

[1] G. R. Patel, P. T. Amin, and S. R. Patel, J. Macromol. Sci.–Chem., A18(6), 939 (1982).

[2] G. R. Patel and S. R. Patel, Ibid., A19(5), 653 (1983).

[3] G. R. Patel and S. R. Patel, Ibid., A19(5), 663 (1983).

[4] G. R. Patel and S. R. Patel, Ibid., A19(5), 673 (1983).

[5] M. Iovu, Rev. Chem., 14(7), 385 (1983); Chem. Abstr., 60, 4263 (1964).

[6] I. V. Niolescu and M. Iovu, Ann. Univ. Bucuresti, Ser. Stii nt Nat., 12(41), 143 (1963); Chem. Abstr., 65, 5600e (1966).

[7] N. K. Moshchinskaya, A. M. Karateev, and N. G. Glukhovtseva, Zh. Prikl. Khim (Leningrad), 41, 660 (1968); Chem. Abstr., 69, 76976 (1968).

[8] G. S. Moronov, M. I. Farbervov, and G. N. Timoshenko, USSR Patent 318,566 (CI(07C)), (October 28, 1971; Appl. July 28, 1969); Chem. Abstr., 76, 45954z (1972).

[9] A. A. Vansheidt, E. P. Mellnikova, and G. A. Gladkovskii, Vysokomol. Soedin., 4, 1176 (1962); Chem. Abstr., 59, 769 (1963).

[10] A. A. Vansheidt, E. P. Mellnikova, and G. A. Gladkovskil, Ibid., 4, 1303 (1962).

[11] R. C. DeGeiso, L. G. Donaruma, and E. A. Tomic, Anal. Chem., 34, 845 (1962); Chem. Abstr., 57, 6653c (1962).

[12] H. S. Patel, S. D. Patel, and S. R. Patel, Angew. Makromol. Chem., 106, 223 (1982).

[13] S. D. Patel, H. S. Patel, and S. R. Patel, J. Macromol. Sci.–Chem., A16(7), 1335 (1981).

[14] B. S. Patel and S. R. Patel, Makromol. Chem., 180, 887 (1979).

[15] J. B. Patel and M. N. Patel, J. Indian Chem. Soc., 58, 491 (May 1981).

[16] L. G. Donaruma (to E. I. du Pont de Nemours and Co.), U.S. Patent 3,052,515 (1962); Chem. Abstr., 57, 13467a (1962).

[17] A. Thorpe, J. Chem. Soc., 91, 1698 (1907).
[18] A. I. Vogel, A Text Book of Practical Organic Chemistry, 4th ed., Longmans, London, 1978.
[19] A. I. Vogel, A Text Book of Inorganic Analysis, 3rd ed., Longmans, New York, 1964.
[20] H. P. Gregor, M. Taiter, L. Citarel, and E. I. Becker, Ind. Eng. Chem., 44, 2834 (1952); Chem. Abstr., 47, 3493e (1953).
[21] R. C. DeGeiso, L. G. Donaruma, and E. A. Tomic, J. Org. Chem., 27, 1424 (1962).
[22] R. C. DeGeiso, L. G. Donaruma, and E. A. Tomic, J. Appl. Polym. Sci., 9, 411 (1965).
[23] F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Wiley-Interscience, New York, 1962.
[24] S. L. Davadov and N. A. Plate, Coord. Chem. Rev., 16(3), 195 (1975).
[25] H. S. Patel and S. R. Patel, J. Macromol. Sci.–Chem., A17(9), 1383 (1982).
[26] B. S. Patel, G. S. Choxi, and S. R. Patel, Makromol. Chem., 180(4), 1159 (1979); Chem. Abstr., 21557f (1979).

Accepted by editor March 10, 1984
Received for publication April 13, 1984