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Friedel-Crafts Polymers. 8. Friedel-Crafts Polycondensation of β-Resorcylic Acid or Resorcinol with p-Xylylene Dichloride, p,p'-Dichloromethyldiphenyl Ether, and p,p'-Dichloroacetyldiphenyl Ether

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ABSTRACT

Friedel-Crafts polycondensation of β-resorcylic acid (BRA) with p-xylylene dichloride (PXDC) or 4,4′-dichloromethyldiphenyl ether (DDE) in dioxane could be effected without simultaneous decarboxylation of BRA. The similar polycondensation of BRA with PXDC, DDE, or 4,4′-dichloroacetyldiphenyl ether (DADE) in nitrobenzene or in the absence of solvent at 150°C was associated with decarboxylation of BRA. Polymers having structures isomeric with those of the polycondensation product of BRA formed with subsequent in situ decarboxylation were prepared by Friedel-Crafts polycondensation of resorcinol with the above dichlorides. All the polymer samples were characterized, and those with related structures were compared. The ion-exchange properties of the polymer sample prepared from BRA and DDE in dioxane were studied.

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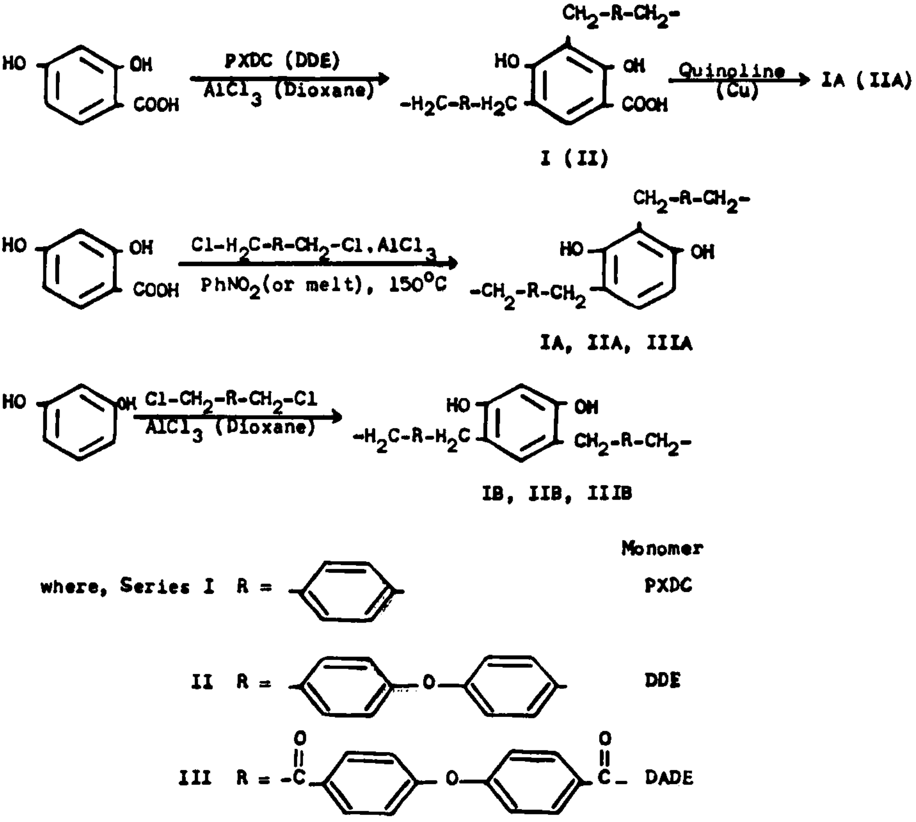
INTRODUCTION

In an earlier communication in this series it was reported that polycondensation of equimolar quantities of β-resorcylic acid (BRA) with p-xylylene dibromide in the presence of ferric chloride in dioxane, affording polymer sample designated as BRA-PXDB, could be effected without decarboxylation of BRA [1]. BRA is reported to undergo decarboxylation in the presence of an acid [2] or a base [3]. The unusual observation of acid-catalyzed polycondensation of BRA occurring without decarboxylation suggested that a study of other similar polycondensation reactions of BRA may provide some interesting information about the reaction. Hence the work described here was undertaken.

The polymerization reactions were effected by using equimolar amounts of the monomers and anhydrous aluminum chloride in dioxane



SCHEME 1.

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at 100°C, in the absence of solvent at 150°C, and in nitrobenzene at 150°C. The polycondensation of resorcinol with the dichloride monomers was effected by using equimolar amounts of the monomers and the catalyst under controlled conditions. These polymer samples were required for comparison with those of polymers of isomeric structure. All the polymer samples were characterized, and those of related structures compared. These reactions are formulated in Scheme 1. The chelating ion-exchange properties of the polymer sample prepared from BRA and DDE in dioxane were measured at various pH values in the presence of a fixed amount of $NaNO_3$ and compared with those of the polymeric ligand, BRA-PXDB, reported in the earlier communication [1].

EXPERIMENTAL

Materials

Resorcinol, anhydrous aluminum chloride, dioxane, and nitrobenzene were laboratory grade reagents. The solvents were purified by distillation. The monomers, viz., β-resorcylic acid (BRA) [4], p-xylylene dichloride (PXDC) [5], p,p'-dichloromethyldiphenyl ether (DDE) [6] and p,p'-dichloroacetyldiphenyl ether (DADE) [7], were prepared and purified by literature methods.

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Friedel-Crafts Polycondensation of BRA with PXDC in the Presence of Anhydrous Aluminum Chloride in Dioxane. Formation of I

The monomers PXDC (1.75 g, 0.01 mol) and BRA (1.54 g, 0.01 mol) were dissolved in dioxane (30 mL). A well powdered anhydrous aluminum chloride (1.33 g, 0.01 mol) was added with stirring to this solution. The reaction mixture was left for 1 h and heated at 100°C for 2 h. The cooled reaction mixture was poured into a stirred 1:1 water:HCL mixture (100 mL). The solid product was filtered and treated three times with boiling 20% HCl (50 mL) and then twice with boiling water (100 mL). The solid was filtered, washed, and dried in air. The dried solid was refluxed with petroleum ether (60-80°C) and filtered to give a yellow powder, soluble in DMF. The yield was 1.2 g. It was designated Sample I.

Following this procedure, BRA was polycondensed with DDE. The polymer, designated as Sample II, was formed in 80% yield. It is a yellow colored powder, partially soluble in DMF.

The polycondensation of BRA with DADE could not be effected by this method.

The decarboxylation of Samples I and II could not be effected completely by refluxing with 10% aqueous NaOH or 10% aqueous HCl. It could be decarboxylated by the well-known method [8, 9] described below.

Decarboxylation of Polymer Sample I

Polymer I (1 g) was suspended in quinoline (10 mL) containing a trace amount of copper powder and heated at 180°C for 3 h. The cooled reaction mixture was diluted with water (100 mL) and steam distilled. The solid was filtered by decantation. It was washed with boiling water and dried (Sample IA).

Sample II was also decarboxylated in a similar manner, affording Sample IIA.

Friedel-Crafts Polycondensation of BRA with DADE in Nitrobenzene

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This was carried out, as described above, with nitrobenzene (30 mL) as the solvent in place of dioxane. The reaction mixture was heated at 150°C for 3 h. Nitrobenzene was removed by steam distillation. The solid product was filtered and treated as described above. The product obtained was a brown solid. The yield was 1.0 g from 1.54 g BRA.

Following this procedure, BRA was condensed, respectively, with PXDC and DDE. In each case there was decarboxylation of BRA. None of these three polymer samples, designated as IA($PhNO_2$), IIA($PhNO_2$) and IIIA($PhNO_2$), exhibited a band around 1 650 cm^{-1} in its IR spectrum.

Friedel-Crafts Polycondensation of BRA with DADE in the Absence of Solvent at 150°C

The reaction was carried out using equimolar amounts of the monomers and anhydrous aluminum chloride at 150°C for 3 h. The reaction mixture was worked up in the manner described above. The yield was nearly 65%. The polymer sample is designated as IIIA(melt).

The polycondensation of BRA with PXDC and also with DDE was carried out in a similar manner, affording polymer samples IA(melt) and IIA(melt) in about 70% yield. None of these three polymer samples showed a band around 1 650 cm^{-1} in its IR spectrum.

Friedel-Crafts Polycondensation of Resorcinol with DDE

A mixture of DDE (1.19 g, 0.005 mol), resorcinol (0.55 g, 0.005 mol), and anhydrous aluminum chloride (0.66 g, 0.005 mol) in dioxane

(20 mL) was heated at 90°C for 1 h. The cooled reaction mixture was poured into a stirred 1:1 water:HCl mixture (100 mL). The solid was filtered and washed free from acid with boiling water. The resultant solid was allowed to dry and then thoroughly washed with benzene. The yellowish product weighed 0.8 g. It is designated as Sample IIB. Other polymer samples, viz., IB and IIIB, were prepared similarly by condensing resorcinol, respectively, with PXDC and DADE as described above.

Characterization for all the polymer samples are given in Table 1.

Apparatus and Methods of Characterization

IR spectra of the polymer samples were measured in KBr on a Perkin-Elmer IR spectrophotometer. The TGA was carried out using a Du Pont 950 TG Analyzer in air at a heating rate of 10°C/min. About 8-10 mg of the dried polymer sample was employed for TGA. For the estimation of the ion-exchange properties, the batch equilibration method developed by DeGeiso, Donaruma, and Tomic was adopted [10]. The rate of metal uptake under specified conditions and the distribution of various metal ions at different pH values were evaluated by their method [10].

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RESULTS AND DISCUSSIONS

Because of the probability of decarboxylation of BRA in an acid-catalyzed reaction [2], there are different possibilities in the Friedel-Crafts polycondensation of β-resorcylic acid with a dichloride monomer. The polycondensation may occur with or without decarboxylation. If decarboxylation occurs, it may be prior to, simultaneous with, or subsequent to polycondensation. The polycondensation of BRA with PXDC in dioxane affords a product I whose properties indicate that there was no decarboxylation. The polymer Sample I shows an IR band at 1 650 cm^{-1}, characteristic of C=O of a salicylic acid derivative [11]. The number-average molecular weight of this sample is estimated to be 1 300 ± 50 by nonaqueous conductometric titration [12]. Sample I was only partially decarboxylated when heated with 10% aqueous HCl or 10% aqueous NaOH. The relative intensity of the band at 1 650 cm^{-1} compared to that at 1 600 cm^{-1} of the so-treated polymer sample decreased very slowly with increasing time of refluxing with either 10% aqueous HCl or 10% aqueous NaOH. When Sample I was refluxed with quinoline in the presence of copper powder, there was complete decarboxylation as indicated by the absence of the band at 1 650 cm^{-1}.

Comparison of the IR spectrum of IA with that of IB (formed by Friedel-Craft polycondensation of resorcinol with PXDC) revealed that the two polymer samples are quite different. The points of linkage

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TABLE 1

Polymer designation	Monomer	Reaction conditions		Elemental analysis		TGA of polymer in air at 10°C/min, % weight loss at				
		Solvent	Reaction temperature, °C	% C	% H	200°C	300°C	400°C	500°C	600°C
I	BRA-PXDC	Dioxane	100	69.2	5.0	24	71	78	93	94
IA ($PhNO_2$)	BRA-PXDC	$PhNO_2$	150	76.2	5.5	-	-	-	-	-
IA (melt)	BRA-PXDC	-	150	76.3	5.6	-	-	-	-	-
IA	[a]			76.8	5.5	18	52	77	89	92
IB	RES-PXDC	Dioxane	100	71.1	5.5	4	13	71	74	76
II	BRA-DDE	Dioxane	100	71.8	4.4	22	66	83	95	98
IIA ($PhNO_2$)	BRA-DDE	$PhNO_2$	150	76.7	4.9	-	-	-	-	-
IIA (melt)	BRA-DDE	-	150	76.4	4.8	-	-	-	-	-
IIA	[a]			76.4	4.9	19	50	79	88	90
IIB	RES-DDE	Dioxane	100	77.7	4.9	4	30	72	80	84
IIIA ($PhNO_2$)	BRA-DADE	$PhNO_2$	150	71.2	4.4	38	65	82	90	93
IIIA (melt)	BRA-DADE	-	150	71.6	4.5	-	-	-	-	-
IIIB	RES-DADE	Dioxane	100	71.7	4.6	9	30	72	79	88

[a] Product of I (or II) decarboxylated with quinoline and Cu powder.

FIG. 1. IR spectra of polymers: (1) II, (2) IIB, (3) IIA.

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of bridges in the polymer chains in the polymer molecules of IA are positions 2 and 4 with respect to the resorcinol hydroxy group. In the polymer molecule of IB, such linkages would be in positions 4 and 6 i.e., para to the hydroxy group of resorcinol. In the IR spectrum of IB but not of IA, a band characteristic of aromatic isolated H atom is observed at 860 cm^{-1}. The polycondensation of BRA with PXDC in the absence of solvent at 150°C and in the presence of nitrobenzene at 150°C, respectively, afforded polymeric samples IA(melt) and IA($PhNO_2$), also without any absorption at 1 650 cm^{-1}. The IR spectra of IA(melt) and IA($PhNO_2$) resembled each other and also that of IA. This indicated that the polymerization of BRA with PXDC under both more vigorous conditions was followed by subsequent decarboxylation.

Exactly similar behavior is observed for the polycondensation of BRA with DDE. In dioxane at 100°C, it proceeded without decarboxylation of BRA, affording polymer Sample II, which showed a strong band at 1 650 cm^{-1} (Fig. 1). Sample II, on decarboxylation by the quinoline-Cu powder method, afforded IIA, whose IR spectrum differed characteristically from that of IIB formed on polycondensation of resorcinol with DDE. The IR spectra of IIA and of the polymer samples IIA($PhNO_2$) and IIA(melt) formed on polycondensation of BRA with DDE under the two more vigorous conditions resembled each other significantly.

Polycondensation of BRA with DADE did not occur in dioxane at 100°C, but did so under the above-mentioned more vigorous conditions, affording IIIA($PhNO_2$) and IIIA(melt). Their IR spectra resembled

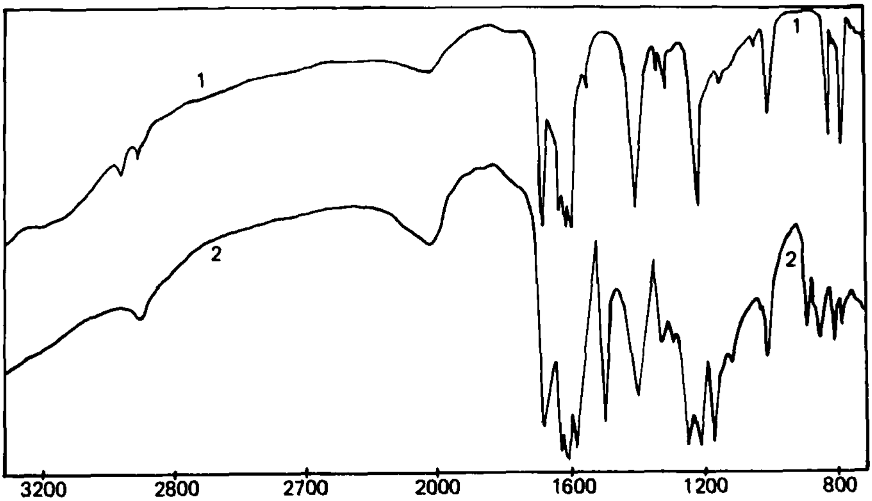

FIG. 2. IR spectra of polymers: (1) IIIB, (2) IIIA($PhNO_2$).

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each other and did not contain a band around 1 650 cm^{-1} and differed characteristically from that of IIIB formed on polycondensation of resorcinol with DADE (Fig. 2). The IR spectra of IIIA(melt),IIIA-$PhNO_2$), and IIIB show a strong band at 1 680 cm^{-1}, which is characteristic of a keto group in conjugation with an aromatic ring system. The C=O band appears at 1 680 cm^{-1} in the IR spectrum of the monomer DADE.

Examination of TGA data (Table 1) and of typical thermograms of polymer samples II, IIA, and IIB revealed that degradation occurred in a single step (Fig. 3). In each case the degradation was very rapid from 200 to 400°C. Comparison of the data for the Series I, II, or III reveals that the polymer prepared by polycondensation of resorcinol with dichloride was more stable than the other members of the series. Among polymers of Series I and II, the decarboxylation product IA (or IIA) was more stable than its parent I (or II).

Rate of Metal Uptake

The rate of uptake of various metal ions by Sample II is shown in Table 2. Examination of these data revealed that nearly 50% equilibrium was established in the first hour with Fe^{3+} ion. Fe^{3+} ions require slightly more than 4 h and the Co^{2+}, Cu^{2+}, and Ni^{2+} ions require slightly more than 5 h to reach equilibrium.

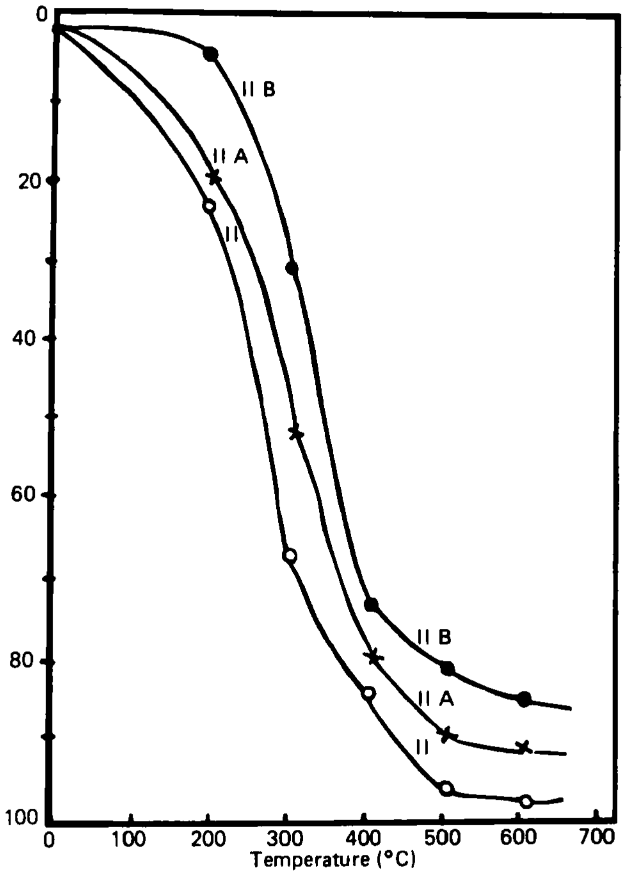

FIG. 3. TGA thermograms of polymers: (1) II, (2) IIB, (3) IIA.

Distribution Ratio of Metal Ions at Different pH Values

The data in Table 3 reveal that the distribution coefficient K_D for various metal ions increases with increasing pH. The selectivity of the polymeric ligand is higher for Fe^{3+} ion than that for the other ions in the order $Fe^{3+} > Ni^{2+} > Cu^{2+} > Co^{2+}$.

Earlier [1] it was shown that K_D for a given metal ion for polymeric ligands differing only in the size of the bridge decreases with increasing size of the bridge. Comparison of those data for the BRA-PXDB

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TABLE 2. Comparison of Rates of Metal Ion Uptake[a] at 30°C

Time, h	Percentage of the relative amount of metal ion uptake,[b] BRA-DDE II			
	Fe^{3+}	Cu^{2+}	Co^{2+}	Ni^{2+}
1/2	40	10	3	22
1	48	17	20	29
2	62	37	36	43
3	70	58	48	52
4	88	72	69	68
5	100	87	89	76
6	-	100	100	100

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

[b] Relative to equilibrium (100%).

TABLE 3. Distribution Ratio, K_D, as a Function of the pH at 30°C for BRA-DDE (II)

pH	Distribution ratio[a] of the ions[b]			
	Fe^{3+}	Cu^{2+}	Co^{2+}	Ni^{2+}
1.0	104	-	-	-
1.5	150	-	-	-
2.0	170	-	-	80
3.0	-	38	39	114
4.0	-	78	48	130
5.0	-	150	68	170
6.0	-	230	100	240

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

[b] Error ± 5%; $[M(NO_3)_2]$ = 0.1 mol/L, volume, 2 mL; $NaNO_3$ = 1 mol/L, volume, 40 mL; 24 h allowed for reaching equilibrium state.

polymeric ligand [1] with the corresponding data for polymeric ligand BRA-DDE (Sample II) supports the above conclusion. In experiments with BRA-PXDB [1], K_D for Fe^{3+} ion at pH 2.5 was reported to be 670 and for Cu^{2+}, Ni^{2+}, and Co^{2+} at pH 6 to be 295, 290, and 140, respectively. It can be seen that all the values for BRA-PXDB are significantly higher than the corresponding values for BRA-DDE, evidently due to the difference in the size of the bridges separating two consecutive BRA units in the polymer chains.

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