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G. R. Patel[a]; S. R. Patel[a]
[a] Department of Chemistry, Sardar Patel University, Vidyanagar, India

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G. R. PATEL and S. R. PATEL

Department of Chemistry
Sardar Patel University
Vallabh Vidyanagar 388120, India

ABSTRACT

Polymers are prepared by polycondensation of 4,4'-dichloromethyldiphenyl ether (DDE) with benzene, toluene, and isomeric chlorotoluenes, respectively, in the absence of any solvent at room temperature and in the presence of dioxane. These polymer samples are found to be insoluble and infusible. IR spectral characteristics and thermal characteristics as revealed by TGA are reported. The polymers are shown to have a complicated cross-linked structure.

INTRODUCTION

Perusal of the literature reveals that Friedel-Crafts polycondensation of p-xylylene dichloride (PXDC) with benzene affords a cross-linked copolycondensation product [1, 2]. Such a condensation is also reported with toluene and xylenes [3, 4]. Vansheidt and co-workers [5, 6] have reported that the condensation of PXDC with p-xylene in the presence of concentrated sulfuric acid affords a polymer containing 1.4% chlorine and melting around 240-250°C. Grace and co-workers

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[7] observed that soluble polymers are formed when PXDC is condensed with o-, m-, and p-xylenes, respectively, in the presence of Friedel-Crafts catalyst. These polymer samples could be cross-linked on treatment with additional amounts of PXDC to yield films of high thermal stability [7]. Overhults and Ketley [8] have reported that the condensation of PXDC with durene yields an amorphous product which is insoluble in all the solvents and which decomposes when heated in air above 250°C. Grassie and Meldrum [9, 10] have reported that polycondenstaion of PXDC with diphenylmethane afforded a polymer which in the later stage of reaction underwent cross-linking. Nicolescu and Iovu [2] reported that Friedel-Crafts polycondensation of PXDC with diphenyl afforded a thermally stable amorphous polymer which was insoluble in benzene [11]. These authors reported that when this condensation was carried out in the presence of $Et_3Al_2Cl_3$, it afforded a highly thermally stable polymer which had properties to improve the viscosity index of lubricating oils. The condensation of PXDC with diphenyl ether is reported to afford a linear polymer of high molecular weight and high thermal stability. These polymers are reported to be soluble in common organic solvents, inflammable, and able to withstand temperatures of around 300°C for a long time [11-13]. Besides these, there are reports of such polycondensation reactions of 1,4-diacetonybenzene and other bz-substituted PXDCs with active aromatic compounds.

Perusal of the literature related to this field revealed that there are two reports [14, 15] about the polycondensation of 4,4'-dichloromethyl diphenyl ether (DDE) with benzene and other active monomers of benzene. Doedens and co-workers [14] have reported that when DDE is condensed with a large excess of m-xylene in the presence of zinc chloride or aluminum chloride, a normal product is formed. In their patent it is reported that DDE affords a normal product and not a polymer on reaction with a large excess of ethyl benzene, toluene, or benzene in the presence of $AlCl_3$ [14]. Oshima [16] reports that the reaction of DDE with a large excess of benzene or toluene in the presence of anhydrous aluminum chloride affords the normal product of reaction and not the polymeric product. The self-polycondensation of DDE affording cross-linked polymer is reported in an earlier communication of the present series. The condensation of DDE with benzene or other active aromatic hydrocarbon would yield a polymer with repeat units comprising both $-Ar-CH_2-Ar$ and $-Ar-O-Ar-$ units. It was thought that such a polymer may have thermal stability intermediate between those of polyarylene methylenes and polyarylene ethers. The syntheses and characterizations of such polymers form the subject matter of the present communication. They are prepared by Friedel-Crafts polycondensation of DDE with benzene, toluene, and isomeric chlorotoluenes. In these reactions of DDE, chances for cross-linking are more than in such polycondensation reactions of PXDC due to the presence of active reaction sites ortho to the aromatic ether linkage. Hence the conditions of the reaction were so chosen as to minimize the possibility of cross-linking.

The Friedel-Craft polycondensations of DDE with benzene, toluene, and isomeric chlorotoluenes, respectively, were effected in the solid phase at room temperature and in dioxane at 100°C. The IR spectral characteristics of these polymer samples have been noted. TGA of all the polymer samples were carried out in air with a view to comparing their thermal properties.

EXPERIMENTAL

All the materials used were laboratory grade reagents. PXDC and DDE were prepared by reported methods [17, 18].

FRIEDEL-CRAFTS POLYCONDENSATION

Polycondensation of Benzene with DDE in the Presence of $AlCl_3$ at Room Temperature: Formation of DB1

To a carefully prepared mixture of DDE (2.67 g) and benzene (0.78 g), finely powdered anhydrous aluminum chloride (4.0 g) was added with vigorous stirring. The reaction commenced on mixing the reactants with the evolution of hydrochloric acid gas. The reaction mass was left aside for 3 h at room temperature and decomposed with 100 mL of an ice water:HCl (1:1) mixture. The product was washed twice with cold water. The dried product was treated with about 40 mL of petroleum ether (40-60°C) to remove the unreacted monomer. The product was a pink-colored powder. The yield was 2.3 g. It is designated as DB1. All other polycondensations of DDE with other aromatic hydrocarbons were carried out in a similar manner at room temperature.

Polycondensation of DDE with Benzene in Dioxane: Formation of DB2

DDE (2.67 g) was dissolved in 22 mL of dioxane. Powdered anhydrous aluminum chloride (3.0 g) was added to this solution with stirring to obtain a homogeneous suspension. Benzene (0.78 g) was added to this suspension. The reaction mass was heated at 60°C for 3 h with occasional stirring. The reaction mixture was then heated at 90°C for 2 h and then at 100°C for 1 h and poured into a 1:1 water:HCl mixture (100 mL). A gummy product separated out. It was filtered and treated with boiling 5% HCl solution (50 mL) and then twice with boiling water. The polymer sample was dried, powdered, and refluxed with petroleum ether (40-60°C). The polymer was a brown-colored powder. The yield was 2.4 g.

TABLE 1

Designation	Condensation of DDE with	Reaction temperature (°C)	Solvent used	Catalyst	Color	Elemental analysis		
						C%	H%	Cl%
DB1	Benzene (1:1)	28-30	-	$AlCl_3$	Pink	77.4	5.14	3.9
DB2	Benzene (1:1)	60-100	Dioxane	$AlCl_3$	Brown	78.5	5.2	3.9
DBB	Benzene (1:5)	60-100	Dioxane	$AlCl_3$	Cream	78.4	5.4	1.9
DT1	Toluene (1:1)	28-30	-	$AlCl_3$	Pink	77.4	5.2	3.8
DT2	Toluene (1:1)	60-100	Dioxane	$AlCl_3$	Brown	84.6	5.8	3.7
DOCT1	o-Cl toluene (1:1)	28-30	-	$AlCl_3$	Pink	75.5	5.2	13.7
DOCT2	o-Cl toluene (1:1)	60-100	Dioxane	$AlCl_3$	Cream	77.6	4.7	12.7
DmCT1	m-Cl toluene (1:1)	28-30	-	$AlCl_3$	Pink	76.7	5.4	12.7
DmCT2	m-Cl toluene (1:1)	60-100	Dioxane	$AlCl_3$	Yellow	77.6	5.6	12.4
DpCT1	p-Cl toluene (1:1)	28-30	-	$AlCl_3$	Pink	74.5	5.3	15.6
DpCT2	p-Cl toluene (1:1)	60-100	Dioxane	$AlCl_3$	Cream	78.1	5.2	13.7

TABLE 2. Thermogravimetric Analysis of Polymer Samples in Air

	% Weight loss at temperatures (°C) of			
Designation	200	300	400	500
DB1	3	5	6	16
DB2	3	4	8	18
DT1	8	8	10	18
DOCT1	6	12	14	24
DMCT1	5	10	12	18
DpCT1	11	12	13	24

All other polycondensations of DDE with other aromatic hydrocarbons were carried out using dioxane as solvent. The polymers were worked up in the manner described above.

APPARATUS AND METHODS

The reaction conditions and elemental analysis are shown in Table 1.

The IR spectra of all the polymer samples were scanned in KBr on a UR-10 IR Spectrophotometer.

Thermogravimetric analysis was carried out in air using a Du Pont 950 Thermogravimetric Analyzer. The sample for TGA was heated at 70°C for 24 h. The amount of polymer used was 10 mg in all experiments. TGA data of all the polymer samples are shown in Table 2.

RESULTS AND DISCUSSION

All the polymer samples reported in the present communication are pink to brown. The polymer samples did not melt when heated but showed signs of decomposition when heated beyond 200°C. They are insoluble in all the common organic solvents. All the polymers prepared contained more than 75% C. The samples prepared from benzene and toluene contain from 1.9 to 3.9% Cl depending upon the nature of the polymer sample. The polymer samples prepared from DDE and isomeric chlorotoluenes contain from 13 to 15% Cl depending upon the nature of the polymer sample.

The polymer samples prepared from equimolar proportions of DDE and benzene at room temperature and also in dioxane showed

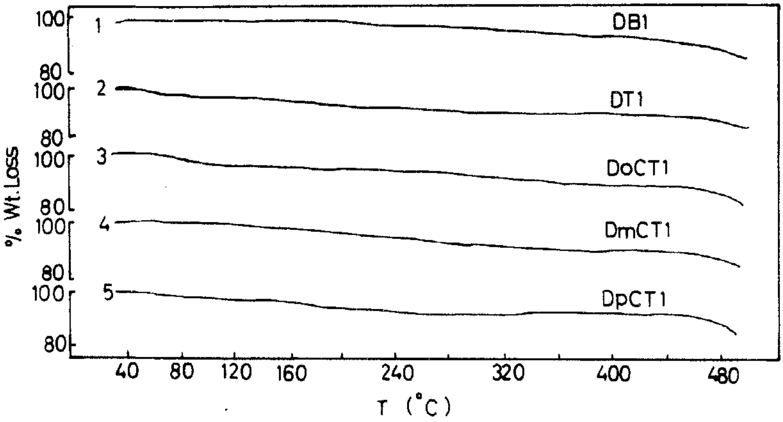


FIGURE 1.

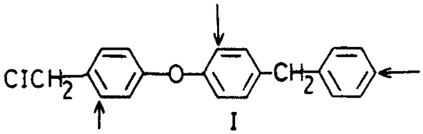
very nearly the same thermal behavior. They underwent 4% weight loss at 300°C and 15% weight loss at 510°C. The polymer sample prepared using DDE and benzene in 1:5 molar proportion in dioxane solution also behaved similarly. The polymers prepared from DDE and toluenes and DDE and m-chlorotoluene using molar proportion of reactants lose 18% of their weight when heated up to 500°C. The polymers prepared similarly from DDE and other p- and o-chloro toluenes lost around 25% of their weight when heated up to 500°C.

Comparison of the thermal behavior of all the polymer samples reported here with those of polymer samples prepared by self-polycondensation of DDE reveals that the polymer samples reported here are distinctly more stable than the polymers prepared by self-polycondensation of DDE as described in the earlier communication of this series. The self-DDE polymer samples lost around 40% or more of their weight when heated in air up to 500°C at a rate of 10°/min [16]. Selected plots are shown in Fig. 1.

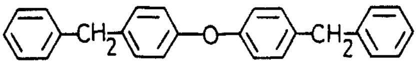
It has been observed that DDE does not undergo self-polycondensation in the presence of anhydrous aluminum chloride in dioxane solution even up to 100°C and in the absence of any solvent at 0° [16]. Under both these conditions, in addition of any one of the aromatic hydrocarbon monomers cited above, the reaction occurs, affording an insoluble and infusible product. This indicated that the copolycondensation reaction of DDE with aromatic hydrocarbon is much more facile than the self-polycondensation of DDE. All the polymeric products reported here contain more than 75% C. A self-polycondensation product of DDE would not contain more than 72 to 73% of C. It is reported in the earlier communication in this series that the self-polycondensation product of DDE contains around 14% of chlorine. The DB and DT polymer samples contain much smaller amounts of chlorine, and DCT polymer samples prepared from isomeric chlorotoluenes contain 13 to 15% Cl. As reported above, all the polymer samples described in the present communication are more stable than the self-polycondensation polymer sample.

The structure of DDE-benzene polymer is considered first. If DDE and benzene condensation were to give a linear product, the product would be the same as that reported to have been prepared from p-xylylene dichloride and diphenyl ether [12, 13]. The latter polymer is reported to be soluble in common solvents and to have very high molecular weight. The DB1 samples reported here are insoluble and infusible. This indicates that the DBs are cross-linked polymers. On the basis of the available information, it is not possible to draw any definite conclusions about the structure of polymer prepared from DDE and benzene or any other aromatic hydrocarbons. It is possible that the reaction will take the following course.

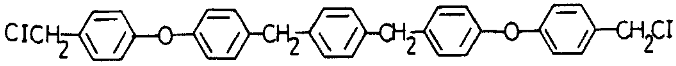
As a result of reaction between DDE and an active aromatic compound, say benzene, the first product would be I. The next stage would be a reaction of I with benzene, leading to formation of II and a reaction of I with DDE at either of the positions shown by arrows on I (other two less reactive positions are not shown), leading to the formation of III and IV. The next stages can be either through reaction of $-CH_2Cl$ end with the monomer, i.e., benzene, or through an attack of a DDE molecule or CH_2Cl endgroup on a position ortho to the ether linkage in Structure I, II, or III, or on a position para to the linkage of the phenyl endgroup on structure I or II and/or on a position ortho to $-CH_2-$ on $-CH_2-Ph-CH_2-$ in Structure III or IV.



I

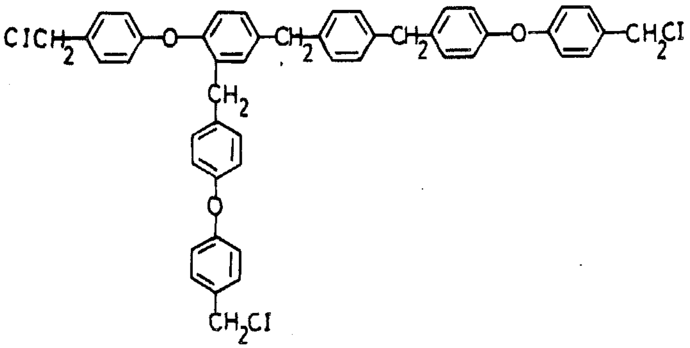


II



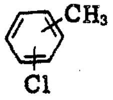
III

or



IV

No definite conclusion can be drawn about the actual event. However, involvement of all the types of reactions cited above, including the infrequent occurrence of the corresponding intermolecular reaction, would be the most probable manner in which the polymer may be built up. The possibility of the reaction with the endgroup would be more in reactions with reactive aromatic monomers like toluene, and that of the intermolecular reaction at the reactive position ortho to the ether linkage would be more in polycondensation reactions of DDE with less reactive monomers. As reported by Oshima [16], polycondensation of DDE with excess bromobenzene affords mostly a self-polycondensation reaction product. On this basis it can be inferred that when any one of the isomeric chlorotoluenes is used, the possibility of reaction on positions ortho to the ether linkage is likely to increase. However, higher chlorine content suggests a definite involvement of one



unit per repeat unit. This indicates that the latter is present in each repeat unit, i.e., the polymer when any one of the chlorotoluenes is used as a monomer is a copolycondensation product.

One point emerging out of the above considerations seems to be definite. The polymeric product is a result of the copolycondensation reaction, i.e., there is simultaneous and random participation of both DDE and the aromatic component in the reaction. It is quite likely that some DDE molecules function as cross-linking agents. The manner in which the DDE and aromatic residues are dispersed in the whole structure of the polymer formed would, however, depend to a

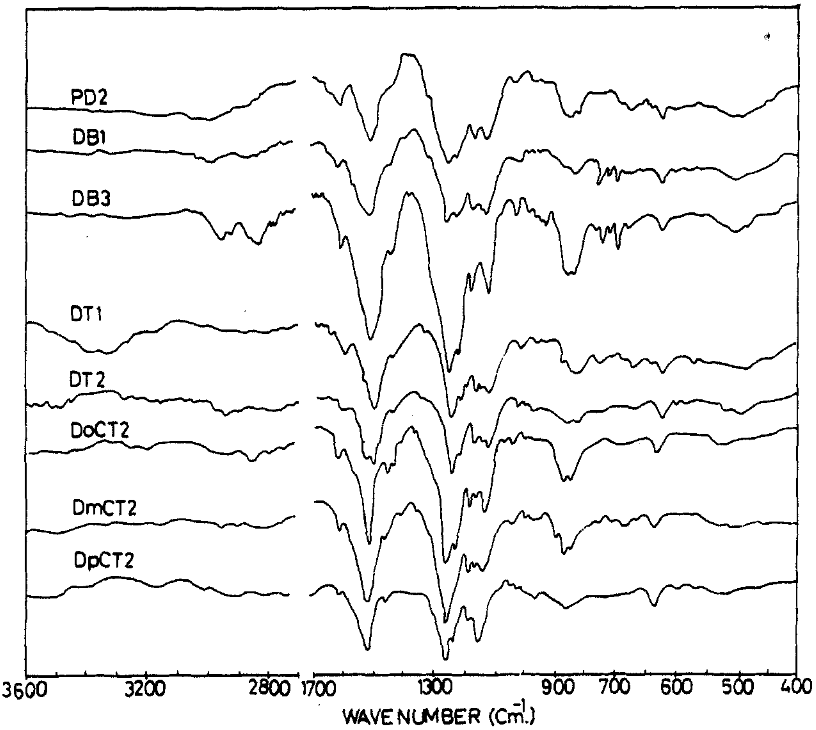


FIGURE 2.

greater extent on the relative reactivity of the reactive position on the two monomers.

The IR spectra of some of the polymer samples are shown in Fig. 2. The bands in the double bond region and the bands characteristic of aromatic C–O–C are quite distinct in the spectra. An examination of the region between 900 to 750 indicates the presence of certain bands which are characteristic of a specific type of aromatic substitution. This information is not that useful in the structure determination of the present polymers because, in a complicated cross-linked structure of each polymer, nearly all types of substitution patterns are expected. In the spectrum of DB sample, bands at 710 and 730 cm^{-1} indicate the presence of phenyl endgroups.

The work reported here has shown that due to higher reactivity of the position ortho to the ether linkage of DDE, cross-linking becomes possible even under milder conditions of reactions and that the copolycondensation of DDE with the aromatic hydrocarbons affords a cross-linked polymer.

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