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Friedel-Crafts Polymers. 4. Friedel-Crafts Polycondensation of 4,4′-Dichloromethyldiphenyl Ether with Salicylic Acid, Salicylaldehyde, and o-Hydroxyacetophenone

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ABSTRACT

Polymers are prepared by condensing 4,4′-dichloromethyldiphenyl ether individually with salicyclic acid, salicylaldehyde, and o-hydroxyacetophenone in the presence of anhydrous aluminum chloride in dioxane. The polymer samples are characterized by elemental analysis, estimation of $\overline{M}_n$ by conductometric titration in pyridine, IR spectral study, and by TGA in air. Ion-exchanging capacities of these polymeric ligands for selected metal ions are measured by the batch equilibration method and compared.

INTRODUCTION

The present authors have reported on the synthesis and characteristics of Friedel-Crafts polymers prepared by self-polycondensation of 4,4′-dichloromethyldiphenyl ether (DDE) [1] and by polycondensation of DDE with benzene, toluene, and chlorotoluenes [2], and with xylenes [3]. The work described in the present communication deals with the synthesis of polymeric ligands based on

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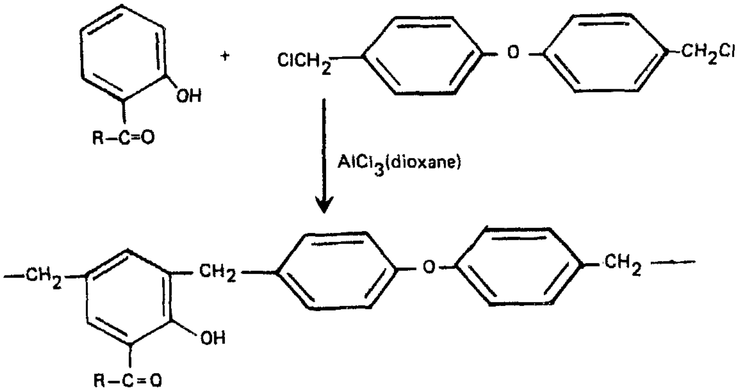
Friedel-Crafts polycondensation of DDE with salicylic acid (SA), salicylaldehyde (SAl), and o-hydroxyacetophenone (OHAC) in the presence of anhydrous aluminum chloride in dioxane and the study of their properties including estimation of number-average molecular weight. The main part of the study of these polymeric ligands is the measurement of their ion-exchanging capacities for selected metal ions and comparison of this property with those of polymeric ligands prepared from each of the above-mentioned 2-hydroxycarbonyl compounds with bridges like $-CH_2-$ and $-CH_2-CH_2$ separating the ligand units in the polymer chains. The latter type of polymeric ligands are prepared by condensation of the required hydroxycarbonyl monomer with formaldehyde [4], methylene dichloride [5], or ethylene dichloride under appropriate conditions [6]. There are no reports about the dependence of the ion-exchanging capacity of a polymeric ligand prepared from the same ligand functioning as monomer and the size of the bridge separating the ligand units in the polymer chains. In the polymeric ligand described in the present communication, both the nature of the bridge and its size have been altered. Ion-exchanging capacities of these polymeric ligands are measured by the application of the batch equilibration method developed by Degeiso et al. [4] and employed by other workers [7].



where R = OH in DDE-salicylic acid (DSA) polymer, H in DDE-salicylaldehyde (DSAl) polymer, and CH_3 in DDE-o-hydroxyacetophenone (DOHAC) polymer.

EXPERIMENTAL

The anhydrous aluminum chloride, dioxane, salicylic acid, salicylaldehyde, and o-hydroxyacetophenone used were laboratory grade reagents.

Materials

4,4'-Dichloromethyldiphenyl ether (DDE) was prepared by the method reported by Doedens and Rosenbrock [8] and modified by the present authors [1].

FRIEDEL-CRAFTS POLYCONDENSATION

Polycondensation of SA with DDE in the Presence of Anhydrous Aluminum Chloride Using Dioxane: Formation of DSA

A well-powdered anhydrous aluminum chloride (14.7 g, 0.11 mol) was added in small lots with stirring to a mixture of DDE (13.35 g, 0.05 mol) and salicylic acid (6.9 g, 0.05 mol) in dioxane (100 mL). The reaction mass was heated at 60°C for 3 h with continuous stirring. The reaction mixture was then heated at 90°C for 2 h and then at 100 °C for 1 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 colored solid thus obtained was dried and powdered. It was refluxed with petroleum ether (40-60° C) for half an hour. The polymer was a cream-colored powder. The yield was 12.5 g. The sample is designated as DSA.

Polycondensation of DDE was effected with salicylaldehyde (SAl) and o-hydroxyacetophenone (OHAC) in a similar manner. The polymer samples are designated as DSAl and DOHAC.

Apparatus and Methods of Characterization

Elemental analyses of the polymer samples were carried out on a Coleman Analyzer. The chlorine content of all the polymer samples was estimated by the Par-bomb method in triplicate.

The IR spectra were taken in KBr on a UR-10 IR Spectrophotometer.

The number-average molecular weight of all the three polymer samples was estimated by nonaqueous conductometric titration using a Metrohm Herisan Konductoskop E 365, following the details described by Patel et al. [9].

Thermogravimetric analysis (TGA) of the polymer samples was carried out on a Dupont 950 Analyzer in air at a heating rate of 10°C/min. The results are presented in Table 1.

Ion-Exchange Properties

Each of the air dried polymer samples DSA, DSAl, and DOHAC was gently ground. The powder, which could pass through a 100 mesh

TABLE 1. Characterization of Polymer Samples

Polymer designation	Elemental analysis			$\overline{M}_n \pm 30$ by conductometric titration	Thermogravimetric analysis in air at a heating rate of 10°C/min. Percent weight loss at a temperature of			
	C%	H%	Cl%		200°C	300°C	400°C	500°C
DSA	73.4	4.53	1.0	3430	10	14	20	40
DSAI	75.9	4.97	1.2	2730	2	8	10	16
DOHAC	96.9	5.1	1.3	2680	7	10	12	18

size sieve, was employed for the study of ion-exchanging capacity. In each of the experiments carried out for the present study, the poolymer sample was swollen under specified reaction conditions as described in the following experiments.

Study of the Effect of Various Electrolytes on the Metal Ion Uptake under Equilibrium Conditions at a Fixed pH

The polymer sample (25 mg) was suspended and stirred in an electrolyte solution (40 mL) of known concentration at the required pH for 24 h at 25°C. To this suspension of the swollen polymeric ligand, 2 mL of a 0.1 M solution of metal ion under study was added. The pH was adjusted and maintained at 5 for the study with Cu^{2+}, Co^{2+}, and Zn^{2+} ions and at 2 for the study with Fe^{3+} ion by adding the required amount of either 0.1 M HNO_3 or 0.1 M NaOH solution. The mixture was stirred at 25°C for 24 h and filtered. The solid was washed. The filtrate and the washings were combined and estimated for the metal ion content by titration against standard EDTA. A blank experiment was also carried out in the same manner without adding the polymer sample. The amount of the metal ion taken up by the polymer in the presence of a given electrolyte of known concentration is equal to the difference between the blank reading and the reading in the actual experiment. Such experiments were carried out in the presence of 0.01, 0.05, 0.1, 0.5, and 1.0 M solutions of electrolytes like NaCl, $NaNO_3$, $NaClO_4$, and Na_2SO_4. As a result of this study it was found that in the presence of 1.0 M $NaNO_3$ comparatively larger amount of metal ion is absorbed than in the presence of any other solutions of $NaNO_3$ and of all other electrolytes. Hence all other experiments for further study were carried out in the presence of 1.0 M $NaNO_3$.

TABLE 2. Comparison of the Rates of Metal (Mt) Ion Uptake[a]

Time (h)	Percentage of the relative amount of metal ion uptake[b]							
	DSA				DSAL		DOHAC	
	Cu^{2+}	Fe^{3+}	CO^{2+}	Zn^{2+}	Cu^{2+}	Fe^{3+}	Cu^{2+}	Fe^{3+}
0.5	12	60	21	8	18	37	17	33
1	21	70	42	16	36	45	55	55
2	33	75	73	33	50	60	68	66
3	41	80	79	58	64	73	76	72
4	54	90	84	83	75	80	86	83
5	83	100	100	100	89	100	93	100
6	100	-	-	-	100	-	100	-

[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+}, and Zn^{2+} = 5 and for Fe^{3+} = 2.

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

Evaluation of the Rate of Metal Ion Uptake

In order to estimate the time required to reach the state of equilibrium under given experimental conditions, a series of experiments of the type described above was carried out in which the metal ion taken up by the polymeric ligand was estimated from time to time to 25°C in the presence of 40 mL of 1 M $NaNO_3$ solution. It is reasonable to assume that under the given conditions, the state of equilibrium will be established in 24 h. The rate of metal uptake is expressed as the percentage of the amount of metal ion taken up after a certain time related to that at the state of equilibrium. These results are reported in Table 2.

Evaluation of Distribution of Metal Ions at Different pH Values

The distribution of each of the metal ions Cu^{2+}, Zn^{2+}, Co^{2+}, and Fe^{3+} between the polymeric ligand DSA and the aqueous phase at equilibrium was estimated in the presence of a 1-M $NaNO_3$ solution at 25°C at different pH values ranging from 1 to 5. Such a study was carried out for polymeric ligands DSAL and DOHAC with only Cu^{2+}

TABLE 3. Distribution Ratios D[a] of Different Metal Ions as a Function of the pH

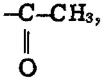
	Distribution ratio of the metal ions ± 5%							
	DSA				DSAL		DOHAC	
pH	Cu^{2+}	Fe^{3+}	Co^{2+}	Zn^{2+}	Cu^{2+}	Fe^{3+}	Cu^{2+}	Fe^{3+}
1	-	52	-	-	-	34	-	27
1.5	4	80	-	-	24	52	16	52
2	20	118	18	-	41	116	57	70
2.5	40	174	44	-	-	145	-	127
3	102	-	56	38	92	-	83	-
4	160	-	70	42	128	-	100	-
5	187	-	-	50	156	-	-	-

[a] D = mg of metal ions taken up by 1 g. of polymer divided by mg of metal ions present in 1 mL of solution at equilibrium. $[Mt(NO_3)_2]$ = 0.1 mol/L, volume 2 mL. $[NaNO_3]$ = 1 mol/L, volume 40 mL. 25°C. 24 h (equilibrium state).

and Fe^{3+} ions. Two independent experiments were carried out. An average of the two values was noted. These results are presented in Table 3.

RESULTS AND DISCUSSION

The polymer samples DSA, DSAl, and DOHAC are yellowish to dull white colored powders. Their number-average molecular weights are found to be 3430, 2730, and 2680, respectively. The observed values of Cl% of these polymer samples agree well with the values of Cl% calculated on the basis of $\overline{M}_n$ and assuming a linear structure with CH_2Cl as an endgroup. These polymer samples are insoluble in common organic solvents and also in aqueous alkali solution.

The important features of the IR spectrum (Fig. 1) of these polymer samples are a broad band extending from 3550 to 2700 cm^{-1} and the inflections in this broad band around 2825 and 2917 cm^{-1}. These inflections are attributed to symmetric and asymmetric stretching of CH of $-CH_2-$ bridges. The carbonyl bands at 1675, 1645, and 1629 cm^{-1} in the IR spectra of DSA, DSAl, and DOHAC are assigned to $-COOH$, $-CHO$, and  $-\underset{\overset{\|}{O}}{C}-CH_3$, respectively. A band at

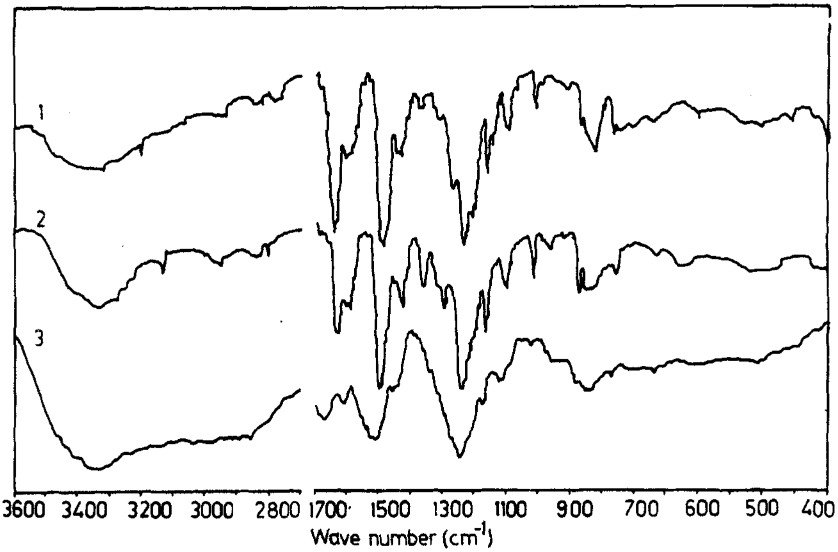


FIGURE 1.

1237 cm^{-1} and the one between 1165 to 1175 cm^{-1} are attributed to the ether linkage of diaryl ether. The bands at 875 and 825 cm^{-1} are assigned to the systems of isolated and two adjacent aromatic hydrogen atoms, respectively. The band at 670 cm^{-1} can be attributed to C–Cl of the CH_2Cl endgroup. Comparison of the results of the TGA of the three polymer samples reveals that the relative order of thermal stability of these polymer samples is DSA > DOHAC > DSA. These polymers lose 16, 18, and 40 wt%, respectively, when heated in air to 500°C.

Results of Ion-Exchanging Capacity

The data presented in Table 2 show that the rate of metal ion uptake by a given polymeric ligand depends on the nature of the metal ion. The order of the rate of metal uptake is Fe^{3+} > Cu^{2+} for all three polymer samples. The results of the study of the rate of uptake of CO^{2+} and Zn^{2+} metal ions by the DSA polymer sample reveal that both these metal ions require nearly equal time to reach the equilibrium state.

Examination of the results of the effect of pH on the amount of metal ions distributed between the two phases indicates that the relative amount of metal ions taken up by the polymeric material increases with an increase in pH of the medium, and the manner in which this happens depends both on the nature of the polymeric ligand and that of the metal ion under study. The trend in the values of the distribution ratio of a given metal ion under the given experimental conditions for different polymeric ligands is the same as the trend in the values of the stability constants of the same metal ion for the respective ligands forming repeat units in the polymeric ligands [10].

Comparison of the ion-exchanging capacities as revealed by the values of the distribution ratios of different polymeric ligands prepared from the same ligand monomer but having different types of bridges (e.g., $-CH_2-$, $-CH_2-CH_2-$ or $-CH_2-Ph-O-Ph-CH_2-$) separating the ligand units reveals that there is no regularity in the dependence of this property on the size and the length of the bridge [11-15].

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