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Friedel-Crafts Polymers. I. Self-Polycondensation of 4,4′-Dichloromethyldiphenyl Ether

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ABSTRACT

Friedel-Crafts self-polycondensation of 4,4′-dichloromethyldiphenyl ether (DDE) is studied under various experimental conditions. These polymer samples are infusible and are insoluble in all solvents. The polymer samples, PDs, are characterized by elemental analysis, IR spectral study, and by TGA. Polymer reaction products of one polymer sample are prepared by subjecting it to Friedel-Crafts reaction with excess benzene and by treating it with triethylamine. Both the polymer reaction products are found to be less stable than the parent polymer sample.

INTRODUCTION

Friedel-Crafts self-polycondensation of benzyl chloride is reported to yield a cross-linked and infusible polyphenylene methylene which is insoluble in common solvents [1]. Such polymerization reactions, starting respectively with 1,4-dichloromethyl benzene, 1,4-dichloromethyl-2,5-dimethylbenzene and 1,3-dichloromethyl-4,6-dimethylbenzene, are reported to yield insoluble and infusible polymer [2]. The polymers prepared from 1,4-dichloromethyl-2,5-dimethyl benzene are reported to have dihydroanthracene unit in the repeat unit of the polymer chains [2]. Besides anhydrous aluminum chloride, other Lewis acids like $SnCl_4$, $TiCl_4$, and $FeCl_3$ have also been employed in these Friedel-Crafts self-polycondensation reactions [2].

Oshima [3] studied the Friedel-Crafts polycondensation reaction of 4,4'-dichloromethyldiphenyl ether (DDE) using benzene, toluene, hexane, bromobenzene, and nitrobenzene as solvents and using various catalysts in molar proportions. The author has reported that DDE affords 4,4'-dibenzyldiphenyl ether and 4,4'-di-p-tolyldiphenyl ether when the reaction was carried out in the presence of a large excess of benzene and toluene, respectively. The author also reported that the reaction of DDE in the presence of a large excess of bromobenzene afforded a polymeric product containing a very low amount of bromine. It is also reported that in the reaction of DDE in the presence of a large excess of hexane and nitrobenzene, a polymeric product containing around 1% Cl is formed. Oshima reports that the polymers formed in these cases are self-polycondensation products containing a chlorine atom as an endgroup. No further report is made about the nature of these products [3].

The present communication deals with a systematic study of the Friedel-Crafts self-polycondensation reaction of DDE. The reaction was studied in the absence of any solvent at room temperature and at 90-100°C in the presence of solvents like carbon disulfide and dioxane. It is observed that the reaction failed when carried out in the absence of any solvent at 0°C and also when carried out using dioxane as solvent at temperatures up to 100°C. The reaction also failed when it was carried out in the presence of PPA at room temperature. Under all the other conditions the reaction proceeded successfully, affording insoluble and infusible polymer samples. These polymer samples are characterized by elemental analysis, IR spectral study, and study of thermal behavior in CO_2 and in air by TGA.

EXPERIMENTAL

Anhydrous aluminum chloride, dioxane, carbon disulfide, diphenyl ether, and other common chemicals used were laboratory-grade reagents.

Material Synthesis

4,4'-Dichloromethyl Diphenylether (DDE)

DDE was prepared by a method suggested by Doedens and Rosenbrock [4] with modifications.

To a well-stirred homogeneous mixture of diphenyl ether (8.5 g), concentrated hydrochloric acid (20 mL), glacial acetic acid, and finely powdered parafamaldehyde (4.5 g), concentrated sulfuric acid (8 mL) was added dropwise over a period of 1.5 h at room temperature. The reaction mixture was then refluxed with stirring on a boiling water bath for 2 h. The cooled reaction mixture was diluted with water (300 mL). The liquid layer was separated from the aqueous layer and washed repeatedly with water and finally extracted with chloroform. The chloroform extract was dried over anhydrous sodium sulfate. Chloroform was distilled off on a water bath. The product in the form of an orange syrup was washed with a small amount of petroleum ether (40-60°C). On cooling in an ice bath, the product turned into a crystalline solid. The solid was vacuum-filtered to squeeze out the adhering liquid containing a mixture of isomers. The solid product was crystallized from ether in the form of white needles, mp 57°C. The yield of the monomer was 45%, and the melting point reported in the literature varies from 52 to 68°C. The product was characterized by oxidizing it to diphenyl ether-4,4'-dicarboxylic acid, mp 331°C [5].

Self-Polycondensation of DDE at 30°C (PD1)

A mixture of 2.0 g DDE and 3.0 g powdered anhydrous aluminum chloride was left at 30°C for 4 h with frequent stirring and decomposed with an ice-cooled concentrated HCl:H_2O (1:1) mixture (100 mL). The solid product was stirred in a 10% HCl solution (100 mL), filtered, and washed with water. It was stirred in acetone (100 mL) for 4 h and the solid was filtered. The solid was treated twice in the same manner with acetone. The acetone extracts were collected. The acetone-insoluble portion, designated as PD2, was a white powder (1.2 g). It was insoluble in all the common organic solvents. It did not melt up to 360°C. The mixed acetone extracts on evaporation left a yellow-colored residue (0.5 g). This sample was treated with excess ether. It is designated as PD1.

When this reaction was carried out in the manner described above at 0°C, the reaction failed.

Self-Polycondensation of DDE at 100°C (PD3)

A mixture of 5.2 g DDE and 8.0 g finely powdered anhydrous aluminum chloride was heated at 100°C for 4 h and worked up in the manner described above. There was no acetone-soluble portion in the product. It was a white powder which did not melt up to 360°C. The yield was 4.6 g. The product was insoluble in acetone, MEK, dioxane, and DMF. The product simply swelled on standing either in dioxane or DMF for a long time.

Self-Polycondensation of DDE at 180-90°C (PD-melt)

A mixture of 2.6 g DDE and 4.0 g well-powdered anhydrous aluminum chloride was heated at 180-190°C for 4 h. The reaction mixture was worked up as described above. The polymer formed was a brown powder. The yield was 2.2 g. This polymer sample is designated as PD-melt. It is insoluble in the common organic solvents. It did not melt up to 360°C.

Self-Polycondensation of DDE in CS_2 PD(SO1)

A suspension of 2.6 g DDE and 4.0 g finely powdered anhydrous aluminum chloride in 50 mL CS_2 was heated on a boiling water bath for 3 h. The reaction mixture was decomposed by ice (100 g) and HCl (5 mL) and left aside to allow CS_2 to evaporate. The solid was filtered and washed with water. The dried solid was washed repeatedly with acetone and finally refluxed in dioxane (50 mL) and filtered. There was no acetone-soluble portion in the product. The polymer was a white powder. The yield was 1.5 g. It was insoluble in all common organic solvents. It did not melt up to 360°C.

This reaction was studied in the manner described above using dioxane as a solvent at temperatures ranging from 30° to 100°C. It was observed that the reaction failed and DDE was recovered.

Treatment of Polymer Sample PD3 with Benzene in the Presence of Anhydrous Aluminum Chloride. Formation of PD3-C_6H_6

A mixture of 0.5 g of the polymer sample PD3 and 0.5 g of anhydrous aluminum chloride was stirred in dry benzene (10 mL) and refluxed at 90°C for 3 h. The mixture was decomposed with a concentrated HCl:water mixture (20 mL). The residue was filtered and washed with water. The dried powder was repeatedly washed with boiling acetone and filtered. It was a dark-colored solid which did not melt up to 360°C. The sample is designated as PD3-C_6H_6. This sample contained 9.3% Cl. This loss in Cl% is due to the reaction with benzene and also due to the additional cross-linking as a result of an intermolecular Friedel Crafts reaction.

Treatment of PD3 with Triethylamine: Formation of PD3-NEt_3

A mixture of 0.5 g polymer sample PD3 and 5 mL triethylamine was refluxed at 80°C for 3 h and poured in water (50 mL). The solid was filtered, washed with boiling water, and finally with boiling acetone. It did not melt up to 360°C. This sample contained 4.7% N and 2.6% Cl.

Methods of Study

IR spectra of all the polymer samples were scanned in KBr on a Beckman Model-4420 IR spectrophotometer. (Fig. 1.)

The thermogravimetric analysis was carried out in CO_2 and in air using a Dupont 950 Thermogravimetric Analyzer. The sample for TGA was heated at 70°C for 24 h. The amount of polymer used in all the experiments was 10 mg.

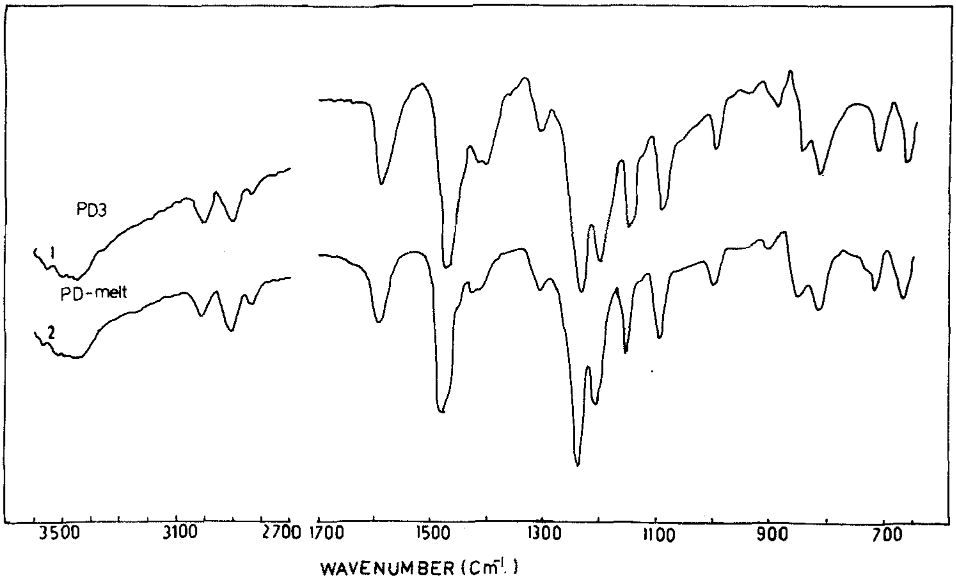


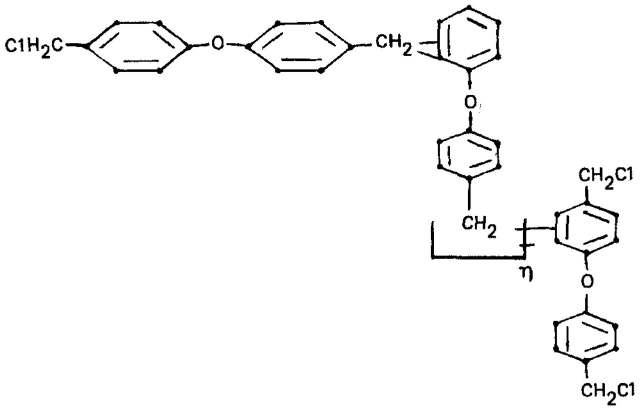
FIGURE 1.

RESULTS AND DISCUSSION

The PD samples, prepared under all conditions ranging from very mild to comparatively more vigorous conditions, are infusible and, with the exception of polymer sample PD1, are all insoluble. The intrinsic viscosity of the soluble polymer sample PD1 at 30°C was found to be 0.03 dL/g in acetone solution. The IR spectra of all the polymer samples exhibit bands at 1590, 1475, and 1450 cm^{-1}, characteristic of aromatic double bond, at 2820 and 2890 cm^{-1}, characteristic of bridge $-CH_2-$ groups, and at 1235 and 1150 cm^{-1}, characteristic of aromatic ether linkage. A band at 670 cm^{-1} is characteristic of C–Cl stretching. The bands appearing at 890 and 820 cm^{-1} are characteristic of aromatic isolated H and two adjacent H atoms, respectively. All the polymer samples contain around 72.5% C and 14.4% Cl; the actual value would depend on the nature of the polymer sample. On the basis of these data, an attempt was made to arrive at the possible structure of the polymers reported here.

Possible Structure

There are two ways in which PD formation can occur. One can consider a simultaneous participation of both the CH_2Cl groups of monomer moiety in the first propagation step and of the monomer moiety forming the endgroup of the growing polymer chain in the subsequent propagation steps. This is ruled out on the grounds that the simultaneous participation of two $-CH_2Cl$ groups is an improbable event and the product formed by such a reaction would contain a very low percentage of Cl. All the PD samples contain around 14% of chlorine. It is possible that in the initial stage a linear polymer is formed by Friedel-Crafts polycondensation between CH_2Cl of the monomer unit or of the growing chain with the active positions ortho to ether linkage on the combining DDE monomer. On the basis of this consideration, a product with linear structure in which each repeat unit has one $-CH_2Cl$ group could result. Considering the possibility of such a structure and assuming various values for the average degree of polymerization, the values of C% and Cl% were calculated. It can be seen that if $P < 15$, C% would be 72.12 but Cl% would be 16.24%. On the basis of observed C%, it was inferred that the average degree of polymerization of the polymer sample is around 15 or even more. But there is a conspicuous difference between the observed Cl%, which is around 14.4%, and the calculated Cl%, which is 16.24%. The properties of the polymer samples, viz., insolubility and infusibility, suggested that there must be sparse cross-linking between polymer chains. Assuming that the average number of cross-links is between 1 to 4 per 15 repeating units, the % Cl was calculated. It was found that if, on an average, 4 cross-links are assumed per polymer chain comprising on an average 15 repeat units, the calculated Cl% would come to a value (14.4%) which is very nearly the same as the observed values of Cl%.



[Possible crosslinking not shown]

The intermolecular cross-linkings may be due to Friedel-Crafts reaction between the $-CH_2Cl$ groups of the repeat unit of one polymer chain and the active position, most probably ortho to the ether linkage, on the repeat unit of another polymer chain. The cross-linking can as well be brought about through the agency of a DDE molecule participating in the Friedel-Crafts reaction between active positions on two vicinal polymer chains. It is possible that the structure can be even more complicated than the one described here. The IR spectral data indicating the presence of both isolated and two adjacent aromatic hydrogen atoms can be explained on the basis of the proposed structure. According to the proposed structure, there would be three types of ether linkages, unsubstituted, monosubstituted, and disubstituted, on position(s) ortho to the ether linkage. An attack on a position ortho to methylene cannot be ruled out during propagation or during cross-linking. Such a cross-linking will, however, be much less facile than the cross-linking due to reaction with a position ortho to the ether linkage.

Examination of the results of TGA of polymer samples in CO_2 reveals that all the polymer samples lose around 40% of their weight when heated up to 800°C at the rate of 10°C/min. However, the polymer sample PD-melt-1 synthesized around 180°C suffers comparatively much lower weight loss at all temperatures up to 600°C than the other three samples reported in Table 1. It has been found that the polymer sample PD3 loses nearly 40 and 93% of its weight when heated in air up to 500 and 600°C, respectively, at the rate of 10°C/min.

In the absence of reports about the thermal stability of related polymers under identical conditions, it is difficult to compare the thermal stability of the polymers reported in the present communication with that of polymers of related structures. Real linear polyphenylene methylene is reported to be less stable than polyphenylene ethers [6]. According to one report, polyphenylene ether samples are stable in air up to a temperature around 450°C [6]. Polyphenylene methylene samples with a cross-linked structure are reported to lose half their weight when heated in vacuum at 500°C [7]. A comparison with these data reveals that the polymers reported in the present communication are less stable then polyphenylene ethers and more stable than the polyphenylene methylenes.

The polymers reaction product PD3-C_6H_6, formed by reaction of the polymer sample PD3 with benzene under Friedel-Crafts conditions, contains about 4% less chlorine than the parent polymer sample. The IR spectrum of PD3-C_6H_6 exhibits bands at 690 and 730 cm^{-1}, characteristic of a phenyl group. The latter type of group is introduced by replacement of some of the end Cl groups in a Friedel-Crafts polymer reaction. The TGA of the PD3-C_6H_6 sample reveals that it suffers around 57% weight loss when heated up to 500°C and in this respect it is less stable than the parent polymer sample.

The polymer reaction product PD3-NEt_3, formed on treating the

TABLE 1. Self-Condensation Polymers and Their Characterization

Polymer designation	Reaction conditions		Elemental analysis				Thermogravimetric analysis % wt. loss at (°C)						
	Reaction temperature (°C)	Reaction time (h)	C%	H%	Cl%	Medium	200	300	400	500	600	700	800
PD1	28-30 (acetone soluble)	4	72.5	5.4	15.2	CO_2	-	6	15	17	32	37	40
PD2	28-30 (acetone insoluble)	4	72.7	5.2	14.2	CO_2	-	2	14	19	28	37	43
PD3	100	4	72.0	5.8	14.4	CO_2	3	8	15	19	33	40	44
PD melt	180-190	4	72.4	4.5	14.5	CO_2	2	5	5	10	19	30	40
PD3						Air	11	15	20	40	93		
PD3 C_6H_6						Air	29	40	44	57	95		
PD3 NEt_3						Air	27	35	44	81	97		

parent polymer sample PD3 with triethylamine, exhibits a band around 1365 cm^{-1}, characteristic of C–N in the IR spectrum. It is found to contain 2.6% Cl and 4.7% N. The parent polymer sample contained 14.4% Cl. It can be shown that the percent molar mass decrease in chlorine is very nearly the same as the percent molar N content of the PD3-NEt_3 sample. This sample loses around 80% of its weight when heated up to 500°C. In this sense it is much less stable than the parent polymer sample.

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