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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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**To cite this Article** Patel, G. R. and Patel, S. R.(1983) 'Friedel-Crafts Polymers. 3. Friedel-Crafts Polycondensation of 4,4'-Dichloromethyldiphenyl Ether with Isomeric Xylenes', *Journal of Macromolecular Science, Part A*, 19: 5, 663 — 672

**To link to this Article:** DOI: 10.1080/00222338308069447

**URL:** <http://dx.doi.org/10.1080/00222338308069447>

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## Friedel-Crafts Polymers. 3. Friedel-Crafts Polycondensation of 4,4'-Dichloromethyldiphenyl Ether with Isomeric Xylenes

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### ABSTRACT

Polymers are prepared by polycondensation of 4,4'-dichloromethyldiphenyl ether (DDE) with isomeric xylenes using such Friedel-Crafts catalysts as anhydrous  $\text{AlCl}_3$ , conc  $\text{H}_2\text{SO}_4$ , polyphosphoric acid, and stannic chloride. The polymer samples prepared under all the reaction conditions are found to be insoluble and infusible. The IR spectral characteristics and thermal characteristics as revealed by TGA are reported. The polymers are shown to have cross-linked structures.

### INTRODUCTION

Overhalts and co-workers [ 1 ] reported that p-xylene dichloride (PXDC) reacts with p-xylene in the presence of a Friedel-Crafts type of catalyst between 40 and 150°C, yielding a soluble polycondensate which with an additional amount of the Friedel-Crafts catalyst could be molded and cured at higher temperature. The polymer which is formed is reported to have high thermal stability and resistance to organic and inorganic solvents [ 1 ]. Grace and Co. [ 2 ] observed that

soluble polymers are formed when PXDC is condensed with *o*-, *m*-, and *p*-xylenes, tetralin, and 1,2,4-trimethylbenzene using Friedel-Crafts catalysts. It is reported that these polymers can be cross-linked on reacting with an additional amount of the dichloro monomer to yield films of high decomposition temperature [2]. Mironov and co-workers [3] prepared bis(3,4-dimethylbenzyl) benzene on condensation of pXDC with *o*-xylene in the presence of anhydrous zinc chloride at 130° [3]. Vansheidt and co-workers [4] reported that when *p*-xylene or durene is treated with 1,4-bisacetoxy benzene or pXDC in anhydrous acetic acid solution containing H<sub>2</sub>SO<sub>4</sub>, condensation products with the composition of  $[-ArCH_2-]_n$  are formed; these

authors report that aromatic hydrocarbons such as *p*-xylene, durene, and isodurene, when heated with formaldehyde in the presence of glacial acetic acid containing H<sub>2</sub>SO<sub>4</sub>, yield similar polymeric derivatives. These authors noted that when pXDC was condensed with *p*-xylene in the presence of Friedel-Crafts catalyst, it yielded a polymer containing 1.4% chlorine which dissolved in anisole above 130°C and melted between 240 to 245°C [4]. Overhults and Ketley [5] reported that high molecular weight copolymers are obtained from pXDC and disubstituted benzenes. These authors observed that the maximum molecular weight and the yield of the soluble copolymers could be expected just before cross-linking took place. Hence it is difficult to obtain a high molecular weight polymer without cross-linking. These authors have observed that because basically the same reaction occurs during chain extension and cross-linking, it is unlikely that any major inhibition to cross-linking can be accomplished without stopping the chain growth. These authors reported that such polymers from *o*-xylene and *m*-xylene soften in the range from 75 to 90°C and those from *p*-xylene soften in the range from 125 to 30°C [5]. These authors reported that the polymer from pXDC and *p*-xylene could be cured at 120-40°C to a thermoset having a high degree of thermal stability if a small amount of Friedel-Crafts catalyst is added [5].

Doedens and co-workers [6] have reported that 4,4'-dichloromethylidiphenylether (DDE) on condensation with a large excess of *m*-xylene in the presence of zinc chloride or aluminum chloride affords a normal product, viz., 4,4'-*m*-xylyldiphenyl ether [6]. Oshima [7] has reported the preparation of the same product based on the condensation of DDE with an excess of *m*-xylene in the presence of conc sulfuric acid. Oshima has reported that this product does not contain chlorine and is a thick liquid soluble in common organic solvents [7].

It was reported in an earlier communication in this series that self-polycondensation of DDE affords a cross-linked polymer which is insoluble in common organic solvents and which is infusible [8]. It was also reported by the present authors that Friedel-Crafts polycondensations of DDE with benzene, toluene, and isomeric chlorotoluenes afford insoluble and infusible polymers [9]. In both the above-mentioned reactions, the high reactivity of positions ortho to

the ether linkage of the DDE residues in the polymer chains seems to be responsible for cross-linking. It was thought that if the reactivity of the active monomer is increased, the chances for linear polycondensation reaction would increase. If this could happen, the formation of linear Friedel-Crafts polycondensation would dominate in such a reaction of DDE with any one of the isomeric xylenes. The work described in the present communication was undertaken with a view to examining this possibility. It deals with a study of the Friedel-Crafts polycondensation of DDE with isomeric xylenes in the presence of various Lewis acid catalysts like anhydrous aluminum chloride, conc sulfuric acid, polyphosphoric acid, and stannic chloride. The reaction of p-xylene with DDE could be carried out in the presence of anhydrous aluminum chloride even at 0°C, affording an insoluble and infusible polymer in very low yield. The polycondensation of DDE with equimolar quantities of each of the isomeric xylenes was effected at room temperature both in the presence of anhydrous aluminum chloride and conc sulfuric acid, affording the corresponding polymer in good yield.

It was observed that the condensation of DDE with each of the isomeric xylenes could not be effected in the presence of stannic chloride and also in the presence of polyphosphoric acid at 30°C. These polycondensation reactions in the presence of stannic chloride and polyphosphoric acid could be effected at 100°C.

All the polymer samples were found to be insoluble in common organic solvents. IR spectral characteristics of these polymer samples have been noted. TGAs of all the polymer samples were carried out in air at a heating rate of 10°/min with a view to comparing their thermal properties.

## EXPERIMENTAL

The anhydrous aluminum chloride, polyphosphoric acid, conc sulfuric acid, and anhydrous stannic chloride used were laboratory grade reagents. 4,4'-Dichloromethyldiphenyl ether (DDE) was prepared by a reported method [10].

### FRIEDEL-CRAFTS POLYCONDENSATION

#### Polycondensation of p-Xylene with DDE in the Presence of AlCl<sub>3</sub> at Room Temperature: Formation of DpX1

To a mixture of DDE (2.66 g) and p-xylene (1.06 g) cooled initially to 0 to 5°C, finely powdered anhydrous aluminum chloride (4.0 g) was added in small lots over a period of 0.5 h. The reaction commenced

15 to 20 min after the addition of the catalyst was over. The reaction mass was left aside for 3 h at room temperature and decomposed with 100 mL of ice water:HCl (1:1) mixture. The product was filtered and washed thoroughly with water and allowed to dry in air. The dried product was treated with boiling acetone to remove unreacted monomer. The product is a pink colored powder. It is insoluble in all organic solvents. Yield 2.0 g. This polymer sample is designated as DpX1.

Both o-xylene and m-xylene were polycondensed with DDE in a similar manner at room temperature using anhydrous aluminum chloride as catalyst. These polymer samples are designated as DoX1 and DmX1 respectively. DDE was copolymerized with o-, m-, and p-xylenes in the presence of conc sulfuric acid at room temperature. These polymer samples are designated as DoX1, DmX2, and DpX2, respectively.

#### Polycondensation of p-Xylene with DDE in the Presence of PPA at 100°C: Formation of DPX3

To a mixture of DDE (2.67 g) and p-xylene (1.06 g), polyphosphoric acid (20 g) was added with stirring. There was no sign of reaction when the reaction was kept aside for 1 h. Hence the reaction mixture was heated at 100° on an oil bath for 3 h with occasional stirring. The reaction mixture was then poured into water and left aside overnight. The gummy product which separated on dilution of the mixture with water turned into a fine powder on standing. The polymer sample was collected and washed twice with boiling water. The polymer sample in the form of dried powder was refluxed with acetone (50 mL) and filtered. It was a pink colored powder, yield 1.0 g. This polymer sample is designated as DpX3. Polymer samples thus prepared from o- and m-xylenes are designated as DoX3 and DmX3, respectively.

#### Polycondensation of DDE with p-Xylene in the Presence of SnCl<sub>4</sub> at 100°C: Formation of DPX4

To a carefully prepared mixture of DDE (2.67 g) and p-xylene (1.06 g), stannic chloride (3.0 mL) was added with vigorous stirring. The reaction mixture was left aside at room temperature for 1 h. However, there was no sign of reaction. The reaction mixture was then heated at 100°C on an oil bath for 3 h with occasional stirring, cooled, and poured with stirring in water (100 mL) containing 10 mL of conc HCl. The polymer sample which separated out was collected and washed with 1:1 water:HCl mixture and then with boiling water (100 mL). The polymer sample was dried and powdered. It was refluxed with acetone (100 mL) for 0.5 h and filtered. The polymer was a pink colored granular material. Yield 2.1 g. It is designated as

DpX4. The polymer samples prepared similarly from *o*- and *m*-xylenes are designated as DoX4 and DmX4, respectively.

## METHODS OF STUDY

IR spectra of all the polymer samples were scanned in KBr on a UR-10 IR spectrophotometer. The thermogravimetric analysis was carried out in air using a Dupont 950 Thermogravimetric Analyzer. The sample for TGA was heated at 70°C for 24 h. The amount of the polymer used was 8 to 10 mg in all the experiments.

## RESULTS AND DISCUSSION

All the polymer samples reported in the present communication are cream to pink to brown in color. These polymer samples, including those prepared under milder reaction conditions, are insoluble in common organic solvents. They are found to contain 80 to 88% of C and 1.8 to 4.2% of Cl depending upon their nature. It may be interesting to note that the self-polycondensation products of DDE have cross-linked structures and they do not contain more than 72 to 73% of carbon [8].

The IR spectra of all the polymer samples are shown in Fig. 1. A comparison of the nature of the bands in the double bond region and of the bands characteristic of aromatic C—O—C in the spectra of all the polymer samples prepared from *o*-, *m*-, or *p*-xylene under different experimental conditions reveals that there are small but significant differences in these spectral trends. This difference is attributed to the difference in the extent of cross-linking of these polymer samples. The IR spectra of all the polymer samples comprise bands at 815 and 880  $\text{cm}^{-1}$ . These bands can be attributed to the presence of systems of two adjacent H atom and isolated H atom. Both these systems would be present in the possible structures (II, III, IV) of the polymers prepared from the three isomeric xylenes. The spectra of all the polymer samples comprise bands around 1365 and 1455  $\text{cm}^{-1}$ . These bands can be assigned to C—H deformation of —CH<sub>2</sub>— bridges and CH<sub>3</sub> of xylene. They appear almost at similar positions. Hence the presence of these bands cannot be employed to prove unequivocally the presence of the —CH<sub>2</sub>— bridge.

Examination of the data of TGA of the polymer samples reported in Table 1 reveals that all the polymer samples lose weight at a comparatively slower rate when heated up to 500°C. Beyond this temperature the samples are found to lose weight at a very rapid rate. The polymers suffer nearly 50 to 60% weight loss when heated from 500 to 700°C. The actual rate of weight loss depends upon the nature of the polymer sample. Examination of the data of TGA also reveals

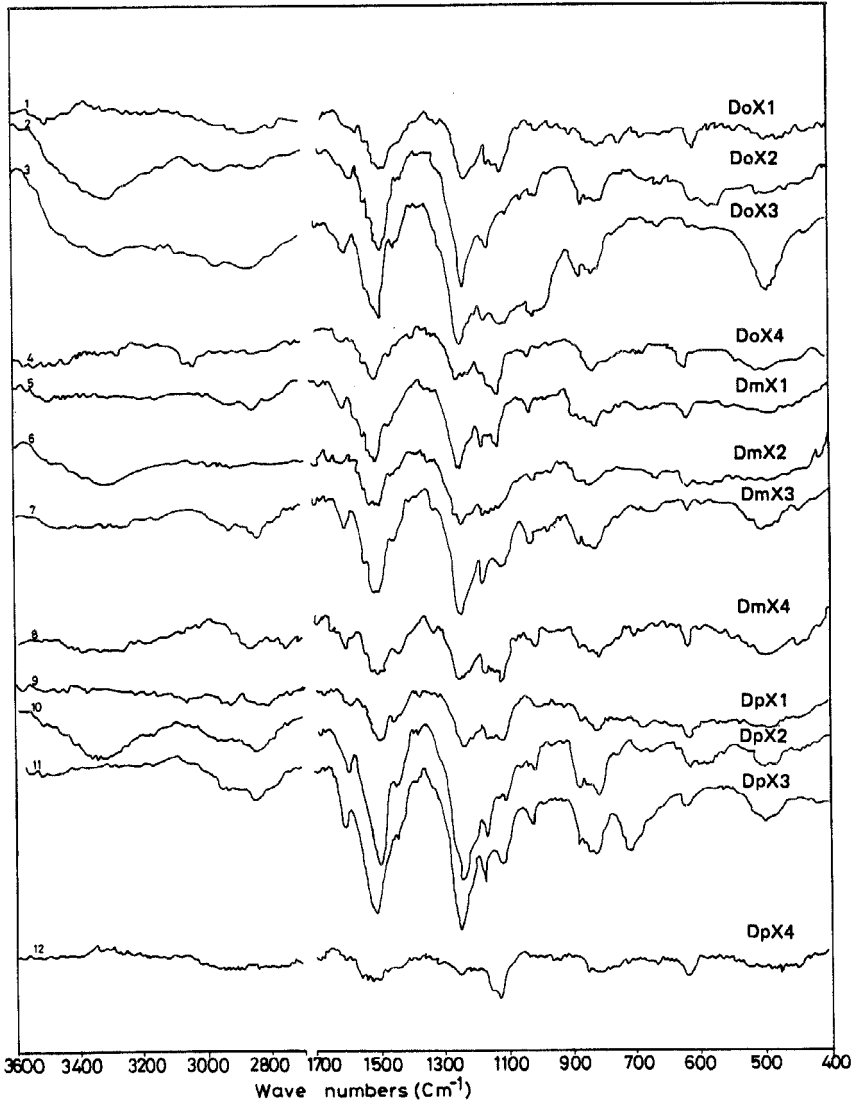


FIGURE 1.

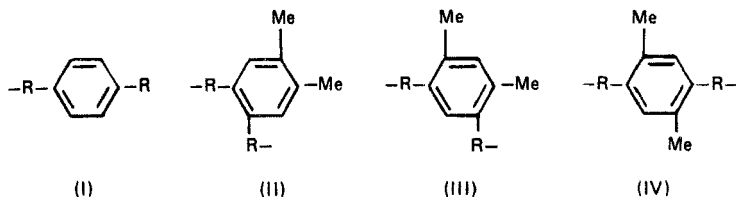
TABLE 1. Characterization of the Polymer Samples

Polymer designation	Color	Elemental analysis			TGA of polymer samples in air medium at a rate of 10°/min. Percent weight loss at temperatures of				
		C%	H%	Cl%	200° C	300° C	400° C	500° C	
DOX1	Brown	82.7	5.8	3.3	8	16	18	27	
DOX2	Pink	84.0	6.4	2.7	19	25	26	39	
DOX3	Cream	87.0	6.0	2.2	12	14	17	24	
DOX4	Pink	83.6	6.0	4.1	2	4	4	5	
DmX1	Brown	82.0	6.2	3.6	12	14	14	20	
DmX2	Brown	80.2	6.6	3.5	16	21	25	32	
DmX3	Cream	83.6	5.2	2.6	4	5	6	17	
DmX4	Pink	87.4	7.2	2.5	-	2	3	4	
DpX1	Brown	87.5	6.2	3.8	15	19	20	34	
DpX2	Pink	84.1	5.0	3.8	8	11	14	25	
DpX3	Pink	80.1	5.4	2.3	1	3	7	20	
DpX4	Pink	85.0	5.4	3.5	1	3	5	19	
[8] PD2	Yellow	72.7	5.2	14.2	11	15	20	40	
[9] DB1	Pink	77.4	5.1	3.9	3	5	6	16	
DT1	Pink	77.4	5.2	3.8	8	8	10	18	

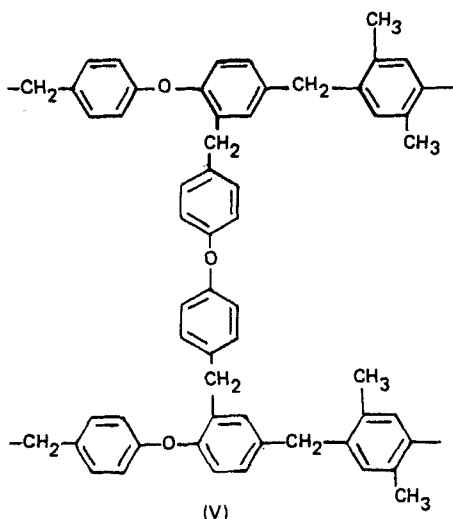


certain general trends. The polymer sample prepared from a given pair of monomers in the presence of PPA or  $\text{SnCl}_4$  is found to be more stable than the polymer sample prepared from the same pair of monomers in the presence of aluminum chloride or sulfuric acid. Comparison of the stability of the polymer prepared from isomeric xylenes under similar conditions reveals that the polymer sample prepared from *m*-xylene is more stable than that prepared from *o*- or *p*-xylene. Comparison of the results of TGA of polymer samples prepared from benzene and toluene reported in our earlier communication [9] with those prepared from isomeric xylenes under similar conditions reveals that the latter are comparatively less stable than those prepared from benzene and toluene.

The results of the present study reveal that even the use of comparatively more reactive xylenes as monomer yields insoluble polymers even under milder conditions of reactions and even when mild Friedel-Crafts catalyst (e.g., stannic chloride) are used. It is interesting to note that Friedel-Crafts polycondensation of *p*-xylylene dichloride (pXDC) with diphenyl ether affords a linear polymer of high molecular weight soluble in common organic solvents [11]. The structure of its repeat unit (I) is shown below. If polycondensation of DDE with *o*-, *m*-, and *p*-xylenes had involved only normal chain



propagation, the structures of the repeat units of the polymer chains would have been II, III, and IV, respectively. Such polymers would have higher solubility than the polymer prepared from pXDC and diphenyl ether due to an increase in the bulk of the intervening aromatic nuclei generated through the xylene unit. The fact that polymeric products are insoluble suggests both normal chain propagation and intramolecular cross-linking has taken place due to the reaction of DDE with each of the isomeric xylenes. It seems that intramolecular cross-linking has taken place between the reactive positions ortho to the ether linkage through the agency of DDE as shown in Structure V for the repeat unit of the polymer prepared from *p*-xylene and DDE.



Higher reactivity of the position ortho to the ether linkage favoring intramolecular cross-linking and increased crowding around the intervening aromatic nuclei generated through isomeric xylene unit retarding normal chain propagation seem to be the reasons for the nature of the polycondensation of DDE with isomeric xylene affording cross-linked polymers. This type of increased crowding also seems to be responsible for the formation of cross-linked polymers in the polycondensation of pXDC and isomeric xylenes [5].

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Accepted by editor August 14, 1982

Received for publication September 14, 1982