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Poly(arylenealkyls)

I.I.Yukel'son and V.S. Glukhovskoi

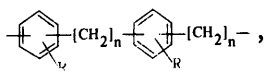
Information on the preparation of poly(arylenealkyls) by polycondensations and on their chemical reactions is surveyed. The chemical reactions of poly(arylenealkyls) can lead to the preparation of materials and products interesting in practical and theoretical respects. There are 75 references.

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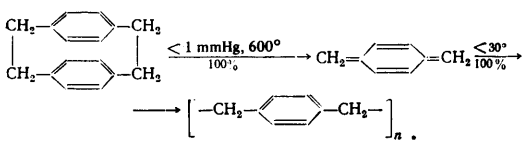
1. INTRODUCTION

It is now known that the methods, mechanism, and conditions of synthesis determine the significant features of the structure of a polymer chain, its structure and the properties of the polymer articles. This is well illustrated by the example of the poly(arylenealkyls)—polymers which contain benzene rings in a chain separated by methylene groups, of the general formula



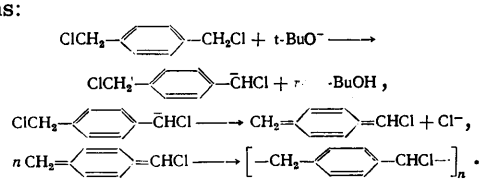
where $n \geqslant 1$ and R = H, CH_3, C_2H_5, C_3H_7, halogen, etc. Poly-(*p*-phenylene-ethylene) prepared by pyrolysis of *p*-xylene, was found to be less thermostable than the same polymer obtained by the reaction of phenyl-lithium with *p*-bisbromomethylbenzene[1]. A considerable number of methods for making such polymers is known and we will only point out some of them.

The preparation of poly-(*p*-xylylene) by the thermal decomposition of di-(*p*-xylylene) in vacuo at 600°C has been described[2]. First two molecules of the intermediate reactive *p*-xylylene are formed, which are spontaneously converted into linear poly-(*p*-xylylene) by the scheme:



Apart from di-(*p*-xylylene), dichloro-, dibromo-, dicyano-, dimethyl-, diethyl-, and tetrachloro-substituted di-(*p*-xylylene) can be used as the initial monomers. Linear, high-molecular-weight sparingly soluble polymers with good physico-mechanical and dielectric properties are formed[3]. Poly-(*p*-xylylene) can be obtained by heating $\alpha\alpha'$-dihalogeno-substituted *p*-xylene with nickel or cobalt powder in the presence of water[4].

A recent paper describes the synthesis of polymers of the poly-(*p*-xylylene) type by the polymerisation of halogenated *p*-xylenes in the presence of bases[5]. α-Chloro-*p*-xylene, by reacting with potassium t-butoxide (t-BuOK), gives poly-(α-chloro-*p*-xylylene) by the following series of reactions:



The polymers thus obtained exhibit considerable thermal stability and good physico-mechanical properties.

The preparation of poly-(*p*-xylylenes) by the electrolytic reduction of $\alpha\alpha'$-dihalogeno-*p*-xylenes has been proposed[6].

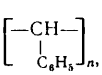
Several investigators[7] have prepared poly-*p*-xylylene with high thermal stability and chemical resistance by heating *m*-methylbenzyltrimethylammonium halides and metal hydroxides in alcohol medium then heating the product in hydrocarbons.

The simplest method for obtaining polymers containing a chain of benzene rings separated by methylene groups is the polycondensation of benzyl chloride and its derivatives, and also of dihalogenoalkanes with aromatic derivatives in the presence of Friedel–Crafts catalysts. However, the poly(arylenealkyls) thus obtained are strongly branched and have a comparatively low molecular weight and low physico-mechanical properties, unlike poly-(*p*-xylylenes).

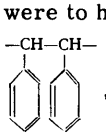
2. SYNTHESIS OF POLY(ARYLENEALKYLS) BY THE FRIEDEL–CRAFTS REACTION

The preparation of polymers with a chain of benzene rings separated by methylene bridges, has been known for a long time. Perkin[8] reported that benzyl chloride reacts with aluminium chloride to form resins and hydrogen chloride. The polycondensation of benzyl chloride has been studied most fully not only in the presence of Friedel–Crafts catalysts, but also of strong acids[9], and even in the presence of such an inert substance as glass[10].

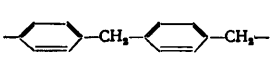
Many workers thought[10,11] that the polybenzyl formed should have a structure of the



type, but did not give any proof in support of this. Mass-spectroscopic analysis of the pyrolysis products of polybenzyl showed that they consist of toluene, benzene, and xylene[12]. If polybenzyl were to have the structure

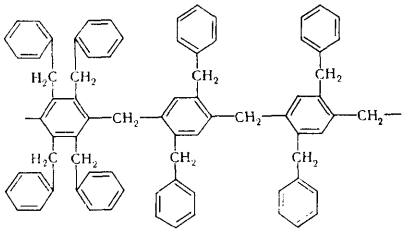


and not



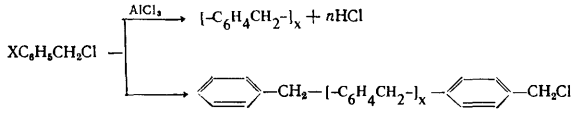
(both structures correspond to the same empirical formula $[-C_7H_6-]_n$) then one of the products of destruction should

be stable. The absence of stilbene shows that the linear structure is correct for polybenzene. The linearity of the polybenzyl structure is also shown by its high thermal stability. In this molecule where the phenyl groups do not enter into the composition of the main chain and there are substituents at each successive carbon atom, all the carbon–carbon bonds of the chain should be weakened by the presence of tertiary carbon atoms. The presence of benzene nuclei in the main chain of the polymer is responsible for its high stability because of the possibility of conjugation. The reason for the high thermal stability of polybenzyl could be a strongly branched structure, which was proposed because of the X-ray diffraction analysis and the infrared spectra:



In pyrolysis of polybenzyl the proportion of volatiles amounts to almost 100%, which shows the absence of a cross-linked polymer or at least of one strongly cross-linked.

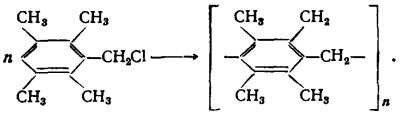
Korshak and coworkers [13] obtained polybenzyl by the polycondensation of benzyl chloride under the action of various Friedel–Crafts catalysts. It was found that in the presence of $AlCl_3$ a powdery product was formed, only partly soluble in benzene, with a softening point of 220–230°C and molecular weight 2000. In the presence of $ZnCl_2$ and $SnCl_4$ a powdery polymer soluble in benzene is formed. The polycondensation proceeds with the formation mainly of a linear polymer:



Owing to secondary alkylation of the same benzene ring the polymer can be branched and the formation of dihydroanthracene rings is possible.

By using the $AlCl_3$.nitrobenzene complex Moore [14] obtained polybenzyl and polyphenethyl with molecular weights not exceeding 1880 by the polycondensation of benzyl chloride and phenethyl chloride in nitrobenzene solution.

Haas [15] showed that the polymer obtained from chloromethyldurene is highly crystalline and has a completely linear structure, unlike the strongly branched and amorphous polybenzyl. The explanation for this difference in the properties of the polymers is that in the polymer based on chloromethyldurene all the positions of the benzene ring except *para*- are blocked:



Overhults and Ketley [16] investigated the effect of substituents in the benzene ring of a chloromethyl-substituted monomer on the formation of a linear polymer. Copolymers of dichloromethyldurene and aromatic compounds were obtained in solution in the presence of $TiCl_4$ catalyst. It was found that if the number of methyl groups present in the second monomer is reduced from 4 (durene) to 2 (*p*-xylene) and to zero ($\alpha\alpha'$-dichloro-*p*-xylene) but the number of methyl groups in the first monomer remains at 4 then the polymers formed are crystalline, insoluble in organic solvents, and have low molecular weights (the degree of polymerisation does not exceed 8). However, when the aromatic ring does not have a substituent, for example, in the copolymerisation of $\alpha\alpha'$-dichloro-*p*-xylene with *p*-xylene, an amorphous product is formed, insoluble in organic solvents and not melting above 500°C. The properties of the polymer show that branching followed by cross-linking occur during the reaction. The polymers obtained from dichloromethyldurene and aromatic compounds in which methyl groups are in positions ensuring *ortho*- and *meta*-addition of the copolymer (for example, a copolymer of dichloromethyldurene) have a small amount of a crystalline product insoluble in benzene and a large amount of amorphous, soluble, low-melting product with degree of polymerisation 4–5. The formation of a low-molecular-weight polymer is evidently due to steric hindrance. If the number of blocking groups is reduced sufficiently to remove the steric hindrance the chain growth prevents cross-linkage. The maximal molecular weight of the soluble polymer is reached immediately before the start of cross-linking. On carrying out the reaction to partial cross-linking, the molecular weight of the soluble part falls from 3800 to 2000 and less. This shows that the longer chains of the polymer are cross-linked first. Attempts to inhibit cross-linking in polycondensation for the preparation of a higher-molecular-weight polymer did not lead to the desired result since chain growth ceases during this.

The polymer obtained from $\alpha\alpha'$-dichloro-*p*-xylene and *p*-xylene can, after separation and purification, be moulded at 120–140°C.

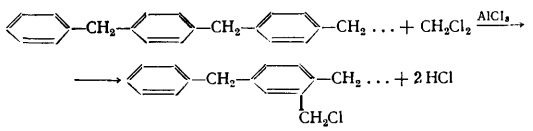
Crystalline polybenzyl, poly-(2,5-dimethylbenzyl), and poly-(α-methylbenzyl) were made by adding a solution of $AlCl_3$ in ethyl chloride to benzyl chloride or to 1-chloroethylbenzene respectively at ~ −130°C. [17] The X-ray powder diagrams of the polymers show their linear structure and high crystallinity. The linear structure is confirmed by an analysis of their infrared spectra (the absorption band of 1,4-disubstituted aromatic rings is at 805 cm^{-1}), and also of the NMR spectra, in which there are signals of aromatic protons with chemical shift 7.05 and methylene protons with 3.08, with relative intensity 2 : 1, which corresponds with the structure $H-[-C_6H_4CH_2-]_n$ for polybenzyl.

High-melting-point crystalline polybenzyls are obtained from benzyl chloride and its derivatives in the presence of $AlCl_3$ at −100°C. The best results in the low-temperature Friedel–Crafts reaction are also obtained with substituted benzyl chloride. Whereas polybenzyl has maximal m.p. 142°C, poly-(2,5-dimethylbenzyl) softens only at 190°C and melts above 300°C. [18] A polymer of the polybenzyl–poly(phenylenemethyl) (PPM) type can be obtained also by the polycondensation of benzene with methylene dichloride in the presence of $AlCl_3$: [19]

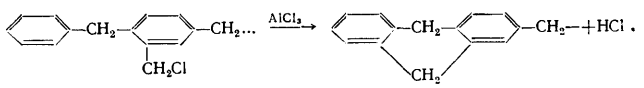


During the polycondensation cross-linked products are not formed at any ratio of the reactants. The reason for

the arrest of chain growth is the formation of dihydroanthracene terminal groups. It is thought that initially branched PPM molecules of the type:



are formed, although compounds with a terminal $-CH_2Cl$ group were not observed. The interaction of the chloromethyl group with a neighbouring aromatic nucleus leads to the formation of a dihydroanthracene ring:



The highest molecular weight of a polymer, 2970, was obtained at a methylene dichloride : benzene ratio of 3.12 : 1 and a catalyst concentration of 4.3 mole %. PPM is a viscous liquid and is soluble in halogenoalkanes and aromatic hydrocarbons.

The possibility of the preparation of PPM [20] by the complete arylation of diphenylmethane under the action of $AlCl_3$ by the reaction:

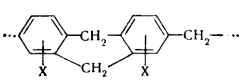


has been shown[20]. The low-molecular-weight product of the complete arylation of diphenylmethane is benzene.

A polymer with the low molecular weight of 1350 is evidently obtained because of the formation of dihydroanthracene rings at the ends of the growing chains which leads to the arrest of chain growth.

The formation of a cross-linked product was observed only on raising the reaction temperature to 170 °C. Increasing the catalyst concentration also leads to an increase in the yield of PPM but an increase in the molecular weight is not observed.

Linear polymers with a molecular weight not exceeding 2500 were obtained by the polycondensation of fluorobenzene, chlorobenzene, and bromobenzene with methylene dichloride[21]. This shows that the activity of halogenobenzenes is less than that of benzene. It could be expected that the formation of dihydroanthracene rings at the ends of the growing polyhalogenophenylenemethyl chains leads to the breaking of the chain

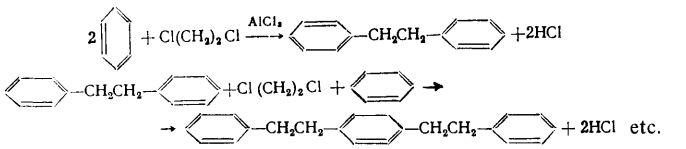


where X is a halogen atom.

A high-molecular-weight polymer is also not formed in the polycondensation of *p*-xylylene dichloride with various aromatic hydrocarbons in the presence of $SnCl_4$ in nitrobenzene at 60 °C. Only gelatinous polymers were obtained[22].

Polymers with benzene rings in a chain separated by $-CH_2-CH_2-$ groups are obtained by the polycondensation of 1,2-dichloroethane with benzene and its derivatives[23-25] in the presence of $AlCl_3$.

Polyphenylene-ethyl (PPE) is formed by polycondensation of 1,2-dichloroethane with benzene in the presence of $AlCl_3$. The molecular weight of PPE increases with decrease in the benzene: dichloroethane ratio and is maximal at the ratio 1.20 : 1,[26] but at 1.10 : 1 the only product of the reaction is insoluble PPE:



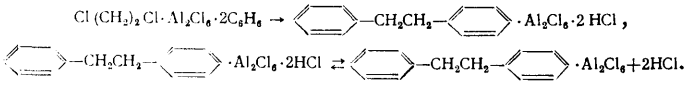
The first stage of the polycondensation of 1,2-dichloroethane with benzene in the presence of $AlCl_3$ is the formation of a complex of $AlCl_3$ with 1,2-dichloroethane[27]:

$$ClCH_2CH_2Cl + Al_2Cl_6 \rightleftarrows ClCH_2CH_2Cl \cdot Al_2Cl_6 .$$

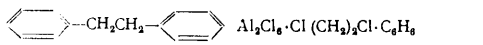
The complex reacts further with benzene, forming a ternary complex:

$$ClCH_2CH_2ClAl_2Cl_6 + 2C_6H_6 \rightleftarrows ClCH_2CH_2Cl \cdot Al_2Cl_6 \cdot 2C_6H_6 .$$

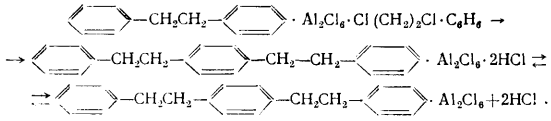
The reaction between 1,2-dichloroethane and benzene takes place inside this complex and leads to the formation of a diphenylethane–aluminium chloride–hydrogen chloride ternary complex.



The complex of diphenylethane and $AlCl_3$ reacts again with dichloroethane and benzene to form:



The reaction proceeds in the ternary complex and leads to the formation of a polymeric chain and the release of hydrogen chloride:



Further increase in the chain proceeds similarly. The yields of the reaction in the ternary complex were confirmed by Garmonov and coworkers[28] who isolated and determined the composition of this complex with the aid of labelled atoms. ^{14}C-Labelled benzene, toluene, ethylbenzene, propylbenzene, and 1,2-dibromoethane, were used.

The mixtures of the components deposited the complexes as dark red, heavy oily liquids. The change in the activity of ^{14}C-labelled radioactive specimens was measured with an end window Geiger counter. The results show that the ternary complexes have the composition:

$$HalCH_2CH_2Hal \cdot (5-7)\,ArR \cdot Al_2Cl_6 .$$

The composition of the complex is almost independent of the molar ratio of the components. Interestingly, with increase in the alkyl groups in the benzene ring the stability of the complex increases. A sufficient excess of one of the initial components is needed to shift the equilibrium

$$ClCH_2CH_2Cl \cdot Al_2Cl_6 + 2C_6H_6 \rightleftarrows ClCH_2CH_2Cl \cdot Al_2Cl_6 \cdot 2C_6H_6$$

to the right.

The polycondensation of aromatic hydrocarbons with dihalogenoalkanes in the presence of aluminium chloride is connected with their transfer from a hydrocarbon layer into a catalytic complex and back again. With this there is

a change in the value of the distribution of the hydrocarbons between the catalytic and hydrocarbon layers, just as in the alkylation of aromatic compounds[29].

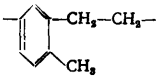
The reaction mass is a heterophase system consisting of a liquid catalytic complex of aluminium chloride with aromatic compounds, halogenoalkanes, and a hydrocarbon layer insoluble in the complex.

Poly(phenylene-ethyl) with a high molecular weight, 60 000, can be obtained by the polycondensation of diphenylethane[30,31]. To obtain a soluble polymer as well as increasing the temperature the reaction time must be shortened, otherwise a three-dimensional product is formed. To produce a high molecular weight the reaction must be stopped before the formation of a cross-linked polymer. An analysis of the infrared spectra of PPE obtained from dibenzyl and dichloroethane gives a basis for considering that a strongly cross-linked product is formed.

Poly(toluylene-ethyl) (PTE) is formed in the polycondensation of toluene with 1,2-dichloroethane[32]:

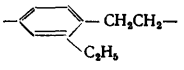
$$(n+1)\,C_6H_5CH_3 + n\,Cl\,[CH_2]_2Cl \xrightarrow{AlCl_3} CH_3C_6H_4\,[-CH_2CH_2C_6H_3(CH_3)-]_nH + 2HCl$$

The maximal molecular weight of PTE (4280) is reached when there is a slight excess of 1,2-dichloroethane and a cross-linked polymer is formed only when there is an excess of the latter. Steric hindrance is responsible for the difficulty in forming a cross-linked polymer. Destructive oxidation of the reaction products offers the possibility of suggesting the structure of the PTE chain:



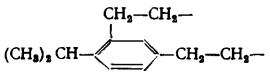
The infrared spectrum of the polymer also shows the presence of a 1,3,4-substituted nucleus in PTE.[33]

Yukel'son and coworkers[34] obtained poly(ethylphenylene-ethyl) (PEPE) by the polycondensation of ethylbenzene with 1,2-dichloroethane in the presence of $AlCl_3$. The highest molecular weight of PEPE is obtained at ethylbenzene : dichloroethane ratios close to 1. An analysis of the infrared spectra of the polymer shows that the benzene ring has predominantly 1,2,4-substitution:



The reaction of cumene with dichloroethane under the action of $AlCl_3$ gives poly(cumylene-ethyl) (PCE) with a low molecular weight even at a cumene : dichloroethane molar ratio[35].

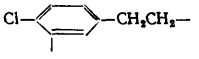
An analysis of the infrared spectrum of PCE shows that the main type of substitution of the benzene ring should be 1,2,4-substitution:



In polycondensation the isopropyl group is completely retained and n-propylbenzene is not formed under the action of $AlCl_3$. This is shown by an analysis of the NMR spectrum.

Shegoev[36] showed that the polycondensation of xylene with 1,2-dichloroethane proceeds smoothly and with a good yield of poly(dimethylphenylene-ethyl) (PDMPE), but in the polycondensation of di-isopropylbenzene with dichloroethane the process stops at the dimer stage owing to the large size of the alkyl substituents. However, the condensation of trialkylbenzene containing an alkyl with 1–3 carbon atoms and a dihalogenoalkane with 2–4 carbon atoms in the alkylene in the presence of $AlCl_3$ leads to the formation of a polymer with a molecular weight of 8000–9000.[37] The reaction of chlorobenzene with 1,2-dichloroethane gave poly(chlorophenylene-ethyl) (PCPE).[38] The greatest increase in the molecular weight to 4250 is observed in approaching an equimolecular ratio of the reactants and the formation of three-dimensional products at the equimolecular ratio. A 1% excess of chlorobenzene gives a mixture of a linear and a cross-linked product.

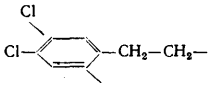
The study of the structure of PCPE by the method of destructive oxidation and an analysis of the infrared spectrum[39] suggests that the benzene ring of the chain is predominantly 1,2,4-substituted:



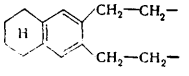
The formation of poly(fluorophenylene-ethyl) (PFPE)[40] proceeds similarly with the only difference that with a 5 mole % excess of fluorobenzene an exclusively three-dimensional infusible and insoluble polymer is formed. The molecular weight of the polymer reaches a maximum at a catalyst concentration of 6 mole % on the fluorobenzene and at a fluorobenzene : dichloroethane ratio of 1 : 1.19.

The PFPE unit cell has the same structure as PCPE.

Korshak and Kolesnikov[41] showed that increasing the substituents in the benzene ring still further hinders the formation of a cross-linked product. Thus in the polycondensation of 1,2-dichloroethane with *o*-dichlorobenzene in the presence of $AlCl_3$ (up to 6 mole %) insoluble products are not formed even when there is a considerable excess of dichloroethane. Poly(dichlorophenylene-ethyl) (PDCPE) of the highest molecular weight (~ 3920) is formed at the equimolecular ratio of the reactants. The polymer is a solid of low melting point (50 °C). Simultaneously with the polycondensation there is a redistribution of the halogen, leading to a decrease in the chlorine content of the reaction product. PDCPE consists mainly of monomeric units of the structure:



Insoluble products are also not formed during polycondensation of tetralin with 1,2-dichloroethane even with an excess of the latter[42]. Tetralin, like *o*-dichlorobenzene, can be regarded as a dialkyl derivative of benzene in which the substituents are in the *ortho*-position. The experimental results showed that the molecular weight of poly-tetralylene-ethyl (PTTE), which is a solid, rises to a maximum (6400) at the dichloroethane : tetraline ratio of 1 : 1.10. It is thought that in PTTE the tetralin residues are linked by $-CH_2-CH_2-$ groups, which occupy both β-positions in the aromatic ring of tetralin:

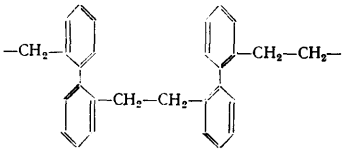


It is interesting to note that the molecular weight of PTTE remains constant in the range of catalyst concentrations 3–12 mole % of the tetralin.

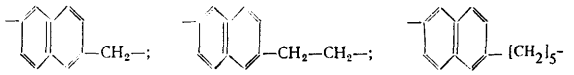
Poly(diphenylene-ethyl) (PDE) isobtained as a result of the reaction of biphenyl with dichloroethane[43,44].

A polymer with a molecular weight of 5120 is formed at a dichloroethane : biphenyl molar ratio of 1 and a catalyst concentration of 10 mole % of the biphenyl. At dichloroethane : biphenyl ratios > 1 and a catalyst concentration of

23 mole %, insoluble PDE is formed. Conclusions about the structure of the polymer are drawn on the basis of an analysis of the infrared spectra of PDE:



Polymers containing naphthalene rings in chains are also obtained under the same conditions:



Kolesnikov and coworkers[45] made copolymers in the dichloroethane–benzene–fluorobenzene and dichloroethane–chlorine–benzene–fluorobenzene systems. The ratio of the units $(-C_6H_4CH_2CH_2-) : (-C_6H_3HalCH_2CH_2-)$ in the polymer obtained by common polycondensation of dichloroethane with benzene and fluorobenzene is less than in the copolymer obtained by the polycondensation of the dichloroethane–chlorobenzene–fluorobenzene system. This shows that the relative activity of fluorobenzene is less than the relative activity of chlorobenzene. The highest molecular weight of a copolymer of dichloroethane with benzene and fluorobenzene is 2610 and that of the copolymer of dichloroethane, benzene, and fluorobenzene is 2120. The rate of the polycondensation process in the dichloroethane–fluorobenzene–chlorobenzene system is appreciably greater than that in the dichloroethane–benzene–chlorobenzene system. The possibility of the synthesis of a ternary copolymer of dichloroethane with cumene and bibenzyl by polycondensation in the presence of $AlCl_3$ was shown by Kolesnikov and coworkers[46]. As expected, the molecular weight increases with the bibenzyl : cumene ratio.

It was found by turbidimetric titration that the polycondensation product is a copolymer and not a mixture of homopolymers. The infrared spectrum of the product of the common polycondensation of cumene and bibenzyl with dichloroethane is similar to that of PCE.

Hence from what has been stated above the following conclusions can be drawn:

1. In the polycondensation of either benzyl chloride or of aromatic hydrocarbons with halogenoalkanes in the presence of a Friedel–Crafts catalyst low-molecular-weight polymers are formed.

2. The highest molecular weight of polyarylenealkyls is reached on approaching the equimolecular dihalogenoalkyl : aromatic compound ratio, which agrees with the polycondensation theory.

3. Since the Friedel–Crafts catalyst is not stereospecific, the polyarylenealkyls obtained are branched and are a mixture of polymeric chains in which the benzene rings have different substitution.

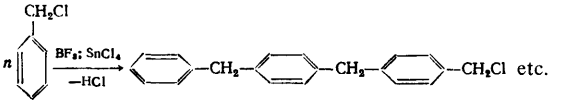
3. CHEMICAL REACTIONS OF POLY(ARYLENEALKYLS)

As a result of polycondensation polymers of low molecular weight and poor mechanical properties are formed. The polymers are either viscous liquids or solids difficult to reprocess. The polyarylenealkyls do not contain functional groups with the aid of which they could be subjected to chemical changes, whereas polyarylenealkyls such as PPM are thermally stable products and withstand heating in the absence of air to 380–400°C without undergoing significant changes[12].

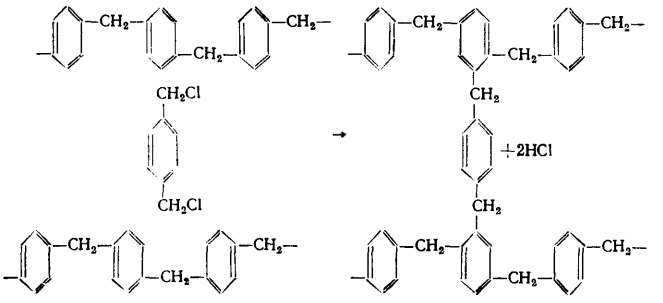
Polyarylenealkyls also exhibit increased resistance to radiation[47]. Thus the viscosity of lubricating oils of polymers obtained by the polycondensation of aromatic hydrocarbons $C_6H_{6-n}R_n$ (where R = alkyl C_1-C_5, $n = 1-5$) with alkylene dihalides C_1-C_4 (for example, $ClCH_2Cl$ or CH_2BrCH_2Br) in the presence of $AlCl_3$, $ZnCl_2$, or BF_3 after the action of a 2×10^9 rad dose of β-radiation increased by 150%, whereas ordinary mineral oil of the same viscosity showed an increase in viscosity of 500%.

A search is now being made for means of the chemical modification of polyarylenealkyls to obtain commercially usable products based on them.

Phillips[48] effected the cross-linking of polybenzyl with a Friedel–Crafts reaction. First the polycondensation of benzyl chloride in the presence of mild catalytic agents (BF_3 or $SnCl_4$) was brought about and fusible and soluble polybenzyl was obtained:



Cross-linking took place when this polymer reacted with *p*-dichloroxylene in the presence of a mild catalyst:



The products were named Friedel–Crafts polymers.

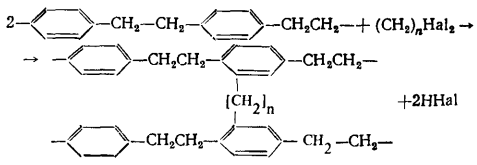
This method of cross-linking, proposed for strengthening polybenzyl and terphenyl, can also be used for other polymers which contain aromatic or heterocyclic rings.

Glass fibre, organic fibre, and siliconorganic fibres are readily impregnated by Friedel–Crafts polymers. The strengthening of these plastics is longer-lasting than, for example, with phenolic resins but the stability of these polymers to the action of chemical reagents is sufficiently high. Thus they do not have the drawback characteristic of phenolic resins—instability towards alkalis, since they do not contain hydroxyl groups arranged in series with methylene bridges. They are also stable to the action of radiation.

A little Friedel–Crafts catalyst is added to the polymer obtained from $\alpha\alpha'$-dichloro-*p*-xylene before moulding and during the moulding at 120–140°C a thermoreactive material which exhibits high thermal stability is formed[16].

The polymers which contain benzene rings in a chain separated by methylene groups, can be cross-linked also by dihalogenoalkanes in the presence of Friedel–Crafts catalysts. PPE with a molecular weight of 5900 was cross-linked with dihalogenoalkanes : methylene dibromide, 1,2-dibromoethane, 1-bromo-3-chloropropane, 1,4-dibromobutane, and 1,6-dibromohexane[49]. The dihalogenoalkanes can be arranged in the following series according

to the rate of formation of the trimer: 1,4-dibromobutane > 1-bromo-3-chloropropane > 1,6-dibromohexane > methylene dibromide > 1,2-dibromoethane. The cross-linking takes place in two stages. Initially a strongly branched polymer is formed, soluble up to a certain stage, and subsequently the branched molecules are converted into cross-linked ones and lose the ability to dissolve:



The higher the molecular weight of the initial polymer the less the need for a cross-linking agent. Initially the longer chains of the polymer molecules are cross-linked, which is shown by the drop in the molecular weight of the soluble part of the polymer.

Another method found for strengthening poly(arylenealkyls) is with the aid of sulphur[50]. In the reaction of poly(arylenealkyls) with sulphur at 200–250°C the sulphur is added to the polymer, hydrogen sulphide is eliminated, the viscosity increases, and double bonds are formed[51]. Most of the polymer becomes insoluble. The vulcanising of PPE, PTE, PEPE, PCE, PCPE, and PDE has been studied[52].

The controlling stage of the vulcanising of poly(arylenealkyls) is the breakdown of inactive sulphur particles into active ones.

The activation energy of the –S–S– bonds in the polysulphide chain of sulphur is 33.4 kcal mole^{-1} and the energy of the fission of $^{\bullet}S_2^{\bullet}$ to the monoradical is 63 kcal mole^{-1}.[53] The activation energy of the vulcanising of polyarylenealkyls lies in the range 37–41 kcal mole^{-1} [52] but the activation energy of the thermal destruction of poly(arylenealkyls)—for example, poly-(*p*-phenyleneethylene) has a value of not less than 58 kcal mole^{-1}.[54] On comparing the values given it can be assumed that the initial active species under the conditions of the reaction is $^{\bullet}S_2^{\bullet}$.

Owing to the formation of new chemical bonds between the poly(arylenealkyl) molecules structuring of the polymer takes place[55]. An analysis of the infrared spectra of vulcanised PPE, PTE, PEPE, and PCE prepolymers in the range of planar deformation vibrations (1225–960 cm^{-1}), of out-of-plane deformation vibrations (below 900 cm^{-1}), and also in the range of the overtones and constituent frequencies (2600–1650 cm^{-1}) shows the absence of changes in the substitution of the benzene ring of the chain[56].

On the basis of the above it has been suggested that in the thermal vulcanising of poly(arylenealkyls) cross-linking takes place by the loss of a hydrogen atom from the methylene groups of the bridge and the alkyl substituents. In the vulcanising of poly(arylenealkyls) owing to the dehydrogenating action of sulphur double bonds are formed conjugated with the benzene ring[57]. The electronic spectra of the vulcanised polymers show that sulphide bridges have the $-S_x-$ structure, where $x \geqslant 2$, and not of type =S= as suggested[58].

The vulcanising proceeds by a radical mechanism[57]:

$$S_8 \xrightarrow{>200^\circ} {}^{\bullet}S_y + {}^{\bullet}S_z,$$

$$PH + {}^{\bullet}S_z \rightarrow P^{\bullet} + HS_z,$$

$$HS_z + HS_z \rightarrow H_2S + {}^{\bullet}S_z,$$

$$P^{\bullet} + HS_z \rightarrow PSSH,$$

$$PS_z + PH \rightarrow PSSH + P^{\bullet},$$

$$P^{\bullet} + {}^{\bullet}S_z \rightarrow PS_z,$$

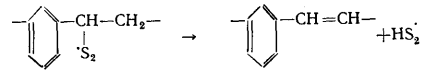
$$PSSH + PH \rightarrow PSP + H_2S,$$

$$PS_z + PS_z \rightarrow PS_4P,$$

$$P^{\bullet} + P^{\bullet} \rightarrow P-P,$$

where PH = poly(arenylalkyl).

The formation of double bonds evidently proceeds thus:



The appearance of absorption bands in the 970–960 cm^{-1} range in the infrared spectra shows the presence of double bonds. After bromination of the poly(alkylenealkyl) this absorption band is not present in the infrared spectrum.

The radical nature of the interaction of sulphur with poly(arylenealkyls) is confirmed by the fact that the products of the thermal vulcanising, subjected to EPR analysis, show a narrow absorption line (~ 10.0e) without signs of hyperfine structure with a *g*-factor of the free electron[59]. The concentration of the paramagnetic species for the vulcanised prepolymers of PPE, PTE, PEPE, PCPE, and PCE falls within the range $(0.12-0.5) \times 10^{20}$ g^{-1}. The EPR signal is unchanged after the products have been stored for several months, but in dissolution in toluene it disappears and does not reappear after removal of the solvent. The intensity of the EPR signal is also reduced on irradiation of the specimens with X-rays. The existence of an EPR signal in vulcanised poly(arylenealkyls) is due to the formation of radicals of the type $R_{arom}-CH_2-\dot{C}H-R_{arom}$ and $R_{arom}-\dot{C}H_2$ produced according to the scheme given above.

Poly(arylenealkyls) react with sulphur at different rates[60]. They are arranged according to hydrogen sulphide liberation in the order PDE > PCE > PTE > PEPE > PCPE and according to the rate of formation of a cross-linked polymer in the order PEPE > PPE > PTE > PCE > PCPE > PDE. Such a difference in the rate of liberation of hydrogen sulphide and the formation of a cross-linked polymer depend on the structure of the initial poly(arylenealkyl). The activating action of the benzene ring on the methylene groups of the bridge ensures that PDE has a high rate of reaction with sulphur. The presence in the benzene ring of the electronegative substituent chlorine reduces the lability of the hydrogen atoms of the methylene groups in the *o*-position to chlorine. Therefore the vulcanisation of PCPE takes place under more severe conditions.

The high rate of gelatinisation for PEPE ensures the presence of a methylene group at the substituent $-CH_2CH_2-$ which should react just like the bridge methylene groups.

The vulcanised poly(arylenealkyls), prepolymers, are solids soluble in aromatic hydrocarbons and halogenoalkanes. Subsequent heating of the prepolymers at temperatures not less than 200°C leads to the formation of cross-linked products.

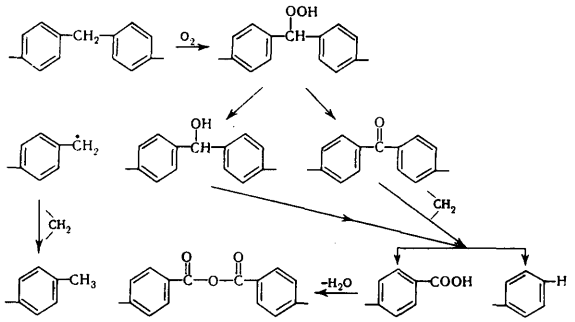
Vulcanised poly(arylenealkyls) can be used as thermoreactive paint constituents[57]. Coatings based on such polymers exhibit good dielectric properties, high chemical stability, and good adhesion to metals.

The prepolymers can be used also as binding agents for plastics, for which purpose glass fibre is impregnated with the prepolymer, pressed and hardened at 220°C or above. The specimens exhibit good thermal stability and chemical resistance and have physico-mechanical indices higher than for plastics based on phenol–formaldehyde resins.

Vulcanised poly(arylenealkyls) have a stabilising effect, like low-molecular-weight antioxidants of the R–S–S–R type[61].

To reduce the temperature of structuring of the poly-(alkylenealkyls) with sulphur, vulcanising under the action of aluminium chloride was studied[62]. The reaction takes place at 80–90°C. Unlike thermal vulcanising, the formation of new chemical bonds in the polymer evidently occurs at the benzene ring. The structured polymer formed in the catalytic vulcanising is a powdery product but the cross-linked polymer after thermal vulcanising is a tough material, ground into powder with difficulty.

Conley[63] studied the thermal oxidation of polybenzyl in air and in oxygen in the temperature range 140–220°C and proposed a mechanism for the oxidation:

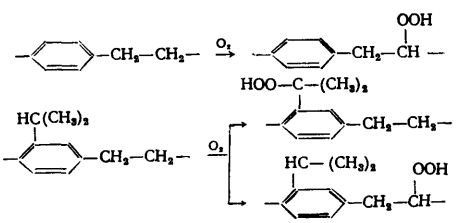


The oxidation, like the vulcanising, takes place at the methylene bridges with the formation of ketonic and carbonyl groups. On the basis of the results on the rate of formation of carbonyl compounds, the initial activation energy of the oxidation was found to be 14.5 ± 3.5 kcal. A vapour-phase chromatographic analysis of the volatile products shows that the main products of the oxidation are benzoic acid and benzophenone; small amounts of toluene, water, and CO_2 are formed. The secondary reactions of the decomposition, which lead to breaking of the chain are considered to be further oxidation of the benzhydrilic and benzophenone bonds.

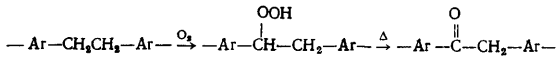
The thermal oxidation of several polymers containing a chain of benzene rings separated by two methylene groups has been studied. It was found that unlike polybenzyl and poly-(*p*,*p*'-diphenylenemethylene) appreciable decomposition of most of the polymers with a $-CH_2-CH_2-$ bond in oxygen is observed in the temperature range 340–410°C.[1] These polymers can be arranged in the following order of thermal oxidation resistance: poly-(2,6-naphthylene-ethylene) > poly-(*p*-phenylene-ethylene) > poly-(9,10-anthrylene-ethylene).

The mechanism given for the oxidation of polybenzyl is evidently correct for the thermal decomposition of these polymers.

Kolesnikov and Chuchin[64,65] oxidised several poly-(arylenealkyls) both in the melt and in solution. The oxidation as far as hydroperoxides proceeds according to the scheme:



An analysis of the infrared spectra showed that the oxidation of poly(arylenealkyls) in the melt goes further than in solution. The spectrum of poly(cumylene-ethyl) oxidised in the melt gave absorption bands characteristic for aromatic acids (1270 cm^{-1}), aldehydes (1715 cm^{-1}), and other oxygen-containing groups. In the oxidation of poly-(arylenealkyls) in cumene the decomposition products of the hydroperoxides do not contain tertiary alcoholic groups. In thermal decomposition poly(phenylene-ethyl) hydroperoxide gives the same products as poly(cumulene-ethyl) hydroperoxide, obtained by oxidation in cumene. Judging by the infrared spectra, the hydroperoxides have the same structure, that is, the oxidation takes place at the methylene groups just as in the thermal oxidation of polybenzyl[63] and the thermal destruction of poly-(*p*-xylylene).[66] The decomposition follows the reaction:



The oxidation of PPE in cumene and tetralin solutions was studied and it was found that the oxidation in cumene is much faster than that in tetralin[67]. Analysis of the infrared spectra showed that oxidation of PPE by atmospheric oxygen at elevated temperatures proceeds like oxidation by oxygen at 80°C, mainly to the hydroperoxide.

Poly(cumylene-ethyl) (M = 1100) oxidised by oxygen in the presence of benzoyl peroxide gave a polymeric hydroperoxide containing 2.4% hydroperoxide groups.

The decomposition of the hydroperoxides is a first-order reaction with an activation energy of 3.5 kcal $mole^{-1}$.

The product of the common polycondensation of cumene and dibenzyl was oxidised[69] and it was found that with increase in the fraction of cumene in this reaction mixture the concentration of peroxide groups in the oxidised poly-(arylene-ethyl) increases, reaching a maximal value in PCE. The reverse picture was observed in the oxidation of poly(arylenealkyls) in cumene solution, when the maximal concentration of hydroperoxide groups was observed in the oxidation of PPE. This difference has been explained[69] by the presence of an alkyl substituent in the benzene ring, which weakens the induction effect, in connection with which there is a decrease in the mobility of the hydrogen atom of the methylene group. Therefore in the common presence in the benzene ring of methylene groups and of groups with α-carbon tertiary atoms a decrease in the rate of autoxidation of dialkylbenzenes and a decrease in the maximal concentration of hydroperoxide was observed. This evidently also explains the increase in the concentration of hydroperoxide groups in poly-(arylene-ethyl) with decrease in the proportion of isopropyl groups in the polymeric chain.

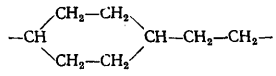
The polymeric hydroperoxides synthesised were used for the production of ion-exchange resins.

Granular sulphonic cation-exchange resins were obtained on the basis of spatially cross-linked copolymers, by the adding on of styrene to polymeric hydroperoxides[70]. For the chain carrier and polymeric initiator respectively the polyarylenealkyl (a product of the common polymerisation of cumene and bibenzyl with dichloroethane) and its hydroperoxide were used; divinylbenzene was the cross-linking agent.

The capacity of the ion-exchange resins, determined by the degree of vulcanising of the specimens, increases with increase in the proportion of poly(arylenealkyl) in the original mixture and of hydroperoxide groups in the polymeric hydroperoxide.

The sulphonic cation-exchange resins obtained are capable of sorbing large organic ions[71].

Poly(arylenealkyls) were subjected to hydrogenation[72], as a result of which poly(cycloalkylenealkyls) of the general formula

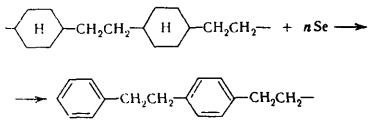


were obtained. The hydrogenation was carried out in the presence of a solvent and in a melt on Raney nickel, according to the reaction:

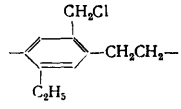
$$[-CH_2-CH_2C_6H_4-]_n + 3n\,H_2 \xrightarrow{Ni} [CH_2-CH_2-C_6H_{10}-]_n$$

The hydrogenation products of the poly(arylenealkyls) retain their initial appearance but their colour is appreciably paler than that of the original polymers. The molecular weight of the hydrogenated poly(arylenealkyls) is almost the same as that of the original polymer.

Dehydrogenation of the hydrogenated PPE with selenium led to the initial poly(phenylethyl):



Polyarylenealkyls are readily chloromethylated. The chloromethylation of PEPE[71,73] gave the polymer



containing up to 19% chlorine.

Water-soluble polyelectrolytes were obtained by the same method. To do this, first the PPE was chloromethylated, then the product was aminated, or vulcanised, or phosphorylated; this was followed by hydrolysis and oxidation[74].

Yukel'son and coworkers[75] nitrated poly(arylenealkyls) and obtained nitro-products with up to 6% free nitrogen. The use of nitropolymers as plasticizers and antioxidants in rubber mixtures based on SKS-30 ARKM rubbers increases the strength properties of the vulcanised products.

Hence the following conclusions can now be drawn:

1. For the improvement of the physicomechanical properties of poly(arylenealkyls) obtainable by polycondensation, several methods for strengthening them have been found.

2. The low melting point and good solubility of the polymers isolated at intermediate stages of the process enables these polymers to be treated rather simply.

3. The introduction of functional groups in poly(arylenealkyls) opens paths for their use for practical purposes.

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