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Vinylphenols and Oligomers and Polymers Based on Them

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The review deals with the methods of synthesis of alkenylphenols and their derivatives whose ethylene bond is conjugated with the benzene ring; data are presented on the polymerisation, copolymerisation, and polycondensation of these compounds and also on the applications of polymeric materials based on them.
The bibliography includes 189 references.

CONTENTS

I. Introduction 1081
II. Synthesis of vinylphenols 1081
III. Synthesis of vinylphenol ethers 1084
IV. Oligomerisation, polymerisation, and copolymerisation of vinylphenols and their derivatives 1086
V. Polycondensation of vinylphenols with aldehydes 1089

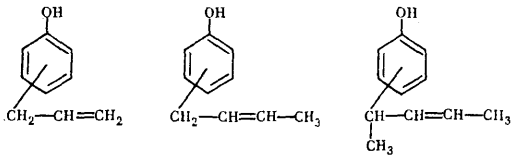
I. INTRODUCTION

The interest in the chemistry of alkenylphenols is due to the fact that their structure contains functional groups of different nature and that reactive oligomers, polymers, and copolymers exhibiting a tendency towards further chemical reactions, particularly in the material moulding stage, can be obtained by standard oligomerisation, polymerisation, copolymerisation, and polycondensation methods; the evolution of volatile products is not observed in their processing. This approach to the preparation of polymers is extremely valuable in the manufacture of materials capable of being used under extreme operating conditions (thermostable and heat resistant plastics, polymers with three-dimensional structures, etc.).

Alkenylphenols are also of independent interest for the chemical modification of industrial polymers during their synthesis and processing.

Vinylphenol oligomers, polymers, and copolymers are used to prepare epoxyresins, in thermoplastic and thermoreactive compositions, in glues, in the manufacture of laminated plastics, press powders and varnishes, cast articles, and adhesives, in the manufacture of laminated electrically insulating materials, as anti-oxidants for rubbers, resins, and oils, etc.

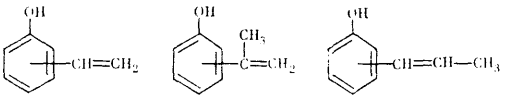
From the standpoint of their reactivity in oligomerisation, polymerisation, and copolymerisation reactions, alkenylphenols can be divided into two main groups. The first group includes alkenylphenols where the ethylene bond of the alkenyl group is not conjugated with the benzene ring, for example:



Alkenylphenols of this series are synthesised by the interaction of phenol or alkylphenol with allyl or methylallyl halides or the corresponding alcohols and with conjugated and non-conjugated dienes in the presence of various catalysts.[1]

Although alkenylphenols of this type can be synthesised comparatively readily, they have not found extensive applications in the syntheses of oligomers and polymers in view of the low reactivity of the allyl group in polyaddition reactions. Alkenylphenols of this type will not therefore be considered in the present review.

The second group include alkenylphenols in which the ethylene bond of the alkenyl group is conjugated with the benzene ring. Typical representatives of this series are vinyl-, isopropenyl-, and propenyl-phenols:



The double bond in alkenylphenols of this series is highly reactive (especially in vinylphenol), which complicates their synthesis and isolation in a pure form.

Vinyl- and isopropenyl-phenols are used to synthesise various reactive oligomers and to modify polymers manufactured industrially. There has been a considerable growth of interest in vinylphenols during the last few years, which is indicated by the numerous publications, mainly patents (especially in Japan, the Federal Republic of Germany, USA, USSR, England, etc.).

The available literature data on the methods of synthesis, properties, and practical applications of vinylphenols and the oligomers and polymers based on them are surveyed and described for the first time in the present review.

II. SYNTHESIS OF VINYLPHENOLS

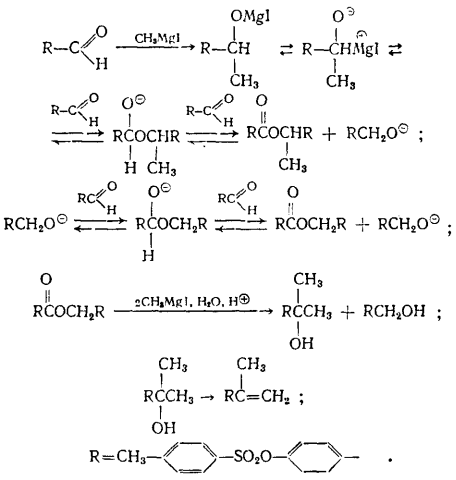
As early as 1931, it was shown that *o*-vinylphenol can be obtained by condensing phenol with epoxyethane, ethylenechlorohydrin,[2] or vinyl acetate[3] with subsequent dehydration of the resulting 2-phenoxyethyl alcohol or the rearrangement of phenyl vinyl ether. However, in practice it is difficult to obtain vinylphenol under these conditions.[4-6] An alcohol which is readily dehydrated to *p*-vinylphenol has been synthesised by the reaction of *p*-hydroxybenzaldehyde with CH_3MgI.[7]

m-Vinylphenol can be obtained in 50% yield by dehydrating *m*-hydroxyphenylmethylmethanol at 300 °C on activated alumina, but the initial alcohol is difficult to obtain.[8]

A method of synthesis of *p*-vinylphenol by cracking 1,1-bis(4-hydroxyphenyl)ethane in the presence of aluminosilicate catalysts at 550–560 °C (yield 60%) was proposed in 1960.[9,10] *o*-Vinylphenol is obtained analogously by the pyrolysis of 2,4-dimethylbenzo-1,3-dioxan at 400–450 °C.[11] The pyrolytic methods of synthesising vinylphenol have attracted attention because of their simplicity and the wide variety of initial compounds which can be used. Thus

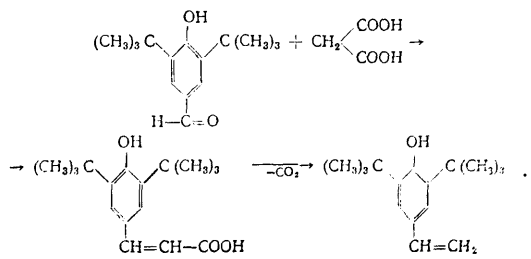
o-vinylphenol can be obtained by the pyrolysis of cyclo-octa-1,3,5-triene-7-one and the product of its irradiation—*cis*-bicyclo[4.2.0]octa-4,7-dien-2-one.[12] Benzene and acetone are formed together with the required product during the pyrolysis. The cracking of 1,1-bis(4-hydroxy-5-methylphenol)ethane leads to 2-methyl-4-vinylphenol.[9] Both *p*-vinylphenol and 2-methyl-4-vinylphenol synthesised in this way readily polymerised on standing in air. The above reaction was later carried out in the presence of iron, manganese, cobalt, copper, thorium, antimony, vanadium, tin, molybdenum, and tungsten oxides. Na_2CO_3, MgO, CaO, BaO, and Cr_2O_3 have been used as promoting agents. In the presence of iron–chromium catalysts promoted by K_2CO_3, a high degree of conversion of the starting material is attained (92–94%) and is accompanied by a high selectivity in the formation of *p*-vinylphenol (85–89%).[13]

It is of interest to note that the organomagnesium synthesis of vinylphenol does not always lead to the desired results. For example, when an attempt was made to synthesise *p*-vinylphenol by the reaction of 4-(4-$CH_3C_6H_4SO_2O$)C_6H_4CHO with CH_3MgI, *p*-isopropenylphenol was obtained instead of the expected product,[14] probably in accordance with the following scheme:

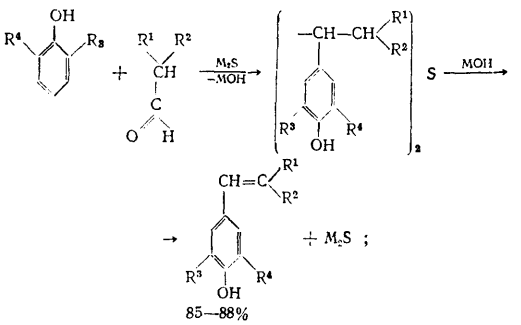


The isolation of vinylphenols in a pure form from the products of the dehydrogenation of ethylphenols and of the cracking of 1,1-bis(4-hydroxyphenyl)ethane presents considerable difficulties. In order to prevent tar formation, it is recommended that the vinylphenols be diluted with an equal volume of ethylene glycol[15] and admixtures of phenol, ethylphenols, hydrocarbons, and vinylphenol polymers are removed from vinylphenols by means of contact counter-current apparatus with aqueous alkaline solutions and organic solvents immiscible with water.[16]

Some methods of synthesis of vinylphenols (decarboxylation of the corresponding hydroxycinnamic acid, dehydration of hydroxyphenylmethylmethanols, pyrolysis of 2,4-dimethylbenzo-1,3-dioxan, etc.) have been described in a monograph.[17] However, since it is difficult to obtain the starting materials, these methods are used only for laboratory purposes. For example, the synthesis of 2,6-di-t-butyl-4-vinylphenol by the condensation of 2,6-di-t-butyl-4-hydroxybenzaldehyde with malonic acid and subsequent decarboxylation of the resulting substituted cinnamic acid has been described:[18]



2,6-Di-t-butyl-4-vinylphenol and its β-alkyl-substituted derivatives can also be obtained[19] by the condensation of 2,6-di-t-butylphenol with aldehydes in the presence of an alkali metal sulphide and the subsequent decomposition of the reaction products in accordance with the scheme



M = alkali metal; R^1, R^2 = H, Alk; R^3, R^4 = t-C_4H_9, etc.

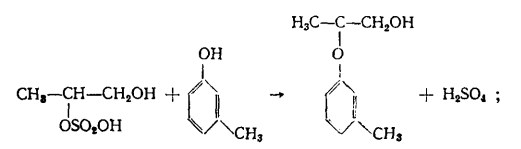
The methods of synthesis of isopropenylphenols are of independent interest. Much attention has been devoted in the literature to their development. According to literature data, the catalytic decomposition of di(hydroxyphenyl)-propane, the alkylation of phenols by acetylene homologues, the dehydrogenation of alkylphenols, etc. are of greatest interest.

The rearrangement of isopropenyl ethers of aromatic hydroxy-compounds leads to *o*-isopropenylphenols. The reaction takes place in the presence of 10% sulphuric acid in glacial acetic acid.[20] The initial ethers can be obtained either by treating isopropenyl bromide with the corresponding potassium phenoxide or from phenol and allyl alcohol. In the latter case the isopropenyl ethers need not be isolated and a mixture of allyl alcohol and the aromatic hydroxy-compound can be used immediately for the synthesis of *o*-isopropenylphenols.

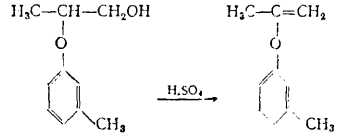
The mechanism of the synthesis of isopropenylphenols, in particular 6-isopropenyl-3-methylphenol from *m*-cresol and allyl alcohol under the influence of concentrated sulphuric acid, is represented in the following manner:[3,20]
a) the addition of sulphuric acid to allyl alcohol with formation of 1-hydroxymethylethylsulphuric acid:

$$H_2C{=}CH{-}CH_2OH + H_2SO_4 \rightarrow CH_3CH(CH_2OH)OSO_2OH\ ;$$

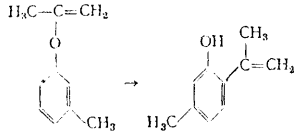
b) the interaction of 1-hydroxymethylethylsulphuric acid with *m*-cresol:



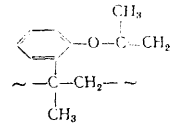
c) the dehydration of the resulting ether by concentrated sulphuric acid:



d) the rearrangement of the unsaturated ether to 6-isopropenyl-3-methylphenol:

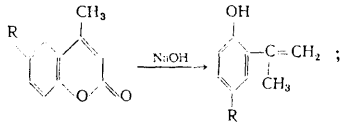


When phenol was allowed to react with methylacetylene in the presence of potassium hydroxide,[21] isopropenyl phenyl ether was isolated as the main product in 57% yield. Isopropenyl ether of o-isopropenylphenol and its trimerisation products (with a molecular weight of ~500), corresponding to the general formula



were also obtained.

Finally o-isopropenylphenol and its ring-substituted derivatives can be obtained by the reaction of 4-methylcoumarin and its derivatives, which are intramolecular phenol esters:[22]



R=H, CH_3, C_2H_5, iso-C_3H_7, OCH_3, Cl, Br

p-Isopropenylphenols are not usually obtained from the alkenyl ethers of aromatic hydroxy-compounds; other reactions are used for this synthesis, in the first place the decomposition of di(hydroxyphenyl)propane. Isopropenylphenols are normally always formed in small amounts (up to 3%) as side products in the manufacture of di(hydroxyphenyl)propane (bisphenol-A), which is based on the condensation of phenol with acetone in the presence of acid or alkaline catalysts.[23] It has been suggested in the literature[24,25] that p-isopropenylphenol is an intermediate in the condensation of phenol with acetone under the conditions indicated. Indeed the possibility of obtaining di(hydroxyphenyl)propane from p-isopropenylphenol in the presence of acid or alkaline catalysts has been demonstrated.[26-28]

A study of the thermal decomposition of di(hydroxyphenyl)methane derivatives showed[24] that one mole of the initial reactant gives rise to one mole of phenol, ~0.5 of a mole of an alkylphenol, and tarry substances. A distillate consisting of phenol, p-isopropylphenol, and tarry products has been obtained from di(hydroxyphenyl)propane in ~80% yield by distillation at atmospheric pressure. The authors[24] believe that the decomposition of di(hydroxyphenyl)propane proceeds initially with the formation of phenol and p-isopropenylphenol and its subsequent disproportionation to p-isopropylphenol and hydrogen-depleted tarry substances. This mechanism of the disproportionation has not been proved.[25]

The decomposition of di(hydroxyphenyl)propane at 100 °C in the presence of concentrated hydrochloric acid leads to a mixture of complex composition consisting of phenol, saturated p-isopropenylphenol dimers, and tarry products. Monomeric p-isopropenylphenol was not detected under these conditions.[24]

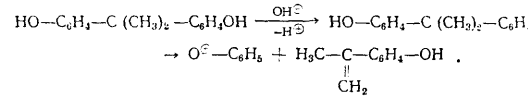
The decomposition of di(hydroxyphenyl)propane in a flow reactor in the presence of an aluminosilicate catalyst at 550 °C and after a contact time of 0.03 s (diluent—water vapour) leads to the formation of p-isopropenylphenol and phenol.[9] However, owing to the disproportionation and isomerisation side reactions, the yield of the required products does not exceed ~46%.

Thus the use of acid catalysts in the cracking of di(hydroxyphenyl)propane promotes the conversion of the cracking products into tars, reducing thereby the yield of p-isopropenylphenol. Side reactions such as disproportionation or oligomerisation of isopropenylphenols takes place to a much lesser extent in the cracking of di(hydroxyphenyl)propane in the presence of alkalis. The use of a vacuum and the continuous removal of the cracking product from the reaction zone also promote an increase in the yield of p-isopropenylphenol under these conditions.

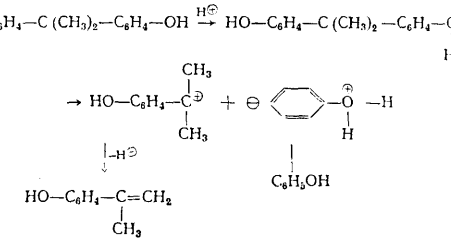
The decomposition of di(hydroxyphenyl)propane and its 2-alkyl derivatives at 170–235 °C *in vaçuo* (2–10 mmHg) in a stream of nitrogen or without it in the presence of NaOH, Na_2CO_3, or CH_3COONa with simultaneous distillation of the decomposition products[29-31] leads mainly to phenol and p-isopropenylphenol, the yield of the latter being 90–98% of theoretical.

It is recommended that cracking of di(hydroxyphenyl)propane in the presence of sodium hydroxide be carried out at 120–180 °C and a residual pressure of 4 mmHg with two injections of alkali.[32] In this case up to 4% of p-isopropenylphenol dimer and trimer is formed together with phenol and p-isopropenylphenol.

The facilitation of the cracking of di(hydroxyphenyl)propane in the presence of alkaline and acid catalysts has been explained in different ways.[27] The hydroxy-group of one of the benzene rings gives rise to the bisphenol anion on treatment with alkali. The π electrons are then redistributed in the hydroxybenzene ring, as a result of which the bond between the central carbon atom and the second hydroxybenzene ring is broken:



When acids are used, the bond between the central carbon atom and the hydroxybenzene ring is weakened owing to the addition of the protons to one of the OH groups, which entails cleavage. The ions formed are stabilised by being converted respectively into p-isopropenylphenol and phenol:



The side products of the manufacture of di(hydroxyphenyl)propane can also be used to synthesise p-isopropenylphenol[33] but the yield of the desired product is low after their thermolysis. The method of synthesis of isopropenylphenol[34] by the thermal decomposition of p-isopropenylphenol

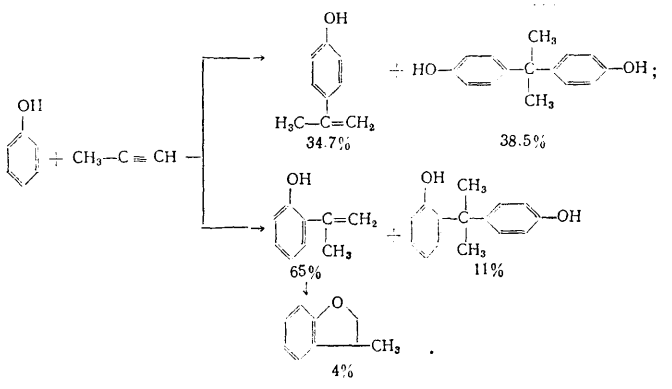
oligomers when these are injected continuously into an inert organic solvent heated to 150–250 °C at a pressure of 10 to 100 mmHg is of interest. *p*-Isopropenylphenol is obtained by this procedure in 98% yield and with a purity of 94.1%. The liquid-phase cracking of bis(4-hydroxyphenyl)alkanes or bis(4-hydroxyphenyl)cycloalkanes in the presence of a basic catalyst proceeds analogously.[35]

In order to prevent the dimerisation of *p*-isopropenylphenol, it is recommended that the vapour of the di(hydroxyphenyl)propane cracking product be irrigated with a polar solvent, for example with monohydric or dihydric alcohols; *p*-isopropenylphenol is isolated by diluting the alcoholic solution with water.[36]

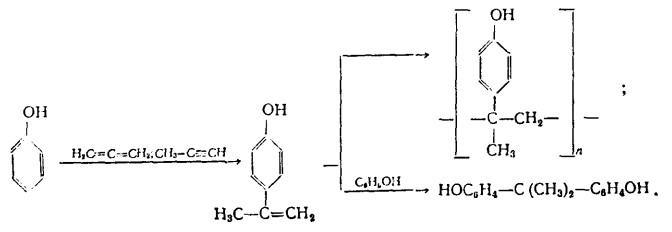
Overall, the cracking of di(hydroxyphenyl)propane in the presence of alkalis[26,29–31] ensures a fairly high yield (~90–98%) of the desired product—*p*-isopropenylphenol and its 2-alkyl derivatives. However, the main deficiency of this method involves the use of pure di(hydroxyphenyl)propane as the starting material which is at the present time a fairly expensive and scarce monomer, used in the manufacture of epoxy-resins. The high cost of di(hydroxyphenyl)propane is due to the complexity of the technology involved in its isolation in a pure form from condensation products and the labour involved in the utilisation of the waste produced.

All this makes the above method of synthesis of isopropenylphenol expensive, although in many instances it is nevertheless used to synthesise *p*-isopropenylphenol, a technically important product, despite being uneconomic.

The next group of methods, which makes it possible to obtain isopropenylphenols, is based on the alkenylation of aromatic hydroxy-compounds by substituted acetylenes.[37] Thus the alkylation of phenol by methylacetylene, phenylacetylene, and t-butylacetylene leads to the desired compounds. In this case of methylacetylene the reaction proceeds with formation of *p*- and *o*-isopropenylphenols, 2,2-di(4-hydroxyphenyl)propane, 2',4''-dihydroxy-2,2-diphenylpropane, and methylbenzofuran:



It is noteworthy that *p*-isopropenylphenol is also formed as an intermediate in the synthesis of di(hydroxyphenyl)propane by the reaction of phenol with allene or methylacetylene:[38]



Among other methods of synthesis of vinyl- and isopropenyl-phenols which are of industrial interest, mention may be made of the alkylation of phenol by ethylene and propene with subsequent dehydrogenation of ethyl- and isopropyl-phenols. The results of a study of the alkylation of phenol by ethylene and propene over aluminosilicates have been published;[39] the resulting mixtures of isomers of ethyl- and isopropyl-phenols were dehydrogenated in the presence of the "styrene-catalyst" (79.5% ZnO, 5.5% MgO, 5% Al_2O_3, 5% CaO, 2.5% K_2SO_4, and 2.5% $K_2Cr_2O_7$). The dehydrogenation of ethylphenols was accompanied in this instance by appreciable coke and gas formation; the yield of vinylphenols was low and their isolation in a pure form was difficult because of tar formation. The dehydrogenation of the mixture of isomeric isopropylphenols proceeds analogously.

When the *m*- and *p*-isomers of ethyl- and isopropyl-phenols are dehydrogenated in the presence of Cr–Al and magnesium, iron, copper, potassium, chromium, and tin oxides in the temperature range 400–700 °C, alkenylphenols are formed in yields of ~48–56%.[6,40,41] The dehydrogenation of isopropylphenols in the presence of catalysts such as the copper–chromium No.4 catalyst, the oxide No.40 catalyst, the "styrene-catalyst", and the "R-1" catalyst without and with a diluent (CO_2, H_2O) at 495–620 °C at atmostpheric pressure[39,42–45] gives rise to satisfactory yields of isopropenylphenol.

When Fe_2O_3 promoted by K_2O is used as the catalyst, both on a carrier (alkaline earth metal oxides) and without a carrier, at 525 °C and a space velocity of 0.3 h^{-1}, the degree of conversion of *p*-ethylphenol is 8% and the selectivity of the formation of *p*-vinylphenol reaches 85%.[46]

The low yield of products, the intensified cracking, the charring of the initial alkylphenols, and rapid coke formation on the catalyst proved to be serious obstacles to further development of this extremely attractive, at first sight, method of synthesis of vinyl- and isopropenyl-phenols. Furthermore, the use of a mixture of isomers of the initial alkylphenols led to the formation of an extremely complex mixture of their dehydrogenation, cracking, and oligomerisation products, which hindered the isolation of the pure isomers of vinyl- and isopropenyl-phenols from it.

Other methods of synthesis of alkenylphenols have also been described in the literature. Thus 2,6-di-t-butyl-4-isopropenylphenol has been obtained in 70% yield by the reaction α-bromoisopropyl 3,5-di-t-butyl-4-hydroxyphenyl ketone with sodium hydroxide in an alcoholic solution.[47] A method of synthesis of *m*-isopropenylphenol by the acid decomposition of di-isopropylphenyl hydroperoxide with subsequent neutralisation of the reaction mixture and distillation in the presence of alkali (pH up to 9) has been proposed.[48]

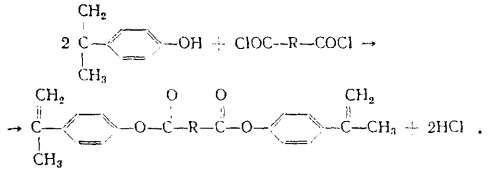
Thus one may conclude that, from the standpoint of its likely usefulness, the method involving the dehydrogenation of alkylphenols is of definite interest. However, the lack of effective catalysts precludes the wide-scale employment of this method in practice. We believe that the method based on the catalytic cracking of di(hydroxyphenyl)propane is most suitable at the present time. Here the yield of the desired product—*p*-isopropenylphenol—reaches 96% and above and the phenol formed as a side product is used to synthesise the initial di(hydroxyphenyl)propane.

III. SYNTHESIS OF VINYLPHENOL ETHERS

The presence of the phenolic hydroxyl in vinylphenols retards their radical polymerisation compared with styrene. On converting them into their ethers, the capacity of the

ethylene bond for polymerisation increases significantly. The difference between the reactivities of the ethylene and ethyl groups makes it possible to carry out the oligomerisation or polymerisation of the vinylphenol ethers strictly via the ethylene group without involving the less reactive centres, which, forming part of the composition of the oligomers or polymers, are capable of subsequent participation in polymer-analogue transformations, imparting new practically important properties to the final polymeric product.

There is limited information in the literature, mainly in patents, about the synthesis of certain representatives of the ethers and esters of vinyl- and isopropenyl-phenols. Reactive monomers containing two isopropenyl groups in the molecule have been obtained[49] in yields up to 80% by the reaction of *p*-isopropenylphenol with the dichlorides of dibasic acids (carbonic, adipic, terephthalic, fumaric, etc.) in the presence of bases according to the scheme



The synthesis of *p*-isopropenylphenyl esters of acetic, propionic, benzoic, diethylphosphoric, and acrylic acids from their chlorides has been used as a classical method of organic chemistry, primarily to characterise chemically these individual compounds.[49-51] However, it was no less convenient to acylate the dimer or trimer of *p*-isopropenylphenol by acetic anhydride in the presence of acid catalysts with subsequent thermal or catalytic (SiO_2) decomposition of the di- and tri-acyl derivatives in order to obtain *p*-isopropenylphenyl acetate.[52] The initial dimers and trimers can be obtained by the cracking of di(hydroxyphenyl)propane in the presence of alkali. Among *p*-vinylphenol esters, 2,6-di-t-butyl-4-vinylphenyl acetate is known.[18,53] The silylation of *p*-vinylphenol by trialkylhalogenosilanes[54] and of 2,6-di-t-butyl-4-vinylphenol by *NN*-bis(trimethylsilyl)-acetamide has also been described.[18]

The synthesis of di[4-(*p*-isopropenylphenoxy)phenyl] sulphone by the reaction of *p*-isopropenylphenol with di(4-bromophenyl) sulphone in the presence of sodium hydroxide at 140 °C has also been described.[55] The yield of the desired product was 98.5%. The ethers of *p*-vinyl- and *p*-isopropenyl-phenols are usually obtained by the reaction of their phenoxides with the corresponding halogeno-derivatives.[56,57]

The methods of synthesis of the glycidyl ethers of vinyl- and isopropenylphenols are complicated by the dimerisation and polymerisation reactions of both the initial phenolic compounds and their glycidyl ethers. For this reason, the usual conditions for the preparation of the glycidyl ethers of phenols, alkylphenols, and allylphenols are unsuitable for the synthesis of the glycidyl ethers of vinyl- and isopropenylphenols. For example, a method of synthesis of the glycidyl ethers of allylphenol involving the gradual addition of a 40–60% aqueous solution of allylphenoxide (1 mole) to a boiling mixture of epichlorohydrin (2–2.1 moles) with benzene (1.1 mole) accompanied by the simultaneous azeotropic distillation of water has been described.[58] The yield of the glycidyl ether of allylphenol reaches under these conditions 95% relative to the allylphenol which has reacted. It has been shown that[59] under identical conditions the yield of the glycidyl ether of *p*-isopropenylphenol does not exceed 80%. This difference is explained in the first place by the characteristic features of the structures of aryl- and isopropenyl-phenols.

Whereas the ethylene bond in allylphenol is not conjugated with the benzene ring, in vinyl- and isopropenyl-phenols the conjugation of the ethylene bond with the aromatic system makes them more reactive and increases their tendency towards polymerisation. For this reason, when the glycidyl ether of *p*-vinylphenol is obtained from *p*-vinylphenol and epichlorohydrin in the presence of alkali, its yield does not exceed 11.1%.[60]

In order to suppress the polymerisation of vinyl- and isopropenyl-phenols and their glycidyl ethers, it is more useful to synthesise the latter in the presence of polymerisation inhibitors [1,4-di(2-naphthylamino)benzene and β-methyl-o-coumaric acid].[61] At the same time it has been recommended that the synthesis be performed in the presence of a large excess of epichlorohydrin and powdered alkali at 90 °C. However, even under these conditions, the yield of the desired product does not exceed 70% for the glycidyl ether of vinylphenol and 80% for the glycidyl ether of *p*-isopropenylphenol.

It is noteworthy that, under the conditions quoted above (elevated temperature, the presence of alkali and phenoxides in the reaction medium),[61] the epoxide ring of the resulting glycidyl ether is comparatively readily opened with an increase of the yield of side products.

The above data exhaust the available information about the synthesis of the glycidyl ethers of vinyl- and isopropenylphenols. Further studies on these lines should be directed towards finding conditions ensuring a high yield of the glycidyl ethers of vinyl- and isopropenyl-phenols and the suppression of the formation of side products. Much attention should be devoted in this connection to the simplification of the technology, a decrease of the consumption of energy and materials in the process, and the development of conditions for the isolation from the reaction products of the final ethers with a high purity and in high yields. Taking these requirements into account, the synthesis of glycidyl ethers of isopropenylphenols in a homogeneous medium at a low temperature (35–60 °C) using mono- or di-hydric C_1–C_3 alcohols as solvents has been investigated and developed recently. The yield of the desired product is 90–98%.[62]

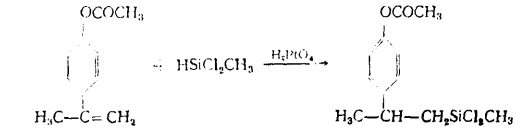
Thus the synthesis of only some esters and glycidyl ethers of vinyl- and isopropenyl-phenols has been described in the literature. These ethers and esters can be used for the modification of known polymeric materials and the synthesis of new ones. The development of convenient, waste-free methods of synthesis of the above monomers from readily available raw materials is therefore important.

The synthesis and study of the rearrangement of esters and allyl ethers of vinyl- and isopropenyl-phenols are of no less interest from the theoretical and practical points of view. Unfortunately the application of these reactions to the ethers and esters of vinyl- and isopropenyl-phenols has until recently been disregarded by investigators despite the abundance of studies on the Claisen rearrangement of allyl ethers[63-77] and the Fries rearrangement of esters[78-96] of phenols and alkylphenols.

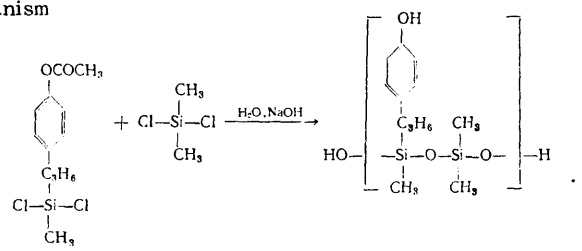
It was not until the 1980's that the first studies on the synthesis and then the photorearrangements and thermal rearrangements of allyl ethers of isopropenylphenols were published.[97,98] These investigations dealt with the reactions of *p*-isopropenylphenol and 2-alkyl-4-isopropenylphenols with allyl halides in acetone, alcohol, and water in the presence of alkali metal hydroxides and potassium carbonate. The conditions for the synthesis of new polyfunctional monomers—the allyl ethers of *p*-isopropenylphenol and 2-alkyl-4-isopropenylphenols in yields of 96.6 to 85%—have been elaborated (temperature 50 °C, *p*-isopropenylphenol : allyl halide molar ratio 1 : 4). It was shown

that the allyl ether of *p*-isopropenylphenol undergoes mainly the Claisen rearrangement both on heating (180 to 240 °C) and on exposure to UV light, with formation of a new polyfunctional monomer—2-allyl-4-isopropenylphenol in 95% yield.

The products of the hydrosilylation of *p*-isopropenylphenyl acetate at the double bond are of independent interest:[99]



The silyl derivative [2-(4-acetoxyphenyl)propyl]dichloromethylsilane can be used as the starting material in the synthesis of hydroxyphenylsiloxanes[99] in accordance with the mechanism

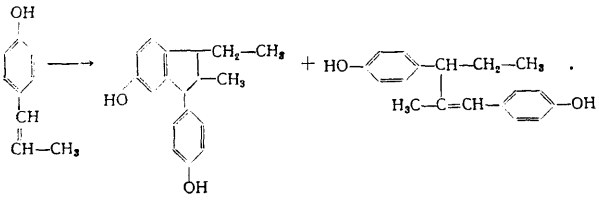


The oligosiloxanes obtained are readily hardened in the presence of hardening agents by a mechanism similar to that of the hardening of phenolformaldehyde oligomers of the novolac type.[100]

IV. OLIGOMERISATION, POLYMERISATION, AND COPOLYMERISATION OF VINYLPHENOLS AND THEIR DERIVATIVES

Studies devoted to the oligomerisation, polymerisation, and copolymerisation of vinylphenols and their derivatives are of definite practical interest.

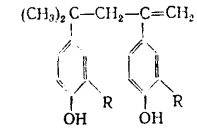
These monomers usually readily dimerise despite the possibility of the inhibiting effect of the phenolic hydroxyl. For example, the spontaneous dimerisation of *p*-propenylphenol (anol) on storage[101] is accompanied by the formation of a product referred to conventionally as "polyanol", which is a synthetic analogue of a female sex hormone:[102]



Vinylphenols readily dimerise and trimerise on heating and also in the presence of acid catalysts.[103–105] The following catalysts have been proposed for the dimerisation of isopropenylphenols (especially the *m*-isomer):[105] H_2SO_4, $AlCl_3$, PCl_3, $C_6H_5SO_3H$, $ClCH_2COOH$, $SnCl_4$, and $BF_3 \cdot O(C_2H_5)_2$. The dimerisation takes place at 110–130 °C. The dimer obtained can be isolated by vacuum distillation. The crystalline dimer is used to synthesise epoxy-resins or novolac resins.[105]

The solid-phase oligomerisation of *p*-isopropenylphenol under UV- or γ-irradiation leads to a low yield (5–10%) of oligomers with a molecular weight of 500–700.[106]

The dimers of *p*-isopropenylphenol and its alkyl derivatives,



where R is a halogen or an alkyl group, as well as their hydrogenation products react with phosgene to form thermoplastic polycarbonates having the general formula $-[-C(O)O-X-O-]_n$, where X is a residue of the dimer or the hydrogenated dimer.[107]

The dimerisation of *p*- and *o*-isopropenylphenols leads to the formation of the following linear and cyclic dimers: 2,4-di(4-hydroxyphenyl)-4-methylpent-2-ene, 2,4-di(4-hydroxyphenyl)-4-methylpent-1-ene, 2,4-di(2-hydroxyphenyl)-4-methylpent-1-ene, 2,4-di(2-hydroxyphenyl)-4-methylpent-2-ene, 1-(4-hydroxyphenyl)-1,3,3-trimethyl-6-indanol, and 2-hydroxy-2,4,4-trimethylflavan.[23]

Linear *p*-isopropenylphenol dimers are obtained in high yields on cracking di(hydroxyphenyl)propane in the presence of alkali.[108] They can serve as starting materials for the synthesis of thermoplastic and thermoreactive compositions. In particular, *p*-isopropenylphenol dimers are used for the modification of phenolic and alkyd resins.[109]

A mixture of dimers, trimers, tetramers, and other oligomers can be obtained by the oligomerisation of *m*-isopropenylphenol in the presence of acids or without them at 135–230 °C. The mixture contains about 50% of dimers and 30% of trimers.[110] BF_3 and alkylbenzenesulphonic acids have also been recommended as oligomerisation catalysts. Mainly tri-, tetra-, penta-, and hexa-mers, used in the manufacture of novolac epoxy-resins with increased mechanical strength, are formed in their presence at temperatures below 20 °C.[111,112]

Linear trimers of *p*-isopropenylphenol have been obtained by the depolymerisation of its linear polymers and also of a mixture of the *p*-isopropenylphenol dimer and polymer in an organic solvent and in the presence of acid catalysts at 0–100 °C.[113,114] These trimers are used in the synthesis of thermoreactive resins and as vulcanising agents for epoxy-resins.

In order to synthesise *p*-isopropenylphenol oligomers with a molecular weight of 500–600, it is best to polymerise the phenol in the presence of iodine in benzene at 30 °C. After 40 h, the degree of conversion of *p*-isopropenylphenol reaches 79.3%.[115] The oligomers obtained can be used in adhesive compositions and in the preparation of ion-exchange resins and high-molecular-weight water-soluble compounds.

In order to obtain polymers with a relatively low molecular weight, isopropenylphenol can be introduced into a preliminary reaction with maleic anhydride[116] and other unsaturated compounds. Propenylphenol reacts analogously with maleic anhydride.[117] Thus, on condensation with maleic anhydride, *o*-propenylphenol gives rise to an adduct with m.p. 308 to 312 °C, which is soluble in alcohol. Under the same conditions, *p*-propenylphenol gives rise to a readily separable product with m.p. 113–114 °C, which has been identified as the *p*-propenylphenyl monoester of maleic acid.[117]

p-Isopropenylphenol and its oligomers are used to synthesise modified phenolformaldehyde resins employed in the manufacture of laminated plastics. For this purpose, *p*-isopropenylphenol and its oligomers are first condensed with unsaturated oils of plant origin and the products obtained, mixed with other phenolic compounds, are then condensed with formaldehyde.[118–128]

Compositions based on *p*-isopropenyl derivatives (consisting of *p*-isopropenylphenol and its oligomers) and compounds in the group of linear unsaturated acids, fats and oils, polydienes, and the products of their "maleic treatment" are used as corrosion- and water-resistant coatings.[115]

Questions concerning the homopolymerisation of vinylphenol are of interest. Specific attention has also been devoted to this problem in the literature. The polymerisation of *p*-vinylphenol has been investigated in the presence of radical initiators and cationic and anionic catalysts with formation of oligomers.[53] In order to synthesise polyvinylphenol, it is necessary to carry out the preliminary polymerisation of *p*-vinylphenyl acetate with subsequent hydrolysis of the resulting poly(*p*-vinylphenyl acetate) with a 10% sodium hydroxide solution containing 5–10% of alcohol. The glass point of the polyvinylphenol formed is 170–180 °C.

The polymerisation of 2-methoxy-4-vinylphenol in an atmosphere of nitrogen in the dark gave rise to di-, tri, and tetra-mers and oligomers with $n > 4$ in yields of 33, 13.4, 11, and 42.6% respectively. It has been shown[130] that, in the presence of azobisisobutyronitrile, the polymerisation reaction is of first order with respect to the initiator; it has been suggested that the oligomer is formed via a cationic mechanism as a consequence of the influence of the acidic phenolic hydroxyl.

The radical polymerisation of vinylphenol in the presence of atmospheric oxygen leads to the formation of dark-coloured polymers.[131] For the preparation of colourless polyvinylphenols, it is recommended that the process be performed in the absence of oxygen.[132] The colourless polyvinylphenols obtained are suitable for esterification [etherification?] and the formation of moulding powders and varnishes.

Poly-*p*-vinylphenol is also readily cross-linked by formaldehyde and hexamethylenetetramine, forming thin films.[133] The polymerisation of *p*-vinylphenol has also been investigated in the presence of $BF_3.O(C_2H_5)_2$, BF_3, $AlCl_3$, $SnCl_4$, $VOCl_3$, $Al(C_2H_5)_2Cl$, etc. in aliphatic or aromatic nitriles and methylene chloride. The molecular weight of the poly-*p*-vinylphenol obtained reaches 116000–530000 and the use of nitriles as solvents makes it possible to obtain polymers with the maximum molecular weight.[134,135]

A poly-*p*-vinylphenol with a comparatively low molecular weight (7000) can be obtained by polymerising *p*-vinylphenol in the presence of P_2O_5, HF, H_2SO_4, H_3PO_4, HCl, and boron, antimony, iron, tellurium, tin, titanium, bismuth, and indium halides.[136,137]

Comparative differential thermal analysis of polystyrene, poly-*p*-vinylphenol, poly-3-methoxy-4-vinylphenol, and their acetates has shown[138] that all the specimens investigated are stable up to 297–327 °C and that the above polymers have the same temperatures of the onset of degradation as polystyrene. The activation energy for the decomposition of poly-*p*-vinylphenyl acetate is highest (70 kcal mol^{-1}) and that for the decomposition of poly-*p*-vinylphenol is lowest (40 kcal mol^{-1}). The activation energy for the decomposition of poly-3-methoxy-4-vinylphenol is 53 kcal mol^{-1}. The glass point increases by 10–50 °C after the introduction of the OH and $CH_3-\overset{O}{\overset{\|}{C}}-O$ groups in the *p*-position in the benzene ring relative to the polymer chain, while the introduction of the $CH_3-\overset{O}{\overset{\|}{C}}-O$ group in the *m*-position entails a decrease of the glass point. This difference between the glass points can be accounted for by the presence of hydrogen bonds and the limitation of molecular mobility in poly-*p*-vinylphenol.[138]

A phosphorus-containing poly-*p*-vinylphenol has been synthesised by the reaction of brominated poly-*p*-vinylphenol with $P(OCH_3)_3$.[139] The resulting phosphorus-containing polymer is used to impart fire resistance to thermoplastic and thermoreactive polymer compositions.

Poly-*p*-vinylphenol is used in polymer compositions for adhesives, hermetic seals, and cross-linking agents and also in the manufacture of laminated and moulded materials.[140]

Polyvinylphenol has been manufactured in the USA under the commercial names Resin-M and Resin-MB under a Japanese licence with an annual production of 100 tonnes. These linear high-molecular-weight powders have found extensive applications as hardening agents, light-sensitive materials, combustion inhibitors, and agents imparting electrical conductivity.[141]

The copolymerisation of vinylphenol with different monomers has also been investigated. Thus copolymerisation with butadiene, isoprene, and chloroprene in emulsion, in bulk,[142] and in solution[143] in the absence of oxygen leads to the formation of light-coloured copolymers capable of being vulcanised via the residual double bonds or via a polycondensation reaction with aldehydes. Such copolymers are suitable for use in casting compositions and varnishes and as cross-linking components.

The synthesis of the copolymers of vinylphenols with cyclopentadiene in the presence of H_2SO_4, HCl, $SnCl_2$, BF_3, $POCl_3$, and $BF_3.O(C_2H_5)_2$ has been described.[144,145] The possibility of using organic peroxides as the initiators of this reaction has also been demonstrated,[122] but these proved to be less effective. The radical copolymerisation of benzyl methacrylate with the phenyl ether of *p*-vinylphenol has been studied[146] and the copolymerisation constant has been determined. In order to obtain a thermoreactive product resistant to water, alkali, and acid, it is recommended that vinylphenol be copolymerised with styrene, methylstyrene, acrylic derivatives, *N*-vinylpiperidine, and allyl derivatives with subsequent treatment of the resulting copolymers with aldehydes in an alcoholic alkaline medium.[147]

Studies[148] on the polymerisation and copolymerisation of 2,6-di-t-butyl derivatives of *p*-vinylphenol, *p*-isopropenylphenol, and *p*-isopropenylanisole with styrene showed that the last two monomers readily polymerise and copolymerise in the presence of $BF_3.O(C_2H_5)_2$, $TiCl_4$, and $Al(C_2H_5)_3$, forming polymers and copolymers with molecular weights of 3900 to 15000. Depending on the monomer ratio, soluble, partly soluble, and completely insoluble copolymers are obtained with styrene or α-methylstyrene. The yield of the polymers (copolymers) varies from 1 to 37%. The copolymerisation constants have been determined for the following pairs of monomers: 2,6-di-t-butyl-4-vinylphenol ($r_1 = 3.4$) and styrene ($r_2 = 0.046$); 2,6-di-t-butyl-4-isopropenylphenol ($r_1 = 1$) and styrene ($r_2 = 0.076$). The copolymerisation of 2,6-di-t-butyl-4-vinylphenol (10.5%) with ethylene or propene (89.5%) in the presence of $TiCl_4$ and $Al(C_2H_5)_3$ gives rise to soluble copolymers.

The copolymers of vinyl- and isopropenyl-phenols with aromatic vinyl monomers have been recommended[149,150] as hardening agents for epoxy-resins (in combination with anhydride hardening agents). The hardened compositions are characterised by an improved mechanical strength, thermal stability, dielectric properties, and resistance to the action of moisture and alkalis.

The copolymerisation of 2-methoxy-4-vinylphenol with fluorinated acrylic monomers in acetone at 60 °C in the presence of azobisisobutyronitrile makes it possible to obtain copolymers characterised by an enhanced resistance to water and oil.[151]

Vinylphenol polymers and copolymers can also be obtained using various vinylphenol ethers. An interesting method of synthesis of ion-exchange resins capable of chelate formation has been described in a British patent.[152] In this case

the vinylphenol ester (*p*-vinylphenyl acetate) copolymerises with divinyl compounds (divinylbenzene, divinyl ether, etc.). The product obtained is hydrolysed and the NO_2, NH_2, COOH, SO_3H, CH_2Cl_2 etc. functional groups are introduced into the "cross-linked" polyvinylphenols formed.

The "cross-linked" polyvinylphenols containing the $AsO.(OH)_2$ groups in the benzene ring, obtained by the reaction of the "cross-linked" polyvinylphenol with diazotised arsenilic acid or by diazotising polyvinylaminophenol and subsequent treatment with sodium arsenite, can be used to extract uranium from dilute solutions.[153]

The polymerisation of the glycidyl ether *p*-vinylphenol in bulk leads to a resin with an intrinsic viscosity of 0.81 dl g^{-1} (in dioxan at 30 °C).[60] The glycidyl ether of *p*-vinylphenol and its polymer are used in the making of cast articles.

Soluble polymers have been obtained by polymerising the allyl ethers of *o*- and *p*-vinylphenols in the presence of $BF_3.O(C_2H_5)_2$ or benzoyl peroxide.[154] The polymerisation in the presence of azobisisobutyronitrile in dilute solution results in the formation of a soluble polymer, while in a concentrated solution the product is an insoluble polymer with cross links. The copolymerisation of these monomers with ethyl vinyl ether and styrene has also been carried out successfully using $BF_3.O(C_2H_5)_2$ as the catalyst. The Claisen rearrangement, cross linking induced by radical initiators, and the formation of epoxides on treatment with C_6H_5COOOH are also possible for polymers obtained by the polymerisation of the allyl ether of *p*-vinylphenol.[154]

The copolymers of vinylphenols also serve as the starting materials for the synthesis of carriers for the catalysts of the oligomerisation of unsaturated hydrocarbons. Thus polymeric carriers with a high swellability in hydrocarbon solvents, a reduced hygroscopicity, and an increased stability have been obtained[155] by using tervalent phosphorus compounds to treat hydroxyl-containing copolymers of styrene with vinylphenols or their glycidyl ethers in organic solvents at 20–110 °C. The carriers obtained contain groups capable of forming complexes with a transition metal compound, in which the central atom is either coordination unsaturated or is bound to other mobile ligands which are readily displaced.

The polymerisation and copolymerisation reactions of isopropenyl- and propenylphenols have been investigated to a much lesser extent than those of vinylphenols. Thus a study has been made[156] of the copolymerisation of *p*-isopropenylphenol (PIP) with butadiene, isoprene, vinyl acetate, and methyl methacrylate, acrylonitrile, methyl acrylate, ethyl acrylate, and styrene in the presence of azobisisobutryronitrile at 60 °C. High-molecular-weight copolymers are not obtained with butadiene, isoprene and vinyl acetate. In the remaining cases the products are copolymers with molecular weights in the range 8000–50000. The reactions of *p*-isopropenylphenol with acrylonitrile and methyl acrylate give rise to alternating copolymers. In all cases an increase in the mole fraction of *p*-isopropenylphenol in the mixture of monomers entails a fall in the rate of copolymerisation. The comonomers can be arranged in the following sequence in terms of the reactivities: acrylonitrile > methyl acrylate > ethyl acrylate > methyl methacrylate. For each PIP–acrylonitrile, PIP–methyl acrylate, and PIP–ethyl acrylate pair, the copolymerisation constants r_1 and r_2 have been determined as 0.07 and 0.02, 0.28 and 0.12, and 0.65 and 0.92 respectively.

A method of synthesis of copolymers of *p*-isopropenylphenol with styrene in acrylonitrile in solution using as catalysts Lewis acids, for example $AlCl_3$, and $ZnCl_2$ or even inorganic acids (H_2SO_4) in an amount of 0.001–5% of the weight of the monomers has been described.[157] The copolymers have a molecular weight of 500–2000 and are readily soluble in many organic solvents and solutions of alkalis. They are suitable for the manufacture of varnishes and plastics.

The reactivity of *p*-isopropenyl phenylacetate in the free radical copolymerisation with butadiene has been estimated.[158,159] The constants for the copolymerisation of *p*-isopropenylphenyl acetate with butadiene were determined in this instance spectrophotometrically and radiometrically (at 60–80 °C). The activity factors Q and e have been calculated for *p*-isopropenylphenyl acetate.

A method for the synthesis of the copolymer of *o*- or *p*-isopropenylphenol 2-alkyl-4-isopropenylphenols with styrene, maleic anhydride, and acrylonitrile in the presence of t-butylperoxide (TBP) and azobisisobutyronitrile (AIBN) has been described.[160,161] For a 1:1 ratio of the isopropenylphenol and maleic anhydride and a 1:2 ratio of isopropenylphenol and acrylonitrile (at 80° and 140 °C), the yields of the copolymers were 37–49% and 92–96% respectively.

The co-oligomerisation of 1–30% of *p*-isopropenylphenol with 70–99% of styrene in the presence of 0.1–0.2% of TBP at 140 °C is completed in 30 h. The yield of the co-oligomers is 93–99%. An increase in the amount of isopropenylphenol in the initial mixture of monomers lowers the rate of copolymerisation and leads to the formation of copolymers with reduced softening temperatures and intrinsic viscosities.

One of the promising applications of the co-oligomers of isopropenylphenols with styrene, maleic anhydride, and acrylonitrile involves their use as hardening agents for industrial epoxydian resins.† The phenolic hydroxyl and the anhydride group in the co-oligomers readily react with the epoxide ring and the OH group of the epoxydian resin, such interaction resulting in a hardening product with an improved heat resistance, adhesive strength, etc.[149].

The allyl ether of *p*-isopropenylphenol copolymerises readily with styrene in bulk and in solution (in ethylbenzene) in the presence of TBP as the initiator.[162] The copolymerisation in bulk is complicated by the formation of a gel-fraction, whose yield increases with temperature and with the amounts of the allyl ether of *p*-isopropenylphenol and the initiator in the initial mixture of monomers. The copolymerisation in ethylbenzene proceeds smoothly with virtually total conversion of the monomers. In the co-oligomerisation in solution, the ethylene bond of the isopropenyl group is more reactive than that in the allyloxy-group, as a result of which the selective synthesis of co-oligomers containing reactive allyloxy-groups becomes possible.[163,164] Studies on the characteristic features of the thermal structure formation in the co-oligomers containing 10, 20, and 30% of units comprising the allyl ether of *p*-isopropenylphenol have shown that their thermal hardening at 180–240 °C proceeds with the opening of the ethylene bond in the allyl group. Coatings based on the above copolymers have improved UV- and thermo-oxidative resistances, adhesive and impact strengths, and elasticities.

The copolymerisation of the glycidyl ether of *p*-isopropenylphenol with styrene and acrylonitrile in bulk in the presence of TBP and AIBN has been studied.[165] The copolymerisation constants for the copolymer of styrene (r_1) and the glycidyl ether of *p*-isopropenylphenol (r_2) are $r_1 = 2.42 \pm 0.78$ and $r_2 \cong 0$.

The copolymers of the glycidyl ether of *p*-isopropenylphenol with styrene are readily hardened by polyethylenepolyamine, *p*-phenylenediamine, and maleic and phthalic anhydrides and also thermally and on irradiation with UV

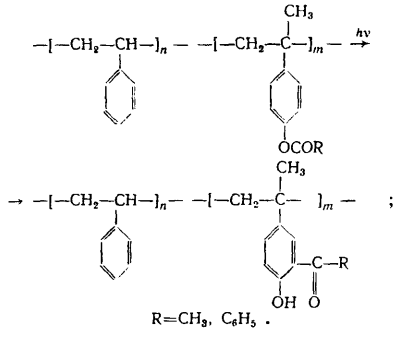
†Dian = 2,2-di(4-hydroxyphenyl)propane (Ed.of Translation).

light. The loss of weight by the "cross-linked" copolymers at 250 °C over a period of 24 h depends on the composition of the product and varies in the range 10–30% (38–40% for polystyrene).[166]

When the co-oligomers of *p*-isopropenylphenol or 4-isopropenyl-2-methylphenol with styrene and acrylonitrile were allowed to react with epichlorohydrin, a reactive oligomer containing simultaneously an epoxide ring and a phenolic hydroxyl was obtained.[167]

The heat resistance and thermal stability of the above plastics can be improved in introducing units comprising the glycidyl ethers of isopropenylphenols into the polystyrene chain with their subsequent thermal hardening. The glycidyl ether of *p*-isopropenylphenol co-oligomerises effectively with maleic anhydride and styrene in the presence of the AIBN initiator and in its absence.[168] The co-oligomerisation of the glycidyl ether of *p*-isopropenylphenol with maleic anhydride (1 : 1) and a mixture of maleic anhydride and styrene (1 : 2 : 1) both in bulk and in solution (in ketones) at 60 °C proceeds with intermediate formation of a charge-transfer complex and leads to the formation of binary and ternary co-oligomers with alternating monomer units respectively. These co-oligomers are readily hardened in the presence of moisture and also amines at 100–180 °C with the opening of the anhydride and epoxy-groups present in the co-oligomer. Coatings based on these co-oligomers are characterised, before and after hardening respectively, by impact strengths of 10 and 50 kg(force) cm^{-2}, elasticities of 1 and 10 mm, hardnesses of 0.72 and 0.9, and adhesive strengths of 4.0 and 89.9 kg(force) cm^{-2}.

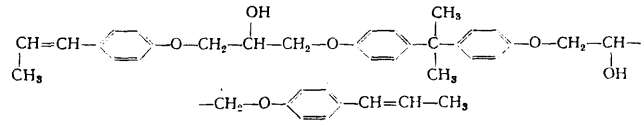
The results for the copolymerisation of *p*-isopropenylphenyl acetate and *p*-isopropenylphenyl benzoate with styrene in bulk in the presence of TBP have been published.[169] Under the influence of UV light, the Fries rearrangement takes place in *p*-isopropenylphenyl ester units of the polymer chain with formation of hydroxyacetophenone and hydroxybenzophenone groups, which improve the photostability of the copolymers:



R=CH_3, C_6H_5 .

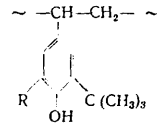
A method for the modification of the *p*-isopropenylphenol–styrene copolymer (hydroxyl index 112–116) by the glycidyl ether of *p*-isopropenylphenol in the presence of sodium hydroxide is also known.[170] The yellow modified resin softens at 85 °C and is soluble in the majority of organic solvents. Di(isopropenylphenyl) ether has also been recommended as a modifying comonomer for the modification of properties, especially for improving the heat resistance of polystyrene.[171] It has also been suggested[172] that the linear *p*-isopropenylphenol homopolymer and epoxy-resins be used for the preparation of thermoreactive polymeric materials with high heat and chemical resistances.

A method of synthesis of "cross-linked" copolymers (Marten heat resistance 87°, Dinstat [DIN static bending test? (Ed.of Translation)] bending strength 976 kg cm^{-2}, specific impact strength 4.3 kg cm^{-2}, and hardness 1415 kg cm^{-2}) by the copolymerisation of ~95% of a vinyl monomer (for example, styrene) with 5% of a tetrafunctional monomer, obtained by the reaction of 2 moles of the glycidyl ether of *p*-propenylphenol with 1 mole of bisphenol, has been proposed in a patent:[173]



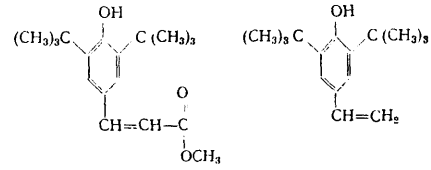
Shielded derivatives of vinylphenols, in particular 2,6-di-t-butyl-4-vinylphenol and 2,6-di-t-butyl-4-isopropenylphenol, are of interest for the synthesis of high-molecular-weight anti-oxidants by their copolymerisation with other monomers.[174] The dimers of 2,6-dialkyl-4-isopropenylphenols and their salts can also be used as anti-oxidants in rubbers and oils.[175]

A composition with an improved resistance to the action of oxidants has been obtained on the basis of polypropylene and poly-t-butyl-p-vinylphenol.[176]



R = H, t-butyl.

In order to improve the stability of the polymers of styrenes, vinyl acetate, vinyl chloride, ethyl acrylate, acrylonitrile, and butadiene, it has been suggested that[177] the latter be copolymerised with unsaturated sterically hindered phenols:



The reactions are carried out under a high pressure in the presence of 0.5% of AIBN in solution in toluene. The phenolic compounds are used in amounts of ~3%.

V. POLYCONDENSATION OF VINYLPHENOLS WITH ALDEHYDES

In contrast to phenol- or alkylphenol-aldehyde resins, alkenylphenolaldehyde resins are capable of being hardened via the alkenyl groups with the evolution of little or no volatile products. Furthermore, they can be structured by vinyl monomers with formation of "cross-linked" copolymers with improved water resistance, chemical resistance, and dielectric properties. Allylphenolformaldehyde resins also have similar properties. Thus allylphenolformaldehyde resins capable of being thermally hardened at 180–250 °C have been obtained by the allylation of a novolac phenol-formaldehyde resin and the polymerisation of the allyl ether of 2,6-dihydroxymethyl-*p*-cresol with subsequent thermal rearrangement of polyallyl ethers.[178–180] The cross-linking of allylphenolformaldehyde resins has also been investigated using cross-linking monomers (styrene, α-methylstyrene, acrylonitrile, and 2-methyl-4-vinylpyridine) in the presence of cationic catalysts.[180] It was shown that the copolymerisation of the allyl ether of novolac in the presence of cationic catalysts proceeds smoothly and at a fairly high rate, while the reaction initiated by free radicals either does not occur or is characterised by a low extent of completion.

Polycondensation resins have also been synthesised using *o*-allylphenol,[126] *trans*-hydroxymethylphenylallyl ether,[181] and cardanol (a monohydric phenol with a C_{15} side chain, containing double bonds, in the *meta*-position) obtained by the distillation of the oil from the seeds of *Anacardium occidentale*.[182]

Allylic resins possess a high thermal stability and moisture and chemical resistances as well as a low toxicity and are used as laminate and moulding materials and also in the form of varnish coatings.[183,184]

In contrast to allylphenolformaldehyde resins, vinyl- and isopropenyl-phenolformaldehyde resins are readily hardened via a free-radical mechanism at lower temperatures.

A method of synthesis of vinyl- and isopropenyl-phenolformaldehyde resins by the polycondensation of *m*-vinylphenol and *o*- and *p*-isopropenylphenols with formaldehyde has been described.[185-187] The unsaturated resin obtained can be readily hardened and can be used in oil-based insulating varnishes and for the preparation of moulding powders and adhesives.

A resin with improved flexibility (without impairment of its electrical properties), thermal stability, chemical resistance, and size stability has been obtained by the polycondensation of *p*-isopropenylphenol and its oligomer with formaldehyde in the presence of an acid catalyst; this resin is used as a binder in the manufacture of electrically insulating laminate materials.[188]

The condensation of *p*-isopropenylphenol or its dimer with formaldehyde can take place in the presence of bases,[189] for example, 28% of an aqueous solution of ammonia at 95 °C. The laminate plastic obtained using the resin thus synthesised is characterised by higher bulk and surface resistivities (4.5×10^{12}) compared with the usual phenolformaldehyde resin (10^9–10^{10}).

These studies exhaust the available literature data on the polycondensation of vinyl- and isopropenyl-phenolformaldehyde resins. Thus the existing possibilities for the synthesis of alkenylphenolformaldehyde resins by the polycondensation reactions have so far been by no means fully utilised. The synthesis of *p*-alkylphenolformaldehyde and ureaformaldehyde resins modified by vinyl- and isopropenylphenols is also of theoretical and practical interest.

The literature data described above permit the conclusion that the chemistry of vinyl- and isopropenyl-phenols has developed vigorously in recent years both in the direction of the creation of effective processes for their synthesis and of the study of their oligomerisation, homopolymerisation, copolymerisation, and polycondensation. Taking into account the differences between the reactivities of the ethylene bond, the phenolic hydroxyl, and the ether and other functional groups, definite advances have been made in the synthesis of new and the modification of existing oligomers and polymers using these polyfunctional monomers. Particular mention should be made of the advances in the creation of unsaturated phenolformaldehyde oligomers, which are hardened without the evolution of volatile products, self-stabilising copolymers, and new composite materials characterised by improved physicochemical and dielectric properties.

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