Friedel-Crafts Polymers. 10. Polycondensation of 4-4'-Dichloromethlydiphenyl Ether with Phenol and Isomeric Cresols

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FRIEDEL–CRAFTS POLYMERS. 10. POLYCONDENSATION OF 4-4'-DICHLOROMETHLYDIPHENYL ETHER WITH PHENOL AND ISOMERIC CRESOLS

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ABSTRACT

Friedel-Crafts polycondensations of 4,4'-dichloromethyldiphenyl ether (DDE) with phenol and isomeric cresols were carried out under different experimental conditions. The molecular weight of the polymer products was estimated by end group analysis, that of soluble products by VPO, and they were characterized by TGA and solution viscosity. DMF solutions of samples prepared from phenol and p- and m-cresols, but not those from o-cresol, showed abnormal viscosity behavior. However, the viscosity behavior of DMF-water solutions was normal. Abnormal viscosity data of DMF solutions were correlated by an empirical relation. Curing of one fusible and soluble DDE-phenol polymer sample with hexamine was studied by measuring the percentage of cured material as a function of time at selected temperatures.

INTRODUCTION

Friedel-Crafts self-polycondensation of DDE [1] and polycondensation of DDE with benzene, toluene, isomeric xylenes, and chlorotoluenes as well as salicylic acid and β-resorcylic acid [2-5] were reported earlier in this series. The commercial Xylok resins are obtained by polycondensation of phenol

with arylyldihalide or diether [5-8]. Poly(phenylene ether)s (PPE) are known to be resistant to oxidation and self-extinguishing. Hence it was thought that a combination of the structural features of Xylok and poly(phenylene ether) in the same molecule might yield a group of polymers with better properties. With this in view, the synthesis and characterization of poly(oxyphenylene methylene phenol)s based on polycondensation of 4,4'-dichloromethyldiphenyl ether (DDE), with phenol and with three isomeric cresols was undertaken. For the sake of convenience, the polymers are designated as DDE-phenol polymers.

EXPERIMENTAL

The polycondensation of phenol or cresol with DDE [1] was carried out using monomers in equimolar proportions in the presence of anhydrous aluminum chloride (3 mol/mol phenol) 1) in the absence of solvent at room temperature, 2) in excess nitrobenzene, 3) in dioxane, and 4) in polyphosphoric acid, according to the details described in earlier communications [2, 3].

Polycondensation of DDE with Phenol in Dioxane under Milder Conditions

A mixture of DDE (5.3 g, 1 mol), phenol (1 g, 1 mol), and powdered aluminum chloride (1.7 g, 2 mol) was suspended in dioxane (40 mL), left for 1/2 h, and then heated at 100°C for 1/2 h. The cooled reaction mixture was poured with stirring into 1:1 water-HCl (100 mL). The solid product was collected, washed with water, and dried. The dried product was extracted twice with petroleum ether (50 mL) to remove unreacted DDE. It was a light yellow powder, fusing from 100 to 125°C. The yield was 5 g. It was completely soluble in MEK and dioxane. This polymer sample is designated as DDE-phenol(sol-1).

Polymer Fractionation

The polymer samples prepared in dioxane and under melt condition were fractionated as follows. Each was Soxhlet-extracted in turn with ethanol, acetone, MEK, and dioxane to give soluble Fractions 1, 2, 3, and 4, respectively, the order of the solvent power of these solvents having been decided by preliminary experiments. The residue which remained unextracted even by dioxane was labeled Fraction 5. Fraction 4 of each sample prepared in dioxane was employed for viscosity study, and Fraction 5 of each polymer

sample prepared under melt condition was employed for thermal study. The measurements of the properties were made as described earlier [1-5].

RESULTS AND DISCUSSION

All the polymer samples were light-colored solids, except those prepared in the melt, which were brownish. None of the samples nor their acetone, MEK, and dioxane-soluble fractions melted below 350°C. The samples prepared in PPA were insoluble in all solvents. Those prepared at room temperature in the absence of solvent were almost completely soluble in MEK and completely soluble in dioxane. The samples prepared in the melt contained a fairly large amount (20%) of the material insoluble in both MEK and dioxane. Those prepared in dioxane contained a small portion insoluble in MEK, a large portion soluble in dioxane, and a very small portion insoluble in dioxane. Only DDE-phenol(sol-1) dissolved completely in MEK and dioxane and fused below 125°C. This sample was employed for the curing study.

The C and H contents of all the polymer samples agree reasonably with those predicted on the basis of the structure of the repeat unit. The agreement between the $\bar{M}_n$ values of the soluble polymer samples obtained by endgroup analysis (EGA) and by VPO supports the assumption made for the endgroup analysis, viz., linear structure of the polymer molecule with a CH_2Cl group at one end. Table 1 reveals that, for all samples prepared in dioxane, $\bar{M}_n$ estimated by VPO is lower than that estimated by endgroup analysis, evidently because the samples dissolve incompletely in dioxane.

Table 1 also reveals the influence of reaction conditions on $\bar{M}_n$ of the polymeric products prepared from the same pair of monomers. In each case the sample prepared in PPA has the highest $\bar{M}_n$ and that prepared at room temperature in the absence of solvent has the lowest $\bar{M}_n$. From the values of $\bar{M}_n$ of polymers prepared from the four phenols and DDE under similar conditions, it is concluded that the reactivity order in the polycondensation is p-cresol > m-cresol > o-cresol > phenol.

The IR spectra of the polymer samples prepared from the same pair of monomers under different conditions were found to be identical. All of them contained the expected characteristic bands: a weak broad band extending from 3650 to 3300 cm^{-1} with a maximum around 3400 cm^{-1}, which is characteristic of bonded —OH groups; bands characteristic of the aromatic and aliphatic C—H stretching at expected positions; bands characteristic of diphenyl ether [9]; a sharp band indicative of the presence of aromatic isolated H atom around 860 cm^{-1}; and a band at 835 and/or 825 cm^{-1} characteristic of two adjacent H atoms.

TABLE 1. Characterization of Polymer Samples

Sample[a]	Elemental analysis			$\bar{M}_n$[b]	
	C %	H %	Cl %	EGA	VPO
DDE-phenol(solid)	82.8	4.6	2.8	1250	1300
DDE-o-cresol(solid)	83.8	5.8	2.3	1550	1600
DDE-m-cresol(solid)	83.7	5.9	2.0	1800	1900
DDE-p-cresol(solid)	84.0	6.0	1.6	2200	2300
DDE-phenol(melt)	82.1	5.5	2.6	1350	—
DDE-o-cresol(melt)	82.9	5.4	2.2	1600	—
DDE-m-cresol(melt)	83.4	5.7	1.4	2500	—
DDE-p-cresol(melt)	83.7	5.6	1.2	2950	—
DDE-phenol(sol-1)	82.0	5.9	3.5	910	950
DDE-phenol(sol)	82.4	6.1	2.1	1700	1600
DDE-o-cresol(sol)	83.8	6.7	1.9	1900	1750
DDE-m-cresol(sol)	83.7	6.8	1.3	2700	2600
DDE-p-cresol(sol)	83.9	6.7	1.2	2950	2800
DDE-phenol(PPA)	82.0	5.2	1.1	3300	—
DDE-o-cresol(PPA)	83.2	5.9	0.9	3950	—
DDE-m-cresol(PPA)	83.5	5.7	0.8	4450	—
DDE-p-cresol(PPA)	83.7	5.8	0.7	5100	—

[a]Conditions: Reaction at room temperature in the absence of solvent (solid); under molten conditions at $150°C$ (melt); in dioxane (sol), and in polyphosphoric acid (PPA).

[b]Estimated error: ±50.

TABLE 2. Solution Viscosity in Different Solvents at 135°C

	$[\eta]$, dL/g		Parameters of Eq. (1) for DMF solutions	
Sample	Dioxane	DMF-water (93.8:6.2 w/w)	A	B
DDE-phenol(sol-4)	0.135	0.105	0.037	0.110
DDE-p-cresol(sol-4)	0.295	0.151	0.042	0.202
DDE-m-cresol(sol-4)	0.285	0.146	0.04	0.190
DDE-o-cresol(sol-4)	0.205	0.122	-0.05	0.255

Suthar [10] observed that solutions of phenol-formaldehyde resins prepared from phenol and isomeric cresols and chlorophenols behave normally in dioxane solutions and show weak polyelectrolyte behavior in DMF solutions with two exceptions. Solutions of o-cresol-formaldehyde and o-chlorophenol-formaldehyde resins in DMF were reported to behave normally [10]. The explanation offered by some authors is that these resins are polyphenols and that their solutions in basic solvents, like DMF, behave as weak polyelectrolytes [5, 10, 11]. According to them, a type of steric effect operates for o-cresol (o-chlorophenol)-formaldehyde polymers that forces them to behave normally in DMF solution. An exactly similar type of behavior is observed for the present polymers.

The dioxane solutions of the four polymer samples listed in Table 2 show normal viscosity behavior. The reduced viscosities of their solutions in DMF, except that of DDE-o-cresol(sol-4), decrease with increasing concentration. The resemblance of this behavior to that of phenol-formaldehyde resins [10] is quite obvious. The intrinsic viscosity of the solution of DDE-o-cresol(sol-4) in pure DMF was 0.186 dL/g.

It is well known that the polyelectrolyte behavior of polymers is suppressed and/or that normal behavior is restored by increasing the solvent power [12], e.g., by the addition of water. In the present case, DMF-water mixtures were used to prepare solutions of DDE-phenol(sol-4), and these were found to show normal viscosity behavior. Extrapolation of the results (shown in Fig. 1) to 0.0 wt% water gave 0.143 dL/g for the hypothetical intrinsic viscosity of DDE-phenol(sol-4) in pure DMF on the assumption that this polymer would behave
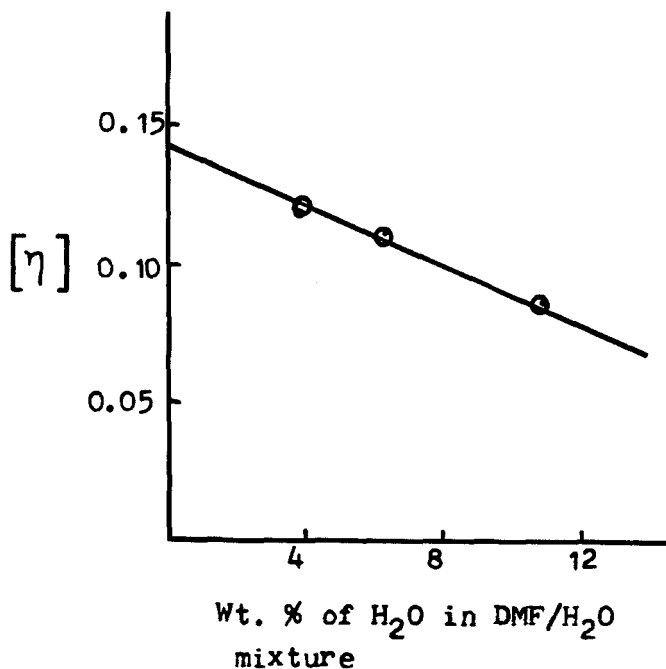
FIG. 1. Intrinsic viscosity of DDE-phenol(sol-4) in DMF/H$_2$O mixtures.

normally in pure DMF. The intrinsic viscosities of the other three polymers in one DMF-water mixture are presented in Table 2.

The viscosity parameters of certain solutions exhibiting polyelectrolyte behavior can be correlated linearly with appropriate concentration functions through empitical relations [13, 14], the simplest of which is that employed by Fuoss and Cathers [13]:

$$\eta_{sp}/\sqrt{C} = A + B\sqrt{C} \qquad\qquad (1)$$

Such plots are shown in Fig. 2. The values of A and B (Table 2) were estimated by linear regression (correlation coefficients 99.5 or more). Interestingly, the value of A is negative for DDE-o-cresol(sol-4) in DMF; it behaved normally in the viscosity experiments.

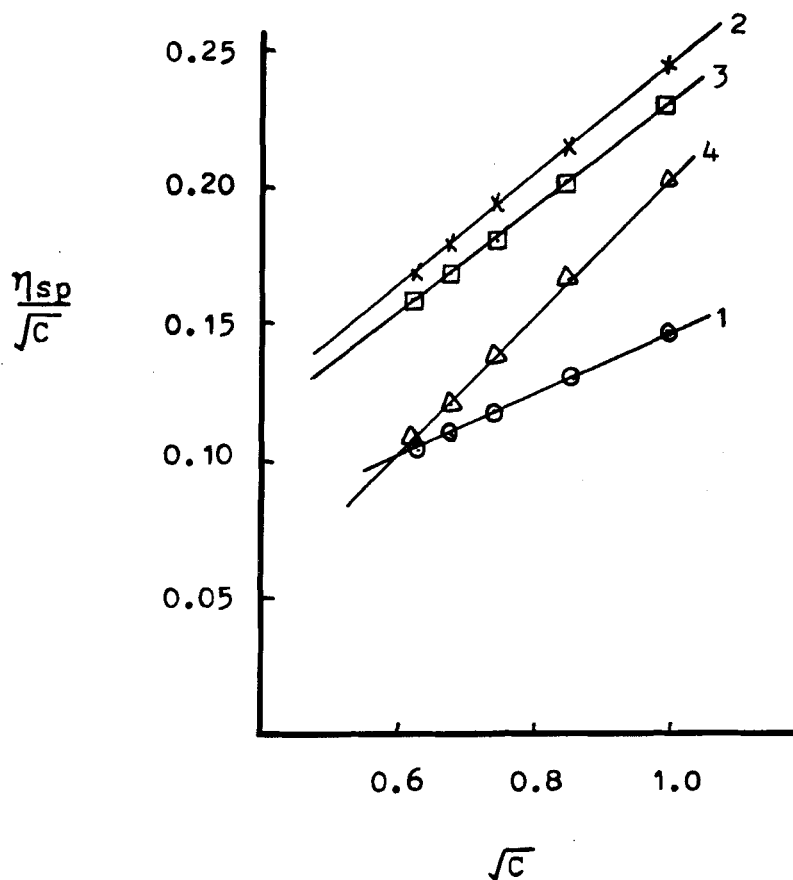The curing of DDE-phenol(sol-1) was studied at 150, 170, and 190°C by

$$\frac{\eta_{sp}}{\sqrt{c}}$$

FIG. 2. Fuoss-Cathers plot: (1) DDE-phenol(sol-4), (2) DDE-p-cresol-(sol-4), (3) DDE-m-cresol(sol-4), (4) DDE-o-cresol(sol-4).

heating an intimate mixture of the sample with 12 wt% hexamethylene tetramine for different time periods [15, 16]. The fractions of cured material (dioxane unextractable) were estimated and showed that DDE-phenol(sol-1) cured almost completely at 190°C in about 10 min.

Examination of the thermograms (Table 3) revealed that all the polymer samples degrade in a single step and that DDE-p-cresol(melt-5) is distinctly more stable than the other (melt-5) samples. It was also observed that the

TABLE 3. TGA of Selected Samples in Air (or CO_2) at a Heating Rate of 10°/min

Sample	Atmo-sphere	Loss, wt% at °C						
		200	300	400	500	600	700	800
DDE-p-cresol(melt-5)	Air	10	10	17	26	36	54	68
DDE-p-cresol(melt-5)	CO_2	4	4	5	18	32	46	50
DDE-p-cresol(PPA)	Air	10	10	26	60	70	80	90
DDE-p-cresol(PPA)	CO_2	3	6	8	14	28	50	65
DDE-phenol(melt-5)	Air	7	10	16	32	50	62	73
DDE-m-cresol(melt-5)	Air	12	16	16	29	45	57	65
DDE-o-cresol(melt-5)	Air	8	110	16	29	46	63	75
DDE-phenol(sol-1)	Air	24	26	30	44	72	78	83
Cured product of DDE-phenol(sol-1)	Air	10	18	19	27	38	43	58

weight loss in air is more than that in CO_2. The cured DDE-phenol(sol-1) sample was found to be thermally more stable up to 700°C than the parent sample.

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