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NOTE
FRIEDEL-CRAFTS POLYMERS. 11. FRIEDEL-CRAFTS POLYMERS FROM 4,4'-DICHLOROMETHYLDIPHENYL ETHER AND CHLOROPHENOLS

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INTRODUCTION

Friedel-Crafts polymers formed on polycondensation of 4,4'-dichloromethyldiphenyl ether (DDE) with benzene, toluene, isomeric chlorotoluenes and xylenes, phenol, and isomeric cresols have been reported [1-4]. The synthesis and characterization of polymers formed on condensation of chlorophenols with DDE are described in the present communication.

EXPERIMENTAL

Friedel-Crafts Polycondensation

Polycondensation was effected in the manner described earlier [1-4] by heating a mixture of the required chlorophenol (0.01 mol), DDE [5] (0.01 mol), and anhydrous aluminum chloride (0.03 mol) under various conditions. The polymer samples are designated in the manner shown in Table 1 so as to suggest the names of the monomers (DDE and *p*-, *o*-, or *m*-chlorophenol) and the reaction conditions.

TABLE 1. Polymer Designation and Characterization

Polymer sample	Dioxane-insoluble portion, %	Properties of the dioxane-soluble fraction		
		Cl, %	$\bar{M}_n$(EGA)[a]	$\bar{M}_n$(VPO)[b]
DDE-pClPh (solid)	3	14.3	900	950
DDE-pClPh (sol)	20	13.3	1300	1250
DDE-pClPh (melt)	25	12.4	2200	2100
DDE-pClPh (PPA)[c]	100	–	–	–
DDE-oClPh (solid)	4	13.6	1200	1250
DDE-oClPh (sol)	25	13.0	1500	1450
DDE-oClPh (melt)	50	12.9	1600	1550
DDE-oClPh (PPA)[c]	100	–	–	–
DDE-mClPh (solid)	5	13.2	1400	1350
DDE-mClPh (sol)	18	13.0	1500	1400
DDE-mClPh (melt)	24	12.9	1600	1500
DDE-mClPh (PPA)[c]	100	–	–	–

[a]By end-group analysis; ± 100.
[b]By vapor-pressure osmometry, ± 100.
[c]These samples are insoluble in all solvents and contain 4.5 to 5.0% chlorine.

Measurements

The characterization of the polymer samples was carried out as described earlier [1-4]. The solubility of these polymer samples in ethanol, acetone, MEK, and dioxane was found to increase in the stated order. The DDE-ClPh (solid) samples dissolve largely in ethanol, completely in acetone and MEK, and quite freely in dioxane. The DDE-ClPh (melt) samples are almost insoluble in ethanol, partly soluble in acetone and MEK, and 70-75% soluble in dioxane. The DDE-ClPh (sol) samples showed a slightly higher solubility in these solvents than the corresponding DDE-ClPh (melt) samples. Polymer samples prepared with PPA as the reaction medium are insoluble in all solvents. The solubility properties of the polymers described here are almost the same as those of the DDE-cresol and DDE-phenol polymers reported earlier [4].

The DDE-ClPh (sol) samples were fractionated into ethanol-soluble (Fraction 1), acetone-soluble (Fraction 2), MEK-soluble (Fraction 3), dioxane-soluble (Fraction 4), and dioxane-insoluble (Fraction 5) by Soxhlet extraction of 1 g of each sample in turn by these solvents in the above order. Fraction 4 of each sample had $\bar{M}_n$ from 2200 to 2400 and $[\eta]$ in dioxane at 35°C of ~0.12 dL/g.

The number-average molecular weights of all the polymer samples freed of dioxane-insoluble material by Soxhlet extraction with dioxane, and of Fraction 4 of the three DDE-ClPh (sol) samples, were measured by VPO and also by end-group analysis based on the chlorine content by assuming a linear polymer molecule with a $-CH_2Cl$ group on one end. The results are presented in Table 1.

RESULTS AND DISCUSSION

All the polymer samples are colored solids. The fact that the $\bar{M}_n$ values estimated by VPO and EGA agree suggests that the dioxane-soluble polymer molecules have linear structures though the insoluble fractions, which have very low chlorine contents, may contain crosslinked molecules. The crosslinking would be brought about by intermolecular Friedel-Crafts polycondensation between linear polymer molecules through DDE [2]. The results reported here and earlier [4] reveal that the high reactivity of DDE in Friedel-Crafts polycondensations causes all the phenols to exhibit nearly similar reactivity.

The DMF solutions of Fraction 4 obtained from the DDE-pClPh (sol) and DDE-mClPh (sol) samples showed weak polyelectrolyte behavior, but that of Fraction 4 of the DDE-oClPh (sol) sample behaved normally. Abnormal viscosity behavior has been observed for DMF solutions of polyphenols [4, 6, 7]. It was further observed that the viscosity data for DMF solutions of Fraction 4 of DDE-pClPh (sol) can be correlated by the empirical relation

$$\eta_{sp}/c^{1/2} = A + Bc^{1/2},$$

proposed by Jones and Dole [8] for polymer solutions exhibiting polyelectrolyte behavior. The constants A and B were found to be 0.032 and 0.07, respectively.

The TGA of Fraction 4 of the three DDE-ClPh (sol) samples was carried out in air at a heating rate of 5°C/min, and that of only one such fraction was carried out in CO_2 at the same heating rate. Examination of the thermograms reveals that these samples start degrading above 175°C and degrade nearly

completely above 800°C. They all suffer 50% weight loss between 500 and 600°C. Comparison of the TGA data of Fraction 4 of DDE-pClPh (sol) in air and in CO_2 at the same heating rate reveals that the sample loses only about 47% of its weight at 800°C in CO_2 as against 84% in air at 800°C. Comparison of the TGA data revealed that the DDE-chlorophenol polymers reported here are less stable than the DDE-phenol and DDE-cresol polymers reported earlier [4].

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