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Diphenyl Ether Derivatives in Condensation Polymers

Resins from chloromethylated diphenyl ether show promise as flame-resistant building materials

DIPHENYL ether has long been known as a heat-stable, relatively unreactive molecule. In fact, its chief use today is as a component of high temperature heat transfer fluids where these properties are used to advantage. While the literature describes many reactions involving diphenyl ether, relatively little work has been reported in which this heat-stable, oxidation-resistant ring system has been put to any other use.

With this in mind, considerable research has been done with diphenyl ether in these laboratories. A "reactive handle" has been provided for this relatively unreactive chemical which allows introduction of the diphenyl ether nucleus into a variety of systems, yielding new chemical combinations but preserving the properties usually associated with diphenyl ether. This discussion is confined to use of the chloromethyl group as the "reactive handle."

A series of new compounds, based on the chloromethylation of diphenyl ether, capable of polymerization to either foams or hard thermosetting resins suitable as binders has been developed. These polymers are extremely tough and are flame and heat resistant.

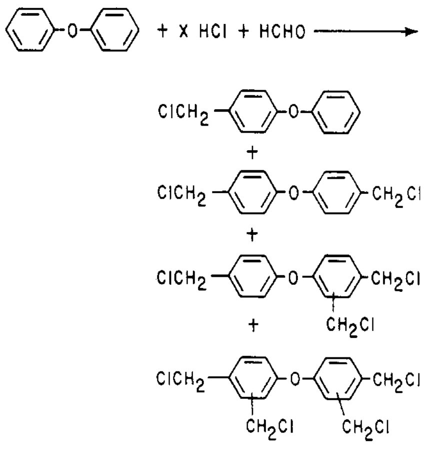
The polymer materials described are suitable for many large-volume applications, especially in the construction industry. For example, unmodified foams are buoyant and provide good insulation, and when combined with inorganic materials these foams produce load-bearing building panels. Still other types of building materials result when unfoamed polymer is used as a binder for inorganic materials. In all these applications, heat- and flame-resistance is an important property.

While this report describes the use of chloromethylated diphenyl ethers as monomers for resin formation, these materials were extremely reactive in other chemical reactions as well. They can be hydrolyzed, aminated, treated with aromatic rings containing active hydrogens, and so on, under certain conditions to produce new and interesting compounds which could find great utility in almost any field of chemistry. The organic chemist can realize the potential of these versatile materials. A further report will be made in detail soon.

Experimental

Chloromethylated diphenyl ether and CMDPO are used as generic terms for a series of compounds produced by reacting diphenyl ether with formaldehyde and HCl to produce different degrees of chloromethylation. The reaction process can be controlled to give products of varying organic chlorine content, depending on the amount of reactants utilized and the reaction time.

The following equation shows in simple form the reaction and the possible products:



The reaction produces a mixture of *ortho* and *para* isomers. However, 4,4′-dichloromethyl diphenyl ether can be isolated in the pure crystalline form. The products of more interest to the resin chemist are the mixtures which can be prepared having specific chlorine contents. The mechanics of preparing these various products are shown (p. 60).

While products having any degree of chloromethylation can be made, efforts were concentrated on the five chloromethylated products shown. These were chosen because they are close to an average chloromethylation of one, two, and three. The pure compounds corresponding to the mono, di, and tri derivatives have the following chlorine content:

CMDPO Derivative	Cl,%
Mono	**16.25**
Di	**26.6**
Tri	**33.6**

All of the products are mixtures, except for the pure 4,4′-dichloromethyl diphenyl ether. The composition of these mixtures is defined in Table I, which shows the isomer composition of CMDPO mixtures containing various amounts of chlorine. As the chlorine content rises or as the degree of chloromethylation increases, the functionality of the molecule becomes greater, or the mixtures contain a greater percentage of polyfunctional entities.

Methods of chloromethylating aromatic nuclei are well covered in the literature, including an excellent review by Fuson and Mckeever (*2*). Tomita and Takahashi (*5*) have described a method for chloromethylating diphenyl ether by reaction of diphenyl ether with aqueous formaldehyde and hydrogen chloride in the presence of $ZnCl_2$. This process involves the use of solvent extraction and distillation to recover

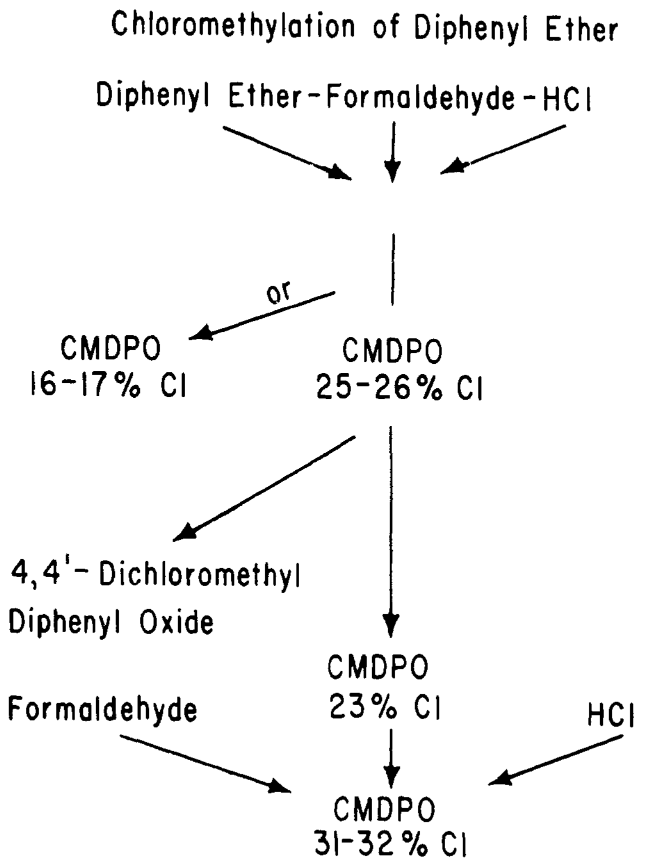


Table I. Typical Analysis of Various Chloromethylated Diphenyl Ethers

As chlorine content increases, the mixtures contain more polyfunctional entities

	Cl Content, Mole %			
Material	17.6	25.2	23.6	30.7
Diphenyl Ether	17.3	0.0	0.0	0.0
***o*-Monochloromethyl DPO**[a]	5.3	0.25	0.5	0.0
***p*-Monochloromethyl DPO**[a]	42.9	2.35	4.7	0.04
***o,p'*-Dichloromethyl DPO**[a]	10.8	17.7	35.4	1.9
***p,p'*-Dichloromethyl DPO**[a]	20.6	69.5	37.7	8.6
Trichloromethyl DPO[a]	2.3	10.5	21.1	89.0
Tetrachloromethyl DPO[a]	0.5-1.0	0.5	0.5-1.0	...

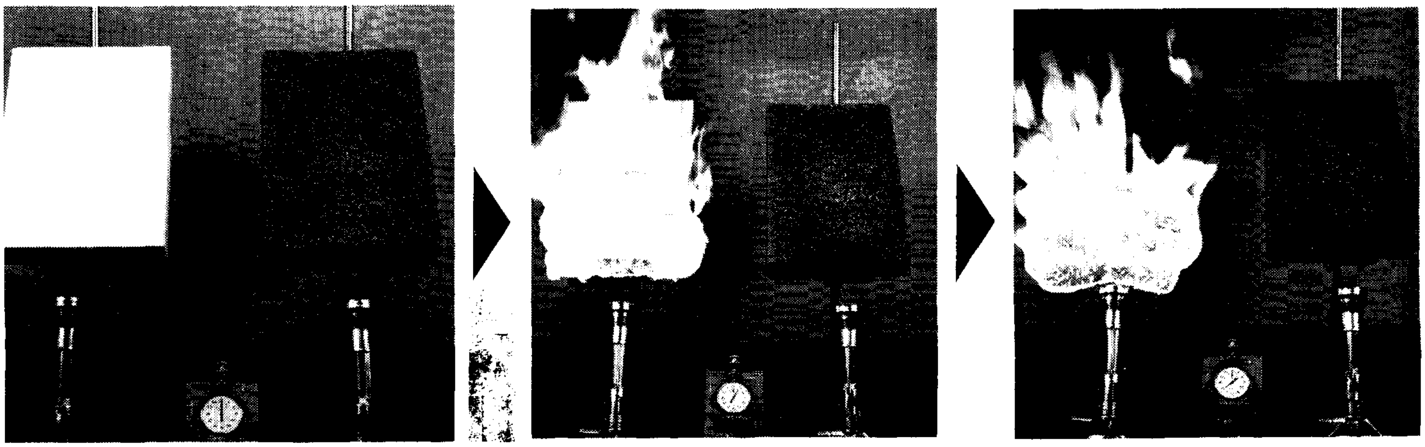
[a] DPO = diphenyl ether.

pure materials. In the process described here commercially available equipment was utilized, involving a minimum of refining techniques. The mixtures previously described resulted. Reaction control was achieved by altering the amount of reactants utilized and the reaction time.

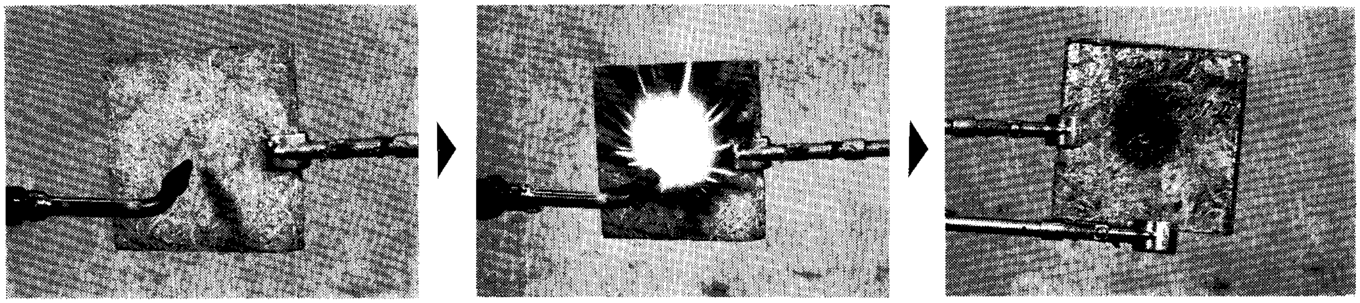
The products are liquids having viscosities slightly greater than water and specific gravities ranging from 1.20 to 1.35, except when the concentration of 4,4'-dichloromethyl diphenyl ether is high. The products become crystalline with melting points ranging from 50° to 65° C. depending on the concentration of the 4,4'-dichloromethyl isomer present. These materials are insoluble in water but are easily emulsified. They are soluble in most organic solvents; however, care must be taken in choosing a solvent to avoid reaction.

Analysis. Chloromethylation of aromatic nuclei is a relatively "old" reaction, and the techniques are well established; however, analysis of the resulting mixtures after chloromethylation was a real problem. Chlorine content, specific gravity, and refractive index were easily attained, but these gave no quantitative indication of the composition. Distillation of the mixtures resulted in decomposition and polymerization. It therefore became necessary to develop an analytical method which would not involve thermal techniques.

The novel analytical technique developed involves treating the chloromethylated compounds with hydrogen to remove the chlorine by hydrogenolysis and analyzing the resulting tolyl ethers by vapor phase chromatography. Analytical data have compared nicely on samples of known composition, and the composition data reported here were



Proof of nonflammability lies in comparison test with foams. Left panel shows chloromethylated diphenyl ether foam (right) and commercially available polyurethane foam just before lighting the Fisher burners. Both burners were lighted simultaneously, and center panel shows progress of flame after 5 seconds. After 30 seconds had elapsed, burners were extinguished; 10 seconds later (right panel), the polyurethane foam is melting down and still burning while the chloromethylated diphenyl ether foam shows only slight evidence of charring

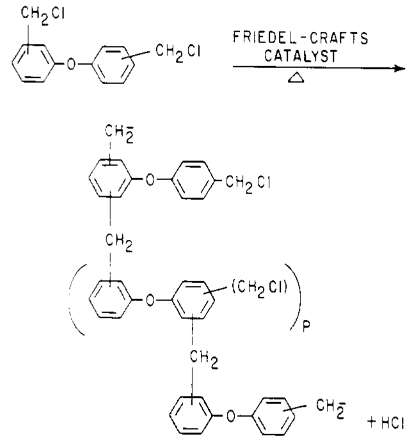


Laminate containing high-silica glass bonded with chloromethylated diphenyl ether is tested with oxygen–natural gas torch. Sample and testing assembly are shown in left panel before the test. The torch was lighted and test assembly photographed (center panel). After 300 seconds, a red glow appeared on back of sample, and flame had penetrated $^1/_8$ inch into front surface. Right panel shows back surface after 300 seconds of flame exposure

achieved by this method. A detailed discussion of this analytical method has been published recently (*6*).

Polymerization

The chief interest in these materials lies in the ability of chloromethylated aromatic compounds to condense on heating to form polymeric materials. Bezzi (*1*), Jacobson (*3*), and Korshak (*4*) have described the polymerization of benzyl halides with heat in the presence of Friedel-Crafts catalysts; however, no literature references have been found relating to the polymerization of chloromethylated diphenyl ethers or to the preparation of thermosetting foams by this route. When material containing 16 to 17% chlorine is treated with a Friedel-Crafts catalyst and heated to 100° to 120° C., polymerization occurs according to the following equation:



A thermosetting foam results. The anhydrous hydrogen chloride evolved acts as the blowing agent for the foam. Catalysts such as $AlCl_3$, BF_3, H_2SO_4, $ZnCl_2$, and $FeCl_3$ are suitable for the reaction. However, $FePO_4$, $Fe_3(PO_4)_2$, and $ZnCl_2$ dissolved in methyl alcohol are more desirable as they are easier to disperse in the monomers.

Initially, it was thought that only chloromethylated diphenyl ether containing 16 to 17% chlorine could be used as the starting material for these foams. However, it has since been proved that any of the materials previously discussed can be foamed and that products similar in properties result.

Foam Properties

The foam has some interesting properties (Table II). Its thermal conductivity (*K* factor) is somewhat better than phenolic foams and is approximately equivalent to that of polystyrene foam. Density can be varied through the use of additives, as well as by varying the foaming conditions. The same is true relative to open or closed cell structure.

One of its most interesting properties is its relatively nonflammable characteristics. The results in Table III were obtained by placing samples of foam against a metal bar heated cherry-red and observing the rate of char—a modification of ASTM test No. 757-49. In none of the tests did a flame appear, but the inches per minute of burning rate reported represents the rate of blackening or charring of the sample.

A more dramatic example of the burning resistance of this foam can be shown when the flame of a Meeker burner is placed against it. Any flame that occurs when touching the surface is completely extinguished immediately upon removal of the source flame. In other words, this foam does not support combustion. Another interesting property relating to flame resistance is that the material will not melt and drip when exposed to a flame; even though charred it will retain its original shape and, surprisingly, some strength. Undoubtedly, the 10 to 20% organic chlorine (depending on the starting material) still remaining in the foam contributes largely to its fire resistance. This remaining chlorine is quite stable, as samples of foam have been strapped to a 150-p.s.i. steam line (approximately 160° C.) for several months without significant loss of chlorine as shown by analysis. Further evidence of the flame resistance of these materials is described below.

Another valuable characteristic of these foams is that they are tougher and less friable than equivalent phenolic foams. Naturally, at foam densities of less than 0.5 to 1.0 pound per cubic foot the materials have little strength and are somewhat friable, but at densities of 1.5 to 3.0 pounds per cubic foot these foams are tough and are not friable. It was found that the density of phenolic foams must be greater than 5 pounds per cubic foot to be equivalent to chloromethylated diphenyl ether foams at 1.5 pounds per cubic foot in these properties.

If the chloromethylated diphenyl ethers are foamed in the presence of inorganic fillers such as glass wool, exploded mica, or rock wool, a somewhat

Table II. Properties of CMDPO Foam

Density	= 0.5–8 lb./cu. ft.
Compressive strength	= 10–100 p.s.i.
Thermal conductivity (*K* factor)	= 0.25–0.27 B.t.u./(hr.)(sq. ft.)(°F.)/ft.
Foam structure	= open or closed cells
Flammability	= will not support combustion

Table III. Nonflammable Properties of CMPDO Foam Were Tested by Contact with a Red-Hot Metal Bar

CMDPO Foam Density, Lb./Cu. Ft.	Charring Rate, In./Min.
2.5	0.1250
1.5	0.0830
6.5	0.1660

heavier structure is formed which has essentially the same or better fire-resistant properties as unmodified foam. In addition, the strength of the foam is greatly improved. Compressive strengths of greater than 200 p.s.i. have been achieved, for example, with foams containing 50% glass wool and 50% chloromethylated diphenyl ether foam at a total density of 5 to 6 pounds per cubic foot.

In an interesting approach to filled foams of this type, the catalyzed chloromethyl diphenyl ether can be sprayed onto the inorganic filler in the desired concentration and cured with heat to produce a foam-filler mat of the inorganic material. By such a procedure, a continuous process for the manufacture of an organic foam filled with an inorganic material is feasible.

In addition to their use in foams, these materials can be polymerized under pressure or vacuum to produce hard, tough, thermosetting resins as binders for inorganic materials. For example, chloromethylated diphenyl ethers have been used to bond MgO, Perlite (a plaster aggregate), flaked glass, asbestos rovings, and the like to form hard, tough, flame-resistant products suitable for construction purposes. When asbestos rovings are used, the product has properties similar to Transite. Flame resistant properties for some of these materials are shown in Table IV.

Again these charring rates were determined by touching a sample of the material to a metal bar heated cherry-red and measuring the length of material blackened or charred in a given time. During all of the tests involving the chloromethylated diphenyl ether binders there was no flame produced at any time. The three additional tests reported in Table IV are of commercially available materials. In these tests, fiber board and the self-extinguishing polyester-glass laminate produced a flame on initial contact with the heated bar; however, the flames disappeared before the 3-minute test was completed. A more striking example of the flame resistance of these materials is illustrated by results of the following test:

A 4 × 4 × 0.5 inch sample was prepared by thoroughly mixing 70 parts of Perlite (a plaster aggregate) with 30 parts of chloromethylated diphenyl ether. The mixture was placed in a mold and cured at 135° C. for 5 minutes at 250 p.s.i. The resulting board, after cooling, was placed on a stand so that the flame tip of an oxyacetylene torch could be touched to the surface. After 6 minutes of such exposure, no hole was burned through the sample, but the test was terminated as a red glow appeared on its back side. The flame had penetrated approximately 0.25 inch into the sample and was less than 0.75 inch in diameter. The Perlite had melted into a glass and did not scatter or flake by flame erosion. High-silica glass was even better as a filler.

Table IV. Flame Resistant Properties of CMDPO-Bonded Inorganic Materials Compared with Commercially Available Building Materials

Material	Charring Rate, In./Min.
CMDPO-bonded glass cloth	**0.1592**
CMDPO-bonded glass fibers	**0.1400**
CMDPO-bonded Perlite	**0.0893**
CMDPO-bonded glass wool	**0.0890**
CMDPO-bonded asbestos	**0.0820**
Fiber board	**0.5000**
Phenolic-bonded glass wool	**0.2500**
Self-extinguishing polyester-glass laminate	**0.2121**

The important point in these tests is that these samples neither burst into flames nor eroded when the better fillers were used. These include glass flakes and high silica glass, such as Refrasil. These results show that a heat- and flame-resistant organic material capable of use as an adhesive or bonding agent for inorganic materials is available.

Through the use of additives and/or modifiers of various kinds, properties can be tailor-made to result in the most desirable material for the application in mind. The use of bases to react with the evolved HCl has received quite a bit of attention in these laboratories, and it has been shown that the greater part of the acid released can be controlled. As previously stated, the organic chlorine in the polymer is stable to hydrolysis or other means of chlorine removal except by extreme conditions.

Applications

Because of the flame-resistance, toughness, and chemical- and moisture-resistance of the unmodified foams, they should attain volume application in the construction industry. Roof decking, sandwich panels, buoyancy applications, and the like should be natural uses for these products.

The combination of organic CMDPO foams with inorganic materials such as glass wool, asbestos, and mica results in tough, hard, fire-resistant materials which should again attain utility in the construction industry as load bearing building materials. One of the most promising areas would be roof decking. Because of its strength it can be used to support a good deal of weight, and because of its flame-resistance and thermosetting nature a coating of hot asphalt can be applied without ill effects.

In addition to the utility described for building panels and roof decking, the unmodified and filled foams should make excellent high temperature insulating materials. The *K* factors are equal to current commercially available materials, and added advantages are that the foams have a high degree of flame-resistance, have no heat distortion temperature, and will not melt or drip when exposed to flame.

If CMDPO is polymerized such that foaming is depressed, utility as a binder or thermosetting adhesive for inorganic materials results. Building panels from CMDPO-bonded asbestos, glass, mica, and MgO are tough and hard, resembling Transite. Because they are fire resistant, they should make excellent building materials for installations where high temperatures will be encountered. Rocket nose cones and missile cases would be more exotic uses. Refactory brick, tank and furnace linings, and commercial oven insulations would be more practical uses.

Acknowledgment

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Correction

Adsorbing Sulfur Dioxide on Dry Ion Exchange Resins

In this article by Robert Cole and H. L. Shulman [IND. ENG. CHEM. **52,** 859 (1960)] the footnote on page 860 is in error. The article was not presented as a paper at the 138th ACS Meeting.