POLYCYCLOCONDENSATION OF ETHYL KETALS OF AROMATIC ACETYL COMPOUNDS—A NEW METHOD OF SYNTHESIS OF POLYPHENYLENES*

V. V. Korshak, M. M. Teplyakov and V. P. Chebotarev

Institute of Hetero-organic Compounds, U.S.S.R. Academy of Sciences

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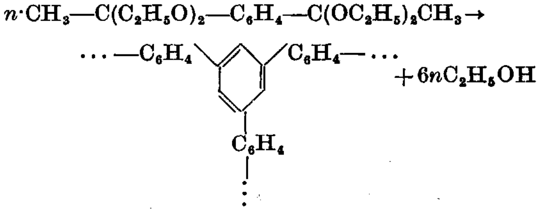
A two stage method has been developed for synthesis of polyphenylenes, based on polycyclocondensation of the ethyl ketals of mono- and diacetylarylenes in the presence of an acid catalyst. Fusible, soluble oligophenylenes with reactive end groups are formed in the first stage, and on heating these are converted to the end products, of the polyphenylene type. It is shown that these polymers are highly resistant to heat.

Promising types of heat resistant polymers are those with a completely aromatic structure especially polyphenylenes [1]. The methods of preparation of polyphenylenes known at the present time [2–5] have a number of important disadvantages, the chief of which are the complexity of synthesis of the starting materials and the difficulty of processing of the polymers. Therefore search for new methods of preparation of polyphenylenes is a very important task.

The cyclotrimerization reaction of ketals of methyl aryl ketones in the presence of acid catalysts, with formation of a 1,3,5-substituted benzene nucleus, has been used for preparation of polyphenylenes [6]. In order to obtain polymers suitable for use in manufacture of articles the process was carried out in two stages. In the first stage fusible, soluble products with reactive end groups were obtained and in the second stage these oligomeric polyphenylenes were converted by heat to crosslinked polymers.

Our results from a study of the cyclotrimerization of a ketal of acetophenone [7] were used for finding the main relationships of copolycyclocondensation of ketals of mono- and diacetyl compounds, leading to formation of polymers of the polyphenylene type.

Examination of the polycyclocondensation of the difunctional diethyl ketal of *p*-diacetylbenzene leads to the conclusion that branching of the polymer begins already in the first stage of the reaction, with formation of a 1,3,5-substituted benzene nucleus, and that subsequently this must result in formation of a network structure



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It is quite understandable that the catalyst concentration will have a considerable effect on this process. It is seen from Fig. 1 that the time to reach the gel point is reduced as the rate of supply of HCl is increased. In order to reach the gel point, however, it is necessary to supply about 1·7 mole of HCl per mole of the ketal of diacetylbenzene, regardless of the rate at which the HCl is supplied. Thus the reaction time can be controlled by varying the catalyst feed rate.

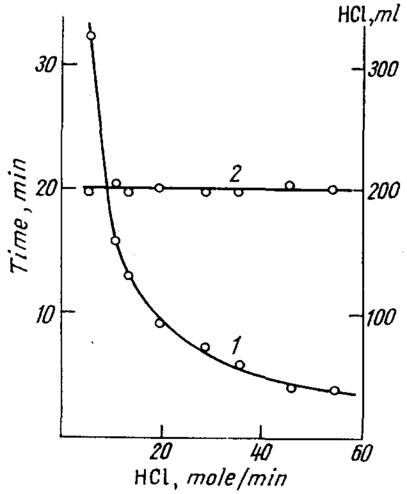


FIG. 1

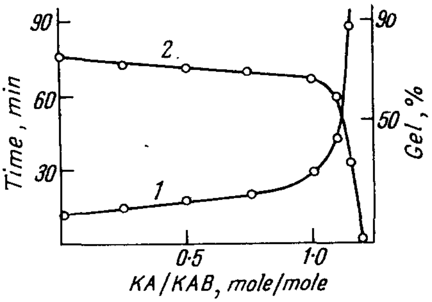


FIG. 2

FIG. 1. Dependence of the gel time (*1*) and consumption of catalyst (*2*) on the rate of supply of dry HCl in polycyclocondensation of the diethyl ketal of *p*-diacetylbenzene.

FIG. 2. Dependence of the gel time (*1*) and quantity of gel (*2*) in copolycyclocondensation of the ketals of acetophenone (KA) and of *p*-diacetylbenzene (KAB) on the molar ratio of the ketals.

PROPERTIES OF OLIGOMERIC POLYPHENYLENES FROM EQUIMOLAR QUANTITIES OF ETHYL KETALS OF DIACETYLARYLENES AND ACETOPHENONE

Diacetyl compound	Elementary composition, %				Mol.wt. (ebullioscopic in chloroform)	Flow temperature,† °C
	found		calculated*			
	C	H	C	H		
$CH_3COC_6H_4COCH_3$	91·12	5·54	91·27	5·65	1800	150–170
$CH_3COC_6H_4C_6H_4COCH_3$	90·56	5·55	91·22	5·72	1400	170–180
$CH_3COC_6H_4CH_2C_6H_4COCH_3$	92·33	6·08	92·83	6·34	2900	100–110
$CH_3COC_6H_4OC_6H_4COCH_3$	85·52	5·18	86·05	5·58	1860	100–120

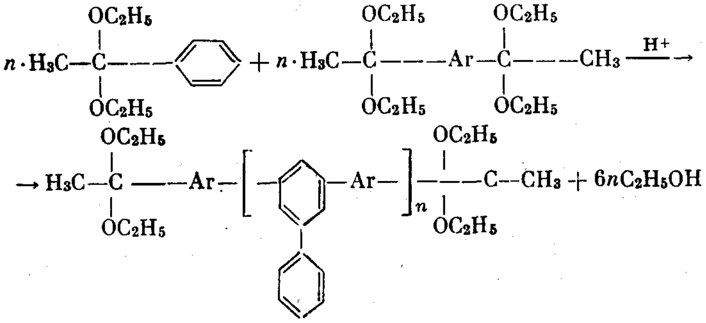
* Calculated for an oligomer with two terminal ketal groups.

† Determined in a plastometer under a load of 100 kg/cm².

The branching reaction can be retarded by blocking a certain proportion of the functional groups. This blocking can be achieved by copolycyclocondensation of ketals of mono- and diacetyl compounds. It is seen from Fig. 2 that as the ratio of mono- to difunctional compound is increased the rate of gel formation decreases and the quantity of soluble fraction increases.

At a molar ratio of 1 : 2 no gel is formed in 2·5 hr. Increase in the quantity of blocking agent results, however, in reduction in the molecular weight of the polymer and decrease in the quantity of functional end groups, which is undesirable for the next stage.

If it is assumed that the reactivities of the ketals of mono- and diacetyl compounds will be similar and that there will be no side reactions, it will be necessary to start with an equimolar ratio of the reactants to obtain a linear polyphenylene. Therefore all subsequent preparations were carried out with an equimolar ratio of the two ketals. In these circumstances the reaction may be represented as follows



For the preparation of polyphenylenes we used the ethyl ketals of *p*-diacetylbenzene, 4,4′-diacetyldiphenyl, 4,4′-diacetyldiphenyl oxide and 4,4′-diacetyldiphenylenethane. The reaction was carried out in solution in dry benzene at 20° and the catalyst was hydrogen chloride. The initial concentration of the solution of monomers was 1 mole/l. The properties of the resulting oligomeric polyphenylenes are presented in the Table.

The suggested structure of the products is supported by the results of elementary analysis and by the infrared and NMR spectra. The infrared spectrum of the polyphenylene from the ketals of *p*-diacetylbenzene and acetophenone contains a band in the region of 880 cm^{-1}, corresponding to the deformation vibrations of a 1,3,5-substituted benzene nucleus, and bands at 1070 and 1680 cm^{-1}, which can be assignd to the valency vibrations of terminal ketal and acetyl groups respectively [9]. The presence of a small quantity of acetyl groups can be explained by partial hydrolysis of the ketal during isolation and treatment of the polymer.

Additional evidence about the structure of the products was obtained by analysis of the NMR-spectra (Fig. 3). Signals of methyl protons and of protons of the benzene nucleus appear at 7·4 and 2·5–2·8 ppm respectively. The fact that there is no signal at 3·25 ppm [10] indicates that the vinylene structure that could be formed as a byproduct by crotonic condensation of the original ketals is absent or present in only insignificant quantity.

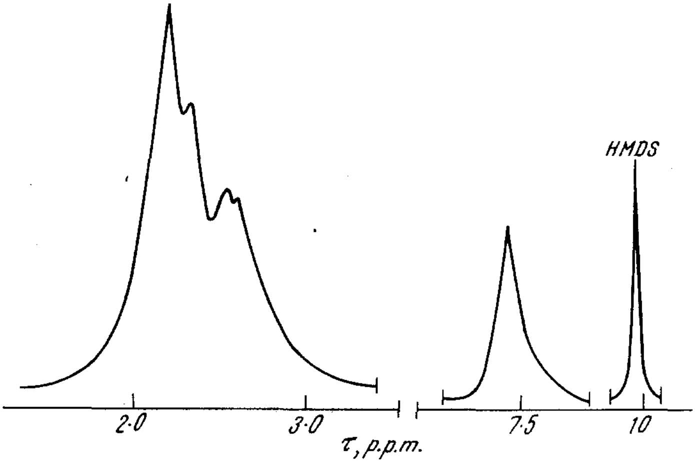


FIG. 3. NMR spectrum of an oligomeric polyphenylene from KA and KAB.

The polyphenylenes were heated in an inert atmosphere at 300°, using p-toluenesulphonic acid as catalyst. This produced dark-brown, infusible and insoluble polymers. The bands at 1070 and 1680 cm^{-1}, assigned to terminal ketal and acetyl groups, disappear completely from the infrared spectra of the final polymers. This indicates that during the heating process further reaction of the end groups occurs, with formation of crosslinked polymer.

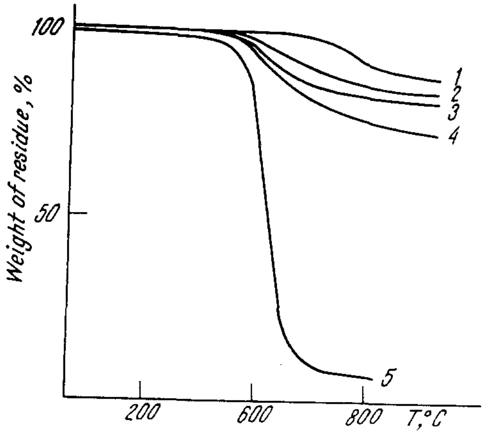


FIG. 4. Dynamic TGA curves of crosslinked polyphenylenes, in an inert atmosphere (*1–4*) and in air (*5*). Polymers prepared from the ketals of p-diacetylbenzene (*1*, *5*), 4,4′-diacetyldiphenyl (*2*), 4,4′-diacetyldiphenyl oxide (*3*) and 4,4′-diacetyldiphenylmethane (*4*).

The chemism of the reactions involved in conversion of oligophenylenes, which is a fairly complex process, is being studied at the present time. The heat-treated polyphenylenes are highly resistant to heat. According to the results of dynamic thermogravimetric analysis the onset of vigorous decomposition in an inert atmosphere occurs in the temperature interval of 480–520° for all the present polymers, and when they are heated to 900° the loss in weight is not more than 12–28% (Fig. 4).

Vigorous decomposition of the polyphenylene from the ketal of *p*-diacetylbenzene occurs in air at 400° (Fig. 4, curve *5*).

It is seen from the above results that the thermal stability of polyphenylenes prepared from ketals of aromatic acetyl compounds is at the same level as the thermal stability of polyphenylenes obtained by the more promising of the previous methods [4, 5]. Moreover the use of easily obtainable ketals of aromatic acetyl compounds provides a comparatively simple and technologically feasible method of producing polymers of this type.

EXPERIMENTAL

Starting materials. The diethyl ketal of acetophenone was prepared by the Claisen reaction [11], by reacting acetophenone with ethyl orthoformate.

The ketals of the diacetylarylenes were prepared by treatment of the diacetyl compound with a 1·2 molar excess of ethyl orthoformate.

The diethyl ketal of *p*-diacetylbenzene is a white, crystalline substance with m.p. 48·5–49°. Found, %: C 69·51, H 9·78. $C_{18}H_{30}O_4$. Calculated, %: C 69·75, H 9·65.

The diethyl ketal of 4,4′-diacetyldiphenyl is a white, crystalline substance with m.p. 78·5–79°. Found, %: C 74·87, H 8·80. $C_{24}H_{34}O_4$. Calculated, %: C 74·60, H 8·81.

The diethyl ketal of 4,4′-diacetyldiphenyl oxide is a colourless, transparent liquid: n_D^{24} 1·5140, d_4^{24} 1·05 g/cm³. Found, %: C 71·52, H 8·50, MR=114·30. $C_{24}H_{34}O_5$. Calculated, %: C 71·5, H 8·45, MR_{calc}=113·95.

The diethyl ketal of 4,4′-diacetyldiphenylmethane is a colourless, transparent liquid: n_D^{24} 1·5090, d_4^{24} 1·07 g/cm³. Found, %: C 75·11, H 9·02, MR=117·0. Calculated, %: C 75·0, H 9·0, MR_{calc} 117·2.

Preparation of oligomeric polyphenylenes. The oligomeric polyphenylenes were prepared by the following general method. The calculated quantities of ketals and solvent to give a solution of concentration 1 mole/l. were placed in a four necked flask, provided with a stirrer, a system for supply of HCl and a thermometer. Then a current of HCl was passed through the reaction mixture at the rate of 11·8 ml/min for 20–30 min. The polymer was precipitated in ethanol and the light yellow product was filtered off, washed on the filter with sodium carbonate solution, with water to neutral reaction then with ethanol, and finally dried *in vacuo* at 60°.

Crosslinking of the polyphenylene oligomers was carried out in boiling tubes in a current of argon. One gramme of polymer and 0·1 g of catalyst were placed in a boiling tube, which was then placed in a heating block where the temperature was raised to 300° and held at that temperature for 4 hr.

Dynamic thermogravimetric analysis was carried out in a DAM B-60, electronic thermal balance, in an atmosphere of argon at a rate of rise in temperature of 4 deg/min.

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SOME CORRELATIONS IN ACCEPTOR-CATALYTIC POLYESTERIFICATION*

V. V. KORSHAK, V. A. VASNEV, S. V. VINOGRADOVA and A. V. VASIL'EV

Institute of Hetero-organic Compounds, U.S.S.R. Academy of Sciences

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A study has been made of the effect on the molecular weight and yield of polyesters of the chemical structure, concentration and order of introduction into the reaction zone of the reactants, and of the temperature and time of acceptor-catalytic polycondensation.

THE polycondensation of dicarboxylic acid chlorides with diols is a typical example of non-equilibrium polyesterification which because of the relatively low reaction temperature has acquired the name "low temperature polycondensation in solution".

In our view this term is unfortunate, because it characterizes only external aspects of the polycondensation.

From study of the mechanism of low temperature polycondensation it has been shown that in one way or another it is a catalysed process, because the tertiary amine is a catalyst for the reaction [1, 2].

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