

MACROMOLECULAR COMPOUNDS

COMMUNICATION 99. POLYCONDENSATION OF DICHLOROMETHANE WITH BENZENE

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In some previous communications of this series [1-7] we described the results of a study of the polycondensation of 1,2-dichloroethane with benzene and other aromatic hydrocarbons in presence of aluminum chloride. The same subject has been studied also by Klebansky and Mironenko [8], Dolgov and Larin [9], and Shishido and coworkers [10-17]. It is evident from the number of papers that have been devoted to the polycondensation of 1,2-dichloroethane with aromatic hydrocarbons that this reaction has aroused considerable interest.

Very much less attention has been devoted to the interaction of dichloromethane with aromatic hydrocarbons in presence of aluminum chloride, and the polycondensation of dichloromethane with aromatic hydrocarbons has not been studied at all. Friedel and Crafts [18] found that reaction of dichloromethane with benzene in presence of aluminum chloride gave diphenylmethane, anthracene, and toluene; when benzene was replaced by toluene, ditolylmethane, dimethylantracene, and a mixture of *p*- and *m*-xylenes were obtained. Adam [19] treated biphenyl with dichloromethane and obtained fluorene and dibiphenylmethane. Reaction of dichloromethane with 1,2,4-trimethylbenzene gave bis-2,4,5-trimethylphenylmethane [20].

It would be expected that polycondensation of dichloromethane with benzene would proceed as in the polycondensation of 1,2-dichloroethane with benzene, since both dichloromethane and 1,2-dichloroethane contain the same number of halogen atoms capable of reacting with benzene in presence of aluminum chloride. With the object of verifying this supposition, we undertook a study of the polycondensation of dichloromethane with benzene.

EXPERIMENTAL

In the first series of experiments the amounts of benzene and catalyst and the experimental conditions were maintained constant, whereas the amount of dichloromethane was varied. The concentration of the aluminum chloride was 2.25 moles per 100 moles of benzene. The initial bath temperature was 50°; this temperature was maintained for one hour, and the temperature was then raised gradually to 100° over a period of 60-90 minutes. The total period of heating was four hours. Reaction was very vigorous and there was a copious evolution of hydrogen chloride. After the usual treatment [1, 2] diphenylmethane (b.p. 110-120° at 3 mm) and dibenzylbenzene (b. p. 190-210° at 3 mm) were distilled off under reduced pressure. The residue in the flask consisted of poly(methylenephenyl). The molecular weight of the poly(methylenephenyl) was determined viscosimetrically. The results obtained are given in Table 1.

It will be seen from Table 1 that with increase in the dichloromethane : benzene ratio the yield of poly(methylenephenyl) rises a little and the yields of diphenylmethane and dibenzylbenzene fall. Two facts become evident from an examination of the results: constancy of molecular weight and nonformation of three-dimensional polymers at equimolecular ratios and even with an excess of dichloromethane.

As is well known, in the overwhelming majority of polycondensation reactions the molecular weight of the polycondensation products increases as the molar ratio of the reactants approaches unity, and we have shown [1-7] that this rule holds for the polycondensation of 1,2-dichloroethane with benzene and other aromatic hydrocarbons. However, the rule does not hold for the polycondensation of dichloromethane with benzene, the

viscosimetric molecular weight of the resulting poly(methylenephenyl) being almost independent of the relative amounts of reactants.

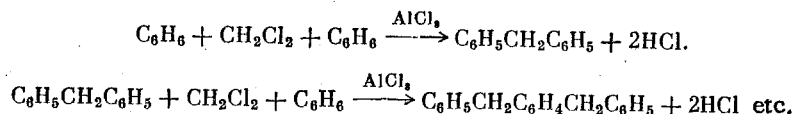
TABLE 1

Polycondensation of Dichloromethane with Benzene

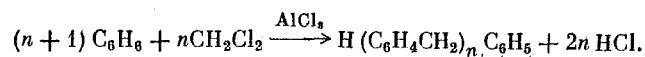
Molar ratio dichloro- methane: benzene	Yield (% on dichloromethane taken)			Molecular weight of poly(methyl- enephenyl)
	Diphenyl- methane	Dibenzyl- benzene	poly(methyl- enephenyl)	
0.50	21.4	13.2	21.6	1370
0.59	18.0	11.6	26.4	1180
0.65	15.7	10.6	24.8	970
0.70	14.4	10.8	27.4	1400
0.75	13.2	11.3	29.5	1280
0.83	10.9	9.5	27.4	1470
0.90	11.0	9.0	28.3	1180
1.00	9.2	7.1	26.1	1100
1.10	8.8*	6.7*	29.8*	1360

* Yield as % on benzene taken.

The above-noted peculiarities of the polycondensation of dichloromethane with benzene can, in our opinion, be explained as follows. This polycondensation can be represented by the scheme:



or in a general form:

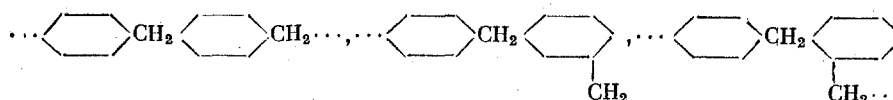


We did not observe the formation of compounds containing a terminal CH_2Cl group, and even when the polycondensation was carried out with excess of dichloromethane the product did not contain chlorine.

The fundamental repeating unit in the linear polycondensation product from dichloromethane and benzene is the group $-\text{C}_6\text{H}_4\text{CH}_2-$, and it may therefore be called poly(methylenephenyl). Elementary analysis showed that the carbon and hydrogen contents of poly(methylenephenyl) obtained from a mixture containing excess of benzene are in close agreement with the values calculated for the repeating unit $-\text{C}_6\text{H}_4\text{CH}_2-$:

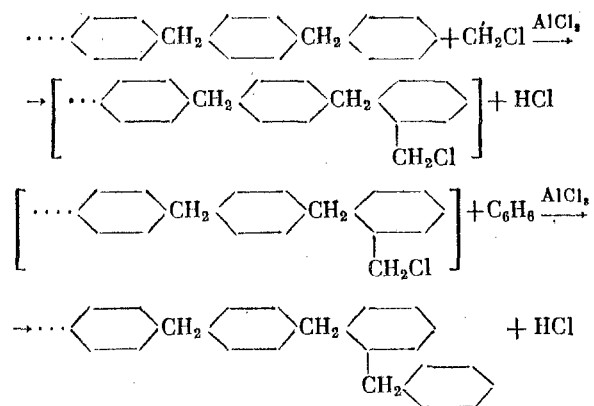
Found %: C 93.07; 93.40; H 6.73; 6.68 C_7H_6 . Calculated %: C 93.29; H 6.71

During chain growth new methylene groups may enter not only para and meta positions, as indicated by the low-molecular-weight polycondensation products, but also in ortho positions to methylene groups already present, i.e., the following structural fragments are possible:

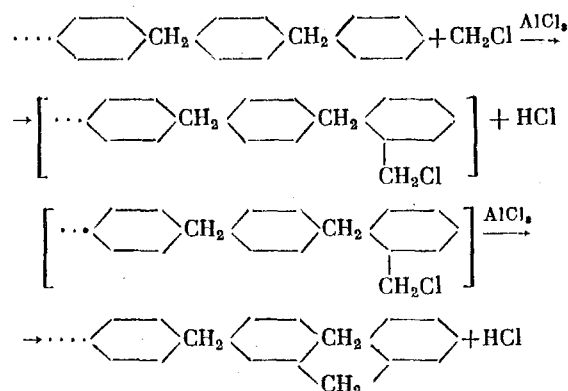


Chain growth is not hindered by para and meta substitution, but this cannot be said of ortho substitution.

In the case of ortho substitution two competing reactions may occur - chain growth, i.e.,



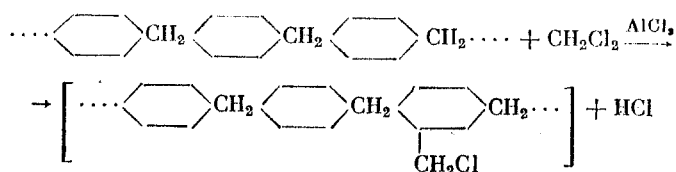
and intramolecular cyclization with formation of a dihydroanthracene residue, i.e.,



We consider that intramolecular cyclization will occur more readily, since, unlike the chain-growth reaction, it does not depend on the occurrence of a collision between molecules of a definite type. The formation of dihydroanthracene ring systems at the ends of growing chains leads to arrest of polymer chain growth, since the alkylation of anthracene and of dihydroanthracene does not occur readily [21]. It would appear that the probability of ortho substitution in the reaction of dichloromethane with benzene in presence of aluminum chloride is independent of the relative amounts of reactants, within the limits indicated in Table 1, so that condensation products of the same chain length are formed in all cases. The formation of terminal dihydroanthracene residues was noted by one of us together with Lebedev and Tsipershtein [22] in the polycondensation of benzyl chloride. In the opinion of the authors, the cause of the arrest in chain growth is the formation of dihydroanthracene end groups.

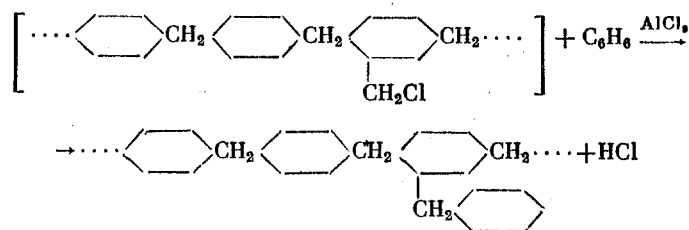
Nonformation of insoluble three-dimensional polycondensation products in the reaction of dichloromethane with benzene may be explained as follows. The formation of three-dimensional products must be preceded by the formation of branched molecules by reaction between linear polymer molecules, dichloromethane, and benzene. The main type of substitution in the polycondensation of dichloromethane with benzene is para substitution. This assertion is based, first, on the fact that the main low-molecular-weight condensation product formed in the early stages of the process is p-dibenzylbenzene and, second, on the analogy shown with the polycondensation of 1,2-dichloroethane with benzene [1,2].

Hence, the formation of branched poly(methylenephenyl) molecules can result from the entry of new methylene groups, and in the great majority of cases these groups will enter positions ortho to existing methylene groups.

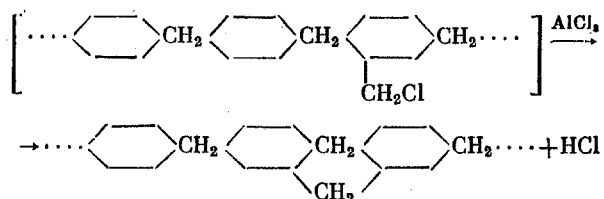


These are two possible ways in which reaction may proceed:

- 1) Reaction of the chloromethyl group with benzene and formation of a branch chain, i.e.,



- 2) Reaction of the chloromethyl group with the neighboring aromatic nucleus and formation of a dihydroanthracene ring system, i.e.,



In our opinion the second way is the more probable, since in this case reaction occurs within the molecule and does not require a collision of the molecule of the intermediate compound with a molecule of benzene or any other molecule of aromatic character.

If this explanation is correct, then we may expect nonformation of three-dimensional polycondensation products even when the amount of dichloromethane is greatly in excess of the equimolecular amount. Experiments designed to verify this suggestion and to determine the effect of the concentration of catalyst showed that no three-dimensional products are formed even when the dichloromethane : benzene ratio is 1.5 : 1; at a ratio of 2 : 1 three-dimensional products are formed only at high concentrations of catalyst, and the amount of such product then formed is not great. The results of these experiments are given in Tables 2-4; the experimental conditions were as indicated above. It was found also that, when the dichloromethane : benzene ratio was raised to 3.12 : 1 at an aluminum chloride concentration of 4.3 moles per 100 moles of dichloromethane, the yield of poly(methylenephenyl) was 64.9% (molecular weight 2970) and no three-dimensional products were formed.

It will be seen from Tables 2-4 that increase in the concentration of catalyst results in an increase in the yield of poly(methylenephenyl) and an increase also in its molecular weight; formation of three-dimensional products is accompanied by reduction in the molecular weight of the poly(methylenephenyl).

The products of the initial stage of the polycondensation of dichloromethane and benzene are diphenylmethane and a mixture of p- and m-dibenzylbenzenes with a preponderance of the para isomer. Diphenylmethane was identified by its melting and boiling points, and it was also oxidized to benzophenone, which showed no depression of melting point in admixture with pure benzophenone. The mixture of dibenzylbenzenes was separated into solid and liquid fractions. The solid was crystallized from alcohol and then melted at 85-86°; the literature [23] gives 85-87.5° for the melting point of p-dibenzylbenzene. Oxidation of the solid with

TABLE 2

Polycondensation of Dichloromethane with Benzene
(dichloromethane : benzene = 1.00)

Catalyst conc. (moles/100 moles of di- chloromethane)	Yield (%)			Molecular wt. of poly (methylenephenyl)
	Diphenyl- methane	Dibenzyl- benzene	Poly(methylene- phenyl)	
2.25	9.2	7.1	26.1	1100
4.50	7.2	6.7	37.6	1710
6.75	7.9	6.2	36.7	1570
9.00	6.7	5.3	37.8	1650
11.25	6.8	2.7	40.2	1820
15.00	5.2	1.6	45.0	2090

TABLE 3

Polycondensation of Dichloromethane with Benzene
(dichloromethane : benzene = 1.50)

Catalyst conc. (moles/100 moles of di- chloromethane)	Yield (% on benzene taken)			Molecular wt. of poly (methylenephenyl)
	Diphenyl- methane	Dibenzyl- benzene	Poly(methylene- phenyl)	
1.50	15.3	5.8	3.9	1020
3.0	16.4	10.7	34.2	1130
6.0	8.1	5.1	43.4	2170
9.0	6.2	3.7	48.1	1940

TABLE 4

Polycondensation of Dichloromethane with Benzene
(dichloromethane : benzene = 2.00)

Catalyst conc. (moles/100 moles of di- chloromethane)	Yield (% on benzene taken)			Molecular wt. of poly (methylenephenyl)
	Diphenyl- methane	Dibenzyl- benzene	Poly(methylene- phenyl)	
1.12	20.7	6.3	5.6	1650
2.25	13.6	4.2	53.6	1710
4.50	7.4	2.8	60.9	2180
6.75	6.7	2.1	63.5*	2130
9.00	3.3	—	49.5**	1820

* Including 1.2% of three-dimensional polymer.

** Including 5% of three-dimensional polymer.

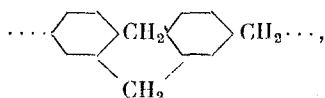
chromium trioxide gave p-dibenzoylbenzene, m.p. 160-161°, identical with the value for p-dibenzoylbenzene in the literature [24, 25].

Found %: C 84.51; 84.34; H 4.70; 4.68 $C_{20}H_{14}O_2$. Calculated %: C 83.88; H 4.89

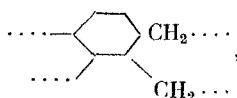
The liquid product was redistilled under reduced pressure and a fraction of b.p. 249-250° (26 mm) was collected. This fraction did not solidify when distilled again, and it was oxidized with chromium trioxide with formation

of *m*-dibenzoylbenzene, m.p. 98-99° (from alcohol); the literature gives 99.5-100° for the melting point of *m*-dibenzoylbenzene [24, 26].

If the above suggestion concerning the formation of dihydroanthracene ring systems in the poly(methylenephenyl) chain and at its end is correct, then this fact should be reflected in the composition of the polycondensation products as expressed by the carbon : hydrogen ratio. When dihydroanthracene residues are completely absent in the polymer, this ratio should be 13.9, and if the polymer chain consists entirely of dihydroanthracene residues linked through methylene groups, i.e.,

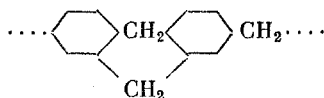


then the carbon : hydrogen ratio should be 14.9. With the maximum possible number of methylene bridges, i.e., when the polycondensation product consists of the units



this ratio should be 15.9.

In order to verify this suggestion we subjected some samples of poly(methylenephenyl) to extraction treatments in order to resolve them into poly(methylenephenyl) soluble in hot alcohol (Fraction I) and of relatively low molecular weight and poly(methylenephenyl) that is insoluble in hot alcohol (Fraction II) and of higher molecular weight. Fractions I and II were analyzed for carbon and hydrogen, and it was found that Fraction II was always richer in carbon than Fraction I. The C : H ratios in Fractions I and II were, respectively, 13.7 and 14.9 for one sample of poly(methylenephenyl) and 13.9 and 14.3 for another. The C : H ratio of Fraction I was close to the ratio calculated for a repeating unit of $-C_6H_4CH_2-$, and that of Fraction II was higher and attained the value calculated for the repeating unit



On the basis of these results we may conclude that the poly(methylenephenyl) obtained by the polycondensation of dichloromethane with benzene in presence of aluminum chloride contains fractions that are richer in carbon than would be expected for poly(methylenephenyl) containing only the repeating unit $-C_6H_4CH_2-$. The high carbon content may be the result of the presence of dihydroanthracene residues in the poly(methylenephenyl) molecule.

The presence of hydroaromatic rings in poly(methylenephenyl) was proved by dehydrogenation of the poly(methylenephenyl) with selenium. It is known that only cycloparaffins are dehydrogenated by selenium, aromatic compounds being formed in the case of six-membered rings [27, 28]. Dehydrogenation of poly(methylenephenyl) with selenium gave a product having a C : H ratio of 15.4, whereas the ratio was 14.3 for the fraction of the original poly(methylenephenyl) that was insoluble in hot alcohol. It was proved, therefore, that poly(methylenephenyl) contains hydroaromatic rings, and in our opinion such rings can only be those of dihydroanthracene residues; we consider that it is scarcely possible that hydroaromatic rings of any other type could be formed.

Poly(methylenephenyl) is a thermally stable substance and can be heated in absence of air to 380-400° without appreciable change. After one hour at this temperature at a residual pressure of 3 mm the polymer showed no appreciable change in molecular weight. Heating to a higher temperature at atmospheric pressure results in pyrolysis, and from the pyrolysis products anthracene was isolated and identified by its melting point, absence of depression of melting point in a mixture test, and results of elementary analysis.

As catalyst for the polycondensation of dichloromethane with benzene, not only aluminum chloride, but also anhydrous ferric chloride, zirconium chloride, and aluminum bromide were tried. The results of these experiments, which were of an exploratory character, are given in Table 5; in all experiments the catalyst concentration was 3.00 moles per 100 moles of benzene and the benzene : dichloromethane ratio was 1.4.

TABLE 5

Polycondensation of Dichloromethane with Benzene

Catalyst	Yield (%)			Molecular wt. of poly (methylene-phenyl)
	Diphenyl-methane	Dibenzyl-benzene	Poly (methylene-phenyl)	
AlCl ₃	12.1	9.3	24.0	1290
FeCl ₃	—	—	—	—
ZrCl ₄	3.1	—	—	—
AlBr ₃	10.8	3.1	17.3	2170

It will be seen from Table 5 that ferric chloride is not a catalyst for the polycondensation of dichloromethane with benzene and zirconium chloride is a very feeble catalyst for this reaction.

SUMMARY

1. A study was made of the polycondensation of dichloromethane with benzene in presence of aluminum chloride.
2. It was shown that in the polycondensation of dichloromethane with benzene a polymer is formed which contains dihydroanthracene residues. The presence of these residues in the polymer chain results in the arrest of chain growth and hinders the formation of branched and three-dimensional polymers.

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